NATIONAL ACADEMY OF SCIENCES

MICHAEL J.S. DEWAR
1918–1997

A Biographical Memoir by

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Biographical Memoirs, VOLUME 77

PUBLISHED 1999 BY
THE NATIONAL ACADEMY PRESS
WASHINGTON, D.C.

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September 24, 1918–October 10, 1997

BY JOSEF MICHL AND MARYE ANNE FOX

MODERN ORGANIC CHEMISTRY would not have been the same without Michael J. S. Dewar. He was one of the first, if not the first, organic chemist to master molecular orbital theory and to apply it to problems in organic chemistry. His sparkling intellect and theoretical insight introduced many of the fundamental concepts that are now taken for granted, and his ceaseless efforts over four decades produced the semi-empirical methods of computation that are still used the world over. He is remembered as a man of marvelously original and unorthodox ideas, a man of impeccable integrity, and a formidable debater.

Michael James Steuart Dewar was born in Ahmednagar, India, on September 24, 1918, of Scottish parents. His father was a district commissioner in the Indian Civil Service, the British government of India. Michael was sent to a boarding school in England at the age of eight, and as a holder of a prestigious scholarship he then studied at Winchester College. He entered Balliol College at Oxford in 1936 and undertook classical studies before developing his intellectual pursuit of organic chemistry. After earning a first-class honors undergraduate degree and his doctoral degree, he stayed at Oxford as a postdoctoral fellow with Sir Robert

Robinson in the Dyson Perrins Laboratory. At Oxford he met, and in 1944 married, Mary Williamson, a historian who later became well recognized as a scholar of English Tudor history. They had two children, Robert and Steuart. Their marriage was one of the world's truly perfect matches, filled with much mutual admiration and support in every part of their personal and professional lives.

In 1945, Dewar accepted an industrial position as a research director at Courtaulds in Maidenhead near London. Although this position permitted him to work with Bamford, the assignment of a newly minted organic chemist as the director of a physical chemistry laboratory was without precedent. Simultaneously, he wrote his first influential book *The Electronic Theory of Organic Chemistry*, which appeared in 1949. The book represented a landmark, as it was the first treatment of organic chemistry in terms of molecular orbital theory.

In 1951, at the age of thirty-three, Dewar accepted a chair at Queen Mary College at the University of London. He was instrumental in establishing a credible research program by hiring aggressively and forming a sound intellectual foundation that has persisted and grown. He stayed until 1959, when he moved to the University of Chicago. In 1963 he accepted the first Robert A. Welch chair at the University of Texas at Austin. Largely because of the presence of Dewar and his former student Rowland Pettit, the University of Texas at Austin became an internationally accepted destination for visitors and sabbatical visitors who wished to work at the frontiers of theoretical chemistry or on physical organic mechanisms. In 1980, the Dewars became U. S. citizens, and in 1983, Michael was elected to the National Academy of Sciences. In 1989, he moved to a half-time appointment at the University of Florida at Gainesville, from which he retired in 1994. He passed away in 1997.

Dewar's reputation for providing original solutions to vexing puzzles first developed when he was still a postdoctoral fellow at Oxford. In 1945, he deduced the correct structure for stipitatic acid, a mold product whose structure had baffled the leading chemists of the day. It involved a new kind of aromatic structure with a seven-membered ring for which Dewar coined the term "tropolone." He then correctly suggested that a similar structure would account for the properties of another problem compound, the alkaloid colchicine. The discovery of the tropolone structure launched the field of non-benzenoid aromaticity, which witnessed feverish activity for several decades and greatly expanded the chemists' understanding of cyclic π-electron systems.

Also in 1945, Dewar devised the then novel notion of a π complex, which he proposed as an intermediate in the benzidine rearrangement. This notion turned out to be extraordinarily fruitful, as it also automatically accounted for the ease of 1,2-shifts in carbocations, as opposed to radicals and carbanions. It also provided a simple explanation for the structure of "non-classical" carbenium ions for which Winstein was starting to provide experimental evidence at the time, and offered the first correct rationalization of the electronic structure of complexes of transition metals with olefins, later known as the Dewar-Chatt-Duncanson model. While at Courtaulds, Dewar displayed an appreciation for the utility of models in practical chemistry. For example, he measured the first absolute rate constants in a vinyl polymerization and in an autoxidation, and performed an array of other kinetic and mechanistic studies, coming close to describing the modern concept of photoinduced electron transfer.

In this period, Dewar developed the key ideas discussed in *The Electronic Theory of Organic Chemistry* at nights and on weekends. When this revolutionary book was published, it was the start of the conversion of organic chemists to a new creed. By 1951, Dewar had succeeded in formulating the molecular orbital theory of organic chemistry in a semiquantitative form, later termed "perturbational molecular orbital theory." This approach was clearly superior to the purely qualitative resonance theory then still in use, but the papers were written in such a condensed manner that the theory was virtually incomprehensible to practicing bench chemists, the intended users. Unlike his more qualitative concepts, it was never enthusiastically adopted by organic chemists as the back-of-the-envelope tool it was designed to be.

At Queen Mary College, Dewar continued his work on the theory of organic chemistry. His startling and provocative views on hyperconjugation stimulated an active debate about the nature of the chemical bond. Although some may feel that his original position later turned out to be somewhat exaggerated, his work served to correct the simplistic descriptions prevalent at the time and formed the basis for the more complicated picture that is accepted today. A list of his experimental projects from the time reveals the incredible breadth of his interests and talents. His group performed a series of significant quantitative experimental studies on aromatic substitution, designed to test theoretical predictions based on his book and on perturbation theory. He elucidated the electronic structure of phosphononitrile chlorides and started a long series of experimental studies of new stable heterocycles, the borazaromatic compounds. He performed the first studies of self-assembled monolayers of thiols on a metal surface, a field that has grown in popularity immensely in recent years. He started a series of investigations of the structure and properties of liquid crystals and developed a novel analysis of substituent effects in aromatic and aliphatic compounds, showing that the classical inductive effect is insignificant. He built an electron paramagnetic resonance spectrometer for use in his research when this kind of spectroscopy was just beginning to be recognized as useful for chemistry applications.

In spite of these burgeoning scientific successes, Dewar did not enjoy the increasingly administrative duties of chairing a modern research-focused department. When they became too much of a burden, he decided to concentrate on chemistry fully by accepting a professorial offer from the University of Chicago. The Dewars had already come to know the United States during a 1957 half-year visit to Yale, which they combined with a long automobile trip all around the country. During that trip, they met many American scientists and established many happy friendships and fruitful collaborations. They were exuberant in praising the United States and the spirit of her best chemists. Even his election as a fellow of the Royal Society in 1960 could not lure him permanently back to England, notwithstanding his frequent summer visits to London to escape Texas summers.

At Chicago, Dewar continued some of his earlier projects and added new ones. In a series of experiments, he showed that charge transfer makes a relatively unimportant contribution to the stability of charge-transfer complexes, contrary to the general belief at the time. Most importantly, at Chicago Dewar started the development of a series of increasingly sophisticated semi-empirical molecular orbital methods for organic chemistry, for which he is probably best known today. Access to the large amounts of computer time that this work required was the main motivation for Dewar's next move. This new direction brought him to the University of Texas at Austin, where he was to spend nearly three decades. He served there as a fulcrum for a strong theoretical chemistry institute that continues to this day.

In Austin, he supplemented his work in theory by continuing his interest in experimental chemistry, examining a wide array of problems ranging from carbenium ions, semiconductors, and liquid crystals to various forms of spectroscopy that now included nuclear quadrupole resonance and photoelectron spectroscopy. Although his experimental program was prolific, the pull of theory gradually became irresistible and dominant. Dewar began to focus his energy totally on the development of increasingly sophisticated semi-empirical methods for quantitative molecular orbital computations on large organic molecules, including novel ions, conjugated systems, and sigma-bonded arrays. This resulted in the development of a series of progressively more accurate methods that have been tested in a wide variety of applications. Although both structure and many molecular properties were treated in these methods, Dewar's primary interest always was chemical reactivity, and he devoted most of his effort to the study of transition states of organic reactions. He was a major contributor to our current understanding of pericyclic reactions, especially in his provocative studies of cycloadditions, electrocyclic rearrangements, and sigmatropic shifts. His work on hydrogen bonding and sigma conjugation continues to be stimulating to experimentalists. Because his methods were computationally much simpler than the non-empirical methods used by others, he was able to treat much larger and more realistic reaction models and to perform full geometrical optimizations of equilibrium and transition state geometries for large and chemically meaningful molecules well before others could even dream of such calculations. In the last decade of his life, he explored a variety of complex phenomena, including superconductivity, the structures in organometallics and reactivity in such biologically relevant compounds as enzymes and carbohydrates. His development of a semi-ab initio (SAM-1) approach to chemistry was based on the calculation of electron-electron repulsions scaled to approximate internuclear distances to allow for electron correlation. He frequently spoke of the utility of his methods, vigorously defending them as “models that work” in real situations.

Today continued advances in computer technology and computer codes permit ab initio calculations for large organic molecules at a level of sophistication that was inconceivable when Dewar developed his semi-empirical methods. Because of this progress, many applications of his semi-empirical approach may have now become obsolete. However, his models are still in use for very large molecules and for rapid preliminary scans. Indeed, in many ways his sequence of SCF-MO, MINDO, MNDO, DEWAR-PI, AM-1, and SAM-1 methods prefigured a whole new generation of parameterized methods, based on density functional theory, that have emerged as a modern replacement of the procedures introduced by Dewar. He would have been pleased to witness this development and the increased sophistication this achievement reflects.

Dewar was a brilliant conversationalist who enjoyed shocking others with his unorthodox ideas, just as he did in chemistry. For instance, he would declare firmly that everyone ought to be taught Latin at school. When challenged to explain why, he would give three reasons with disarming charm: (1) Latin is sufficiently complex to provide superb intellectual training, teaching young people how to reason through intricate problems; (2) children tend to hate Latin, so they learn at an early age to face and overcome adversity; and (3) almost without exception Latin will be totally useless for them in later life (one would not wish to make children hostile to something that might be useful to them later!). He offered similar analyses on such topics as traffic speed limits, the use of DDT, and preferred techniques for the reform of incarcerated convicts.

Dewar viewed argument as a stimulating intellectual challenge and as the best way of arriving at a reasoned solution, much in the spirit of medieval scholasticism. To be worthwhile, an argument had to be led ruthlessly, with no holds barred, but also without malice or anger. For all his bluster and disdain for the politically correct, he was a warm and happy person, truly dedicated to science and his students. Dewar's wide interests in chemistry were matched by an equally wide range of interests outside his discipline. He was keen on many subjects—from astronomy and geology to oriental cooking—and he loved to discuss them all with wit and passion. In his early years, Dewar was also an avid outdoorsman, but a back injury forced him to abandon rock climbing and other physical exercise other than carrying large pitchers of Manhattans and martinis at the legendary parties he and Mary loved to give.

Dewar’s outspokenness was not limited to science, and he found it increasingly difficult in his later years in Austin to deal with blind bureaucracy and arbitrary regulations. The disruption associated with his move to Gainesville preempted the completion of what might have been some of his finest work, and the premature death of his beloved wife Mary left him personally devastated. The irony of her death by lung cancer after lifelong opposition to smoking was particularly painful. Some of the difficulty of his transition to retirement is reflected in his memoirs published by the American Chemical Society, “A Semi-Empirical Life,” which uncharacteristically provides a seemingly embittered and convoluted picture of a truly great man.

Dewar’s professional recognition started early with his scholarships to Winchester and Balliol and his designation as a Gibbs Scholar in his second year at Oxford, a university-wide prize never previously won by so young a student. His first major award (from the Chemical Society in 1954) was largely in recognition of the influence of *The Electronic Theory of Organic Chemistry* and a stunning 1952 series of six back-to-back articles in the *Journal of the American Chemical Society* that explained the implications of molecular orbital theory in organic chemistry. Elected a fellow of the American Academy of Arts and Sciences in 1966, and a member of the National Academy of Sciences soon after accepting U.S. citizenship, Dewar was also named an honorary fellow of Balliol College (Oxford) and of Queen Mary and Westfield College (University of London).

Despite his dislike of flying, Dewar accepted 32 named lectureships and visiting professorships around the world and served as a stimulating consultant to industry both in the United States and abroad. His list of professional society awards serves as a nearly complete list of those available to organic chemists:

1954	Tilden Medal of the Chemical Society
1961	Harrison Howe Award of the American Chemical Society
1974	Robert Robinson Medal, Chemical Society
1976	G. W. Wheland Medal of the University of Chicago (first recipient)
1977	Evans Award, The Ohio State University
1978	Southwest Regional Award of the American Chemical Society
1982	Davy Medal, Royal Society of London
1984	James Flack Norris Award of the American Chemical Society

1986	William H. Nichols Award of the American Chemical Society
1988	Auburn-G. M. Kosolapoff Award of the American Chemical Society
1989	Tetrahedron Prize for Creativity in Organic Chemistry
1990	World Association of Theoretical Organic Chemists Medal
	Chemical Pioneer Award, American Institute of Chemists
1994	American Chemical Society Award for Computers in Chemistry

As a recipient of the Davy Medal, he is one of only six Americans to have been so selected. But his principal personal reward was in the achievements of his more than 50 doctoral students and 60 postdoctoral fellows, whose collaborative work is reflected in the more than 600 refereed scientific papers and 8 books that Dewar published.

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