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Jack D. Dunitz (1923–2021): a chemists' crystallographer

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Abstract

Jack D. Dunitz (1923–2021) was Professor of Chemical Crystallography at the Swiss Federal Institute of Technology, Zurich. He received his degrees from Glasgow University, was at the ETH Zurich since 1957, and retired in 1990. His research interests included crystal structure analysis as a tool for solving chemical problems, polymorphism, solid state reactions, and a broad area of structural variations during chemical events under the umbrella term of structure correlation.

Keywords Chemical crystallography · Structure correlation · Dorothy Hodgkin · Linus Pauling · ETH Zurich

Jack D. Dunitz (1923–2021) was born in Glasgow into an East European Jewish immigrant family ([1], Fig. 1). His father's family came to Britain at the end of the nineteenth century from a small town north of Bialystok, called Grajewo, close to what is today the borders of Poland, Lithuania, and Belarus. A part of the family, Dunitz's paternal grandparents, went to Palestine around 1900 and stayed there until the end of their lives. Dunitz's father was brought up by an aunt in London, and the father served in the British Army in World War I. He had an appreciation of music and literature, but did not have a formal education. Dunitz's maternal grandfather, Morris Grossman, came to London from Zhitomir, from the Ukraine. Dunitz's mother was the eldest of his seven children, was brought up in poverty in London's East End, and lived to the age of 101.

Dunitz received his BSc degree in 1944 from Glasgow University and stayed on for his doctoral studies. J. Monteah Robertson (1900–1989), a leading figure in X-ray crystallography, was his mentor. Robertson taught him the fundamental scientific approach to structure analysis and to crystal structures. Robertson was a pioneer of the technique of isomorphous replacement in X-ray crystallography, which made it possible to reach the spectacular results in protein crystallography by future Nobel laureate researchers, such as Max Perutz and John Kendrew, and others. Dunitz received his PhD degree in 1947. He then joined Dorothy Hodgkin (Fig. 2) at Oxford to learn about her structural studies of large biologically important molecules in which Hodgkin employed Robertson's technique. Dunitz's stay with Hodgkin at Oxford was the beginning of his decade-long peripatetic

Fig. 1 Jack D. Dunitz, 1999, in his office at the ETH Zurich. Photograph by I. Hargittai

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Fig. 2 A later encounter of Jack D. Dunitz with Dorothy Hodgkin, 1989, in Los Angeles (courtesy of Jack D. Dunitz)

existence during which he moved from laboratory to laboratory and learned from the best representatives of structural chemistry.

A succession of his stations included Glasgow–Oxford–Pasadena (Caltech)–Oxford–Bethesda (NIH), Maryland–London (Royal Institution)–Zurich. The individuals with whom he connected up included Robertson, Hodgkin, Gerhard Schmidt, Linus Pauling, Verner Schomaker, Alex Rich, Sydney Brenner, W. Lawrence Bragg, and many other big names with whom his interactions were less intense, but still most beneficial. Dunitz and Barbara Steuer married in 1953 and the marriage was followed by a desire to settle down. They had two daughters, Marguerite (b. 1955) and Julia Gabrielle (b. 1957).

Dunitz's wanderings were dotted by research achievements of his own and being witness to some of the most exciting developments in structural chemistry, which was also fast transforming into structural biology. One of the structural problems Dunitz worked on in Oxford and Pasadena was the intriguing variations of the carbon–carbon bonds observed in small-ring systems. He determined the crystal structure of tetraphenylcyclobutane and had found long bonds in the cyclobutane ring, 1.57 Å, instead of the "standard" 1.54 Å. Just about that time, Charles Coulson and Bill Moffitt had developed their "bent bond" theory, which explained why bonds in small strained rings should be shorter than normal, as 1.51 Å, in cyclopropane. There appeared to be a controversy and the question was why were the bonds in tetraphenylcyclobutane long instead of short? Dunitz and his colleague at Caltech, Verner Schomaker, decided to determine the structure of the free cyclobutane molecule itself by gas-phase electron diffraction. They found long bonds, 1.57(2) Å, and proposed an explanation in terms of non-bond repulsions, which was a novel concept [2]. Not only has this concept stood the test of time, today it is receiving added attention and significance.

Another example of Dunitz's structural studies was the determination of the crystal molecular structure of ferrocene done jointly with Leslie Orgel [3]. They embarked on this project out of disbelief in the sandwich structure by Robert B. Woodward et al. [4]. They ended up with a reliable structure determination, which confirmed Woodward's sandwich structure. Although the initial suggestion for the ferrocene structure by Kealy and Pauson was wrong [5], Dunitz recognized its value in initiating further studies. These are his words from 2015: "Pauson's paper was so interesting to discerning readers because the structure suggested was seen by them to be obviously incorrect. A new type of structure was needed." [6].

Dunitz first met Linus Pauling (Fig. 3) during the winter of 1947–1948 when Pauling was Visiting Professor in Oxford. *The Nature of the Chemical Bond* was the most influential book in Dunitz's scientific education. He developed a "tremendous hero-worship admiration for the man" [7]. During the stay at Caltech (1948–1951), Dunitz witnessed some of Pauling's work on protein structures and his spectacular discovery of the alpha-helix structure. It was crucial in the investigation, what Pauling considered important and what he decided to ignore [8]. He ignored the limitation to consider only integral number of amino acids per turn of the screw of the protein molecule. On the other hand, he included as a crucial condition that the peptide group had to be planar. He knew this from his structural studies on small molecules containing the peptide group and from his resonance theory. He was a pioneer in recognizing the importance of intramolecular hydrogen bonding in proteins, and his approach of model building was most forward-looking.

Pauling talked to Dunitz about his models and used the term "spiral." At one point, Dunitz pointed out to Pauling that the right term in this case would be "helix," and henceforth, Pauling would always use "helix." Dunitz liked to think that he helped to give the alpha-helix its name—he considered this to be his personal contribution to molecular biology.

At Caltech, he came into contact with Max Delbrück and the biologists working around him. Their discussions centered about bacteriophage and about DNA. By then, DNA was accepted by most as the hereditary substance, but its structure and the mode of its operation was still unknown. When Dunitz went back to Oxford, he had sufficient background in molecular biology to appreciate the developments that he witnessed there. He was back in Hodgkin's group

Fig. 3 Jack D. Dunitz and Linus Pauling, 1977, at the ETH Zurich (courtesy of Jack D. Dunitz)

when one day, in spring 1953, a telephone call came from Cambridge with an invitation to visit the Cavendish Laboratory and see Crick and Watson's new model of the DNA structure. It was to be the double helix. It was not only the answer about the structure, it also implied the solution of the hereditary puzzle—the copying mechanism.

A decisive change in Dunitz's situation happened in 1956. Leopold Ruzicka (1887–1976), the internationally renowned Nobel laureate chemistry professor at the ETH Zurich, decided to establish X-ray crystallography at his Organic Chemistry Laboratory. His first choice was Dorothy Hodgkin to head this new laboratory, but it became soon obvious that she was not available. In her stead, she recommended Jack D. Dunitz. He was invited for a visit in 1956, and in October 1957, he assumed the position of extraordinary professor at the ETH. With this, his wanderings ended and he stayed at the ETH for the rest of his days. This happened at the same time as Ruzicka was retiring and was succeeded by the future Nobel laureate natural products chemist and stereochemist Vladimir Prelog (Fig. 4, 1906–1998) [9]. Prelog was no less interested in developing a strong group of crystallography than was his predecessor. Dunitz's activities at the ETH covered a great variety of chemical problems providing solutions by means of crystallography. Only a selection will be mentioned here.

Above, I have already mentioned Dunitz's early recognition of the importance of non-bond interactions. This remained one of his principal interests. Other developments in chemistry and biology further emphasized the necessity to develop this concept and its applications. In chemistry, the progress in supramolecular chemistry showed the fruitfulness of this concept in the understanding of both intramolecular and intermolecular interactions. The same has been valid for the understanding of the function of large biological systems. The mere determination of bond lengths and bond angles no longer suffices for the complex description and understanding of structures. It is also noted that the bond lengths and bond angles can often be computed with similar accuracy as measured but with considerably smaller efforts and especially at much lower costs as far as human labor is concerned. Emphasis has moved to the monitoring and understanding of the *variations* of the structures, for example, during a chemical reaction, or during the performance of a biological function.

The term "structure correlation" aptly expressed this new approach even if it has not penetrated the science of structures as Dunitz might have hoped for upon its introduction. He defined it as follows: "Structure correlation is based on the recognition that the various functional groups in chemistry are not fixed and rigid. When one examines the distribution of the structural parameters of a group observed in different crystal and chemical environments, one often finds correlations among these parameters. These correlations are characteristic of the group, they tell us something about the energy surface and in many cases they can be interpreted in terms of supposed mechanisms of chemical reactions" [10]. Dunitz and Hans-Beat Bürgi edited a two-volume treatise in which they collected a broad spectrum of examples of structure correlation by a stellar collective of contributing authors [11].

Fig. 4 Istvan Hargittai, Jack D. Dunitz, and Vladimir Prelog, 1995, at the ETH Zurich, as part of a larger company in the university canteen (by unknown photographer)

Dunitz's research program on the elucidation and understanding of medium ring structures was a direct consequence of his joining the ETH. Vladimir Prelog had written an essay about medium rings, which influenced Dunitz whose structure determination of medium ring molecules coincided with other efforts to develop force fields for hydrocarbons. The two research directions interacted and strengthened each other. It occurred to Dunitz that from a systematic set of related structures, it is possible to come to some conclusions about the shape of the potential energy function for a variety of events. For example, he and his associates started deriving the potential energy function for out-of-plane deformations of the amide group. They began with the small-ring lactams and worked their way toward the larger rings. The medium ring size turned out to be very interesting for hydrocarbons and so did the lactams. Here, they saw another excellent example of structure correlation. The production, examination, and understanding of the electron density maps was yet another area of having great significance for the chemical behavior of crystal and molecular systems, and Dunitz was deeply and long involved in these studies [12].

Jack D. Dunitz was in a unique position in the world of crystallography having been shaped by an extraordinarily broad international outlook, both by the venues he had worked at and the scientists he had worked with. When he was preparing for his first encounter with Aleksandr Kitaigorodsky (or, Kitaigorodskii, Fig. 5), the great Soviet-Russian crystallographer, he was full of trepid anticipation. Dunitz had never visited the Soviet Union and had never met a Russian crystallographer. Kitaigorodsky did work of milestone importance, but operated in complete isolation with almost unsurmountable barriers to international travel (see, e.g., [13]). He was allowed to make his first trips to the West quite late in his career. Thus, the two had had very different backgrounds in their scientific antecedents. Dunitz expected Kitaigorodsky to be a Doctor Zhivago-kind of an individual, perhaps difficult to initiate a conversation with, and so on. When the two did meet, a rapport developed between them almost instantaneously [14]. Both were outgoing and vivacious, eager to communicate, and both looked at X-ray crystallography as more than a narrow branch of science; rather, as a tool of getting to know our broader world.

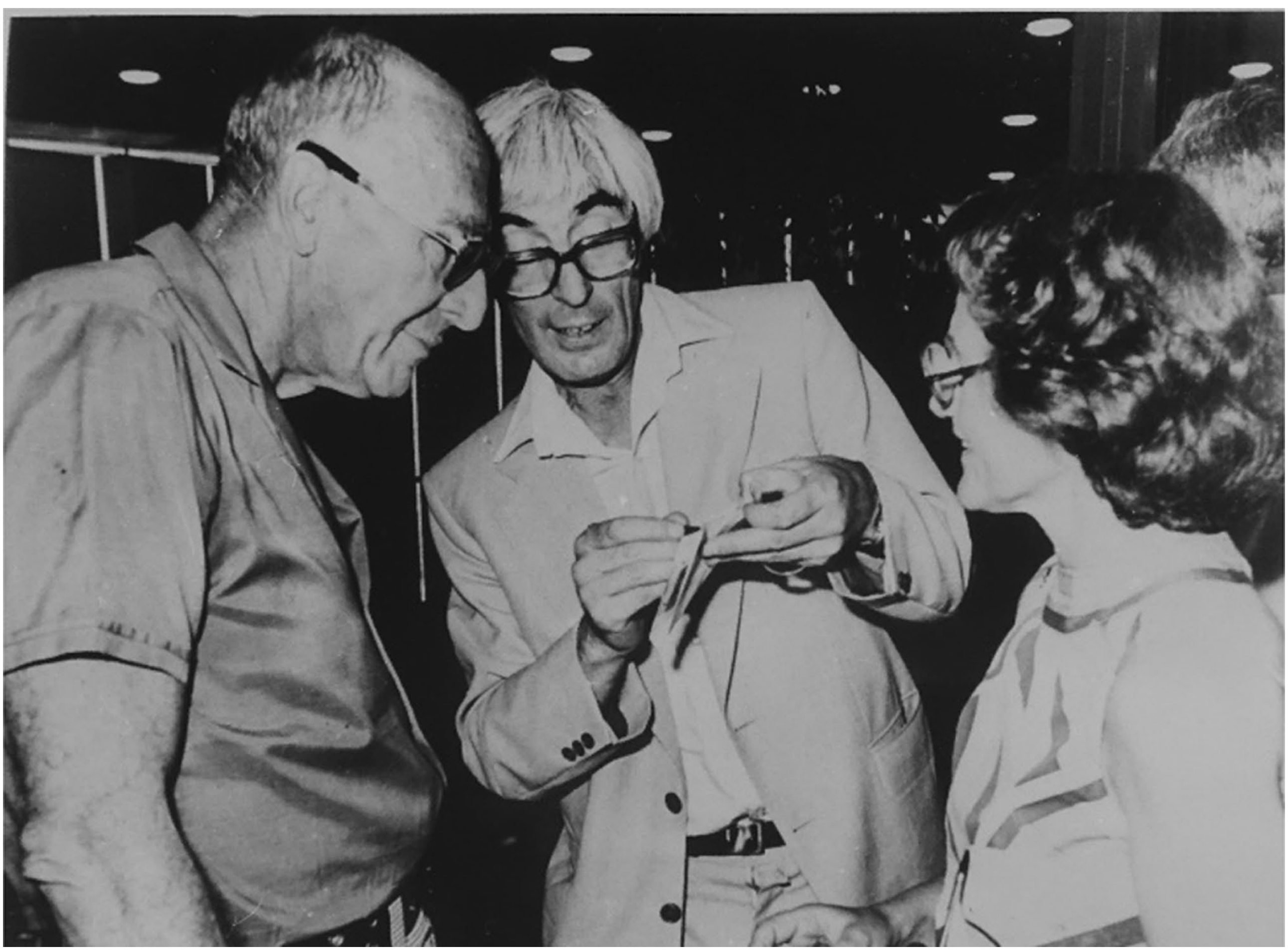

Fig. 5 From left to right: Aleksandr I. Kitaigorodsky, Jack D. Dunitz, and Olga Kennard, 1975, in Amsterdam, at the Congress of the International Union of Crystallography (courtesy of Jack D. Dunitz)

One of the outlets of Dunitz's interest in the intricacies of structures was his work along with Joel Bernstein (1941–2019) on the so-called disappearing polymorphs [15]. There may be cases when it proves difficult to produce a particular polymorphic form of a crystal even though it had already been produced before somewhere else or even in the same laboratory. Instead, another polymorphic form appears, it does consistently, and the initial form does not form ever again. Determining thermodynamic and kinetic factors of the crystallization process need to be understood, but they often become clear after the fact rather than in advance. The phenomenon of disappearing polymorph has considerable theoretical interest, but may also have tremendous industrial and economic interest [16].

Dunitz had a deep interest in symmetry and this interest was also common with Kitaigorodsky, spiritually, that is, because they never worked together. Jointly with the noted Swiss chemist, Edgar Heilbronner, Dunitz produced a book on symmetry demonstrating their broad grasp of the concept and its omnipresence in all areas of chemistry [17].

He was recognized by a number of most distinguished learned societies, which elected him to membership and only a partial list follows. He was elected Fellow of the Royal Society (London, 1974), the German science academy "Leopoldina" (1979), and the Academia Europaea (1979). He was an international member of the National Academy of Sciences of the U.S.A. (1988) and a foreign member of the Royal Netherlands Academy of Arts and Sciences (1979). He received the Paracelsus Prize (Swiss Chemical Society, 1986), the Gregori Aminoff Prize (Royal Swedish Academy of Sciences, 1990), the M.J. Buerger Award (American Crystallographic Association, 1991), and the Bijvoet Medal (University of Utrecht, 1989). He had honorary doctorates of the Technion, the Weizmann Institute, and the University of Glasgow. Another much coveted recognition was the George Fisher Baker Non-Resident Lectureship in Chemistry at Cornell University in 1976 from which he compiled and published a monograph on X-ray crystallography [18]. Characteristically, Dunitz started each chapter with a quotation from *Alice in Wonderland*.

I conclude with another quote from Dunitz in which he summarized his feelings about his career at the age of 76, having already been in retirement for almost a decade, at a time when he would carry on for two more decades: "I have the good fortune, and I call it fortune rather than luck, in having had a career in science in the second half of the twentieth century. I know it has been a terrible century in many ways. But in the last 50 years a person of modest talents could have a great time in science. He could be supported by the public to be paid to do things that he liked. That's been for me a marvelous piece of good fortune." [19].

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Declarations

Conflict of interest The author declares no competing interests.

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