Professor Henry J. Shine

A Tribute

Henry J. Shine was born on January 4, 1923, in a district of London, England, known as the East End. Like the East Side of New York, the East End had a working class population. His schooling began at the Stepney Jewish Boys School, in 1926. The system in England at that time was for working-class children to leave elementary school at the age of 14 and begin a working life, unless they did well enough in the exam for 11-year olds to go to either a Central or Secondary School (higher standard) for continuing education. From Stepney Jewish Boys School, Shine went in 1934 to Mile End Central School, a school of high caliber in which children began learning German, chemistry, botany, geography, English literature and even Greek mythology from age 11 on. In 1936, however, his family moved from the East End to the West End, a more sophisticated, commercial part of London, close to the cinema and theatre businesses, and with the move came a new school, the Lyulph Stanley Central School. Lyulph Stanley provided excellent teaching in German, chemistry, physics, and math, as well as carpentry and metalwork, but, nevertheless, did not expect its working-class students to go further in education.

Shine left Lyulph Stanley in 1938 to go to work as a clerk, first with an import-export firm in the City of London, where his ability in German got him a job, and later with Warner Brothers and First National Films in Wardour Street, within walking distance of his home. In the film company's offices, Shine was a member of the rentals team, keeping accounts of the weekly film rentals from cinemas throughout the country. Keeping accounts meant being able to tally rapidly columns of rentals in pounds, shillings and pence by eye (no calculators), a feat that Shine can still perform even if the old sterling currency is obsolete. During these jobs, Shine continued schooling at evening classes, planning to take the national examinations to become a civil servant. Lacking any form of parental guidance in careers, Shine had decided to follow his schoolmates, the Doggett twins, in studying for the civil service. The outbreak of war in September, 1939, ended that ambition, because the national exams were called off. The war and work with Warner Brothers were the turning points that led Shine into chemistry, however.

On the day (September 3, 1939) war was declared by Great Britain, the Shine Family moved from what was thought to be a precarious location in Charlotte Street, in London's West End, to the village of Sunbury-on-Thames, a peaceful place 17 miles up river from London. That move turned out to be a misjudgement in one respect, because Charlotte Street was untouched in subsequent bombing, whereas parts of Sunbury close to Shine's home were destroyed by bombers following the river on moonlit nights. The move was propitious in another respect, because Warner Brothers abandoned London in the early stages of bombing and moved its offices to the film studios at Teddington, coincidentally a few miles from Sunbury, also on the Thames. When bombing of London became so commonplace as to be acceptable, however, Warner Brothers moved back to Wardour Street, but Shine chose not to go. Instead, he sought a new job from the local Labour Exchange (Employment Commission) and, because he had studied chemistry in school, was offered a job as a laboratory assistant with Macleans, the makers of a well-known toothpaste. There, by happenstance, began Shine's career in chemistry.

In the lab at Macleans were young men who were studying at night school for degrees in chemistry, albeit external degrees for students who could not attend full-time classes. This was an entirely new world to Shine, having no knowledge whatsoever of universities and for whom Oxford and Cambridge had been, until then, a boat race held every year between light- and dark-blue crews on the river Thames. Shine began such studies, also at night school, with the courses for the Intermediate B.Sc. Certificate (called by the tongue-in-cheekers the Inter Course). In 1940, Shine moved from Macleans to Pears, the makers of transparent soap and other cosmetics, located in Isleworth nearer to Sunbury, continuing studies at Twickenham Technical College at night, and later at weekends when nightly bombing became too severe to hold classes safely. The work at Pears was a dream in analytical chemistry for Shine, and included a daily climb to the water tower to take samples for softness measurements. It was in the Pears lab that Shine learned, with the appearance of a university summer intern (John Bush), that students could go full time to a university and did not necessarily have to work for a living.

In 1941, having become 18, Shine received his draft notice. He appeared before the draft board in London to ask for a deferment of six months to finish the Inter Course, only to be told

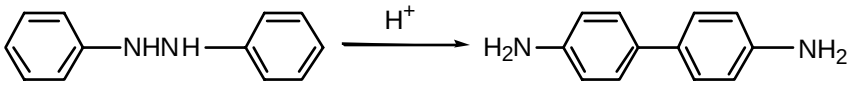
that he could not only have six months, but a further two years if he would go the university full time for a degree in chemistry. To do that required financial support, unavailable at home. But, a grant from Middlesex County, in which Sunbury was located, and a loan from the Society of Friends took care of that problem. That is how Shine became a university student. He was accepted by University College, London, the home of Ingold and Hughes, evacuated at that time to University College of Wales in Aberystwyth, on the west coast of Wales, remote from the war's bombings. It was an ideal place to study and learn. From UCL, Shine received a B. Sc. with 1st Class Honours in 1942. Appearing again before the draft board and expecting to be drafted, Shine was told that, to the contrary, he was to find a job in chemistry, where he could put to use the degree he had been allowed to pursue, an extraordinary enlightened attitude for those times. Shine found a job with Shell Oil Co. in its lubrication labs in the small town of Hook, near to his home on the Thames.

The work with Shell turned out to be boring and undemanding and Shine looked for a way to make a change. That came with the chance to do a wartime project with Prof E. E. Turner at Bedford College for Women, situated idyllically in Regents Park in London. Turner had a grant for the synthesis of pure hydrocarbons, supported by one of the Ministries and Anglo-Iranian Oil Co. (later British Petroleum). The idea was to make hydrocarbons of known structure and to characterize them with infrared spectroscopy, at Cambridge University. That was before the days of nmr spectroscopy and gas chromatography. The project was linked with the analysis of German jet fuels, new to the British. EET turned the project over to Shine, with the instruction to work out a way to make a given class of simple hydrocarbons. That was accomplished with an undergraduate's knowledge of chemistry, namely Grignard reactions to make alcohols, non-isomerizing dehydrations, and subsequent hydrogenations.[1,2] But, in the preparations of alcohols, Shine learned that Grignard reactions weren't as straightforward as textbooks made out. Instead, enolization, condensation and reduction of ketones were encountered, and that became the focus of Shine's investigations.[3,4] It was those reactions that formed the basis of a Ph. D. dissertation and led, eventually, to Shine's move to the U. S. A.

Shine had a mission "to solve the mechanism of Grignard reactions" and to do that he felt that he had to go to Iowa State College in Ames, Iowa to work with the world-eminent organometallic chemist, Henry Gilman, which he did in January of 1948. In retrospect, it was a hopeless mission, because neither Shine nor Gilman had any knowledge of electron-transfer reactions or of epr spectroscopy, both of which proved essential in later years for such a mission. The mission was hopeless in other respects. Henry Gilman was no longer really interested in the Grignard reaction, and when Shine arrived in Iowa, Gilman was in California having retinal surgery, surgery that was to keep him away from the chemistry building for many months. He and Shine parted company eventually after falling out over whose chemistry should be studied, Gilman's or Shine's.

The mission to Iowa was a boon in other respects. While Gilman was kept away from the chemistry building with retinal trouble, and before he parted company with Shine, he assigned Shine to look after his large research group of graduate students and other postdocs.

That proved to be invaluable training in helping research students. Also, because Gilman had been the only organic teacher in the department, another was hired, George Hammond, and it was a boon for Shine to meet him. Having been dismissed by Gilman, Shine was given financial support by the Department Head, Ralph Hixon, enabling a continuation of the Grignard reaction study.[5] In return for that support, Shine took on a quiz section in undergraduate organic chemistry, in the course of which an undergraduate asked how the benzidine rearrangement took place, a question that neither Shine nor Hammond could answer and one that set both of them on years of research in benzidine reactions. The story has been recorded in detail.[6,7] At Iowa State University, at Hammond's suggestion, Shine undertook to measure the kinetic order in acid of the rearrangement of hydrazobenzene, a task that appeared to have been overlooked by others. The result was the now seminal discovery of second-order acid kinetics.[8] The benzidine rearrangement was to play a large role in Shine's research life when he joined Texas Tech in later years.



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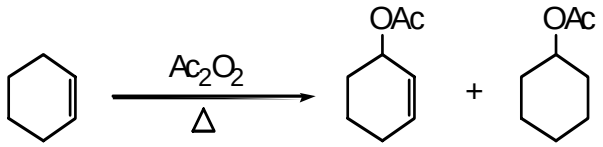
From Iowa State, Shine went, in 1949, to a postdoctoral fellowship with Carl Niemann at the California Institute of Technology in Pasadena, California, doing kinetics in the chymotrypsin-catalyzed hydolyses of tyrosineamide. From there, in the fall of 1951, he joined the United States Rubber Company, in Passaic, New Jersey. U. S. Rubber had done pioneering studies in free radical polymerizations in the hands of prominent researchers, such as Frank Mayo, Cheves Walling, and F. M. Lewis. The atmosphere for fundamental research was diminishing in 1951 after the free radical group had mostly dispersed, but still prevailed to some extent in the group of Pliny O. Tawney , managed by Robert H. Snyder. Shine worked in that group for three years, studying mainly the free-radical oxidation of hydrocarbons in acid anhydride solutions.[9,10]

In 1954, however, recognizing that industrial chemical research was not his cup of tea, Shine left U. S. Rubber to go to do his own thing at Texas Technological College (now Texas Tech University) in Lubbock, Texas. Shine relates, that having accepted a position at Texas Tech, sight unseen at the 1954 ACS National Meeting in New York, he had to go to the library on 42nd Street to find a map large enough to show Lubbock's location. He stayed at Texas Tech thereafter.

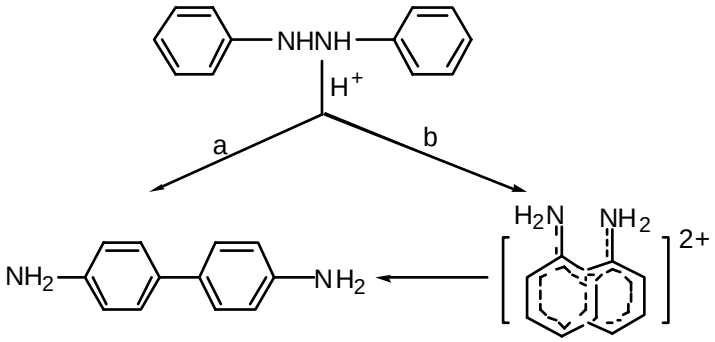
Texas Tech in 1954 was primarily an undergraduate college in which teaching loads were extraordinarily high, a way of life that didn't bother Shine because he was unaware of any other way. The Department Head at that time, Joe Dennis, had the ambition to build a research and graduate department, and Shine and William Wesley Wendlandt, later to become recognized internationally for his work in thermal analysis, were the first of Dennis' choices to try to do that.

Shine began research, himself, on the thermal rearrangement of hydrazonaphthalenes,[11] while students and postdocs took up the reactions of acetyl peroxide in cycloalkenes, work that

followed from the oxidation studies at U. S. Rubber, and from which the unexpected involvement of the acetoxy radical, thought until then to be too short-lived to survive for reaction, was deduced.[12,13]



The studies of the acid-catalyzed and thermal benzidine rearrangements continued over many years. The discovery of second-order acid kinetics by Shine and Hammond triggered a resumption of studies of the benzidine rearrangements in other laboratories, particularly by the world-renowned groups of Ingold and Hughes, on the one hand, and M. J. S. Dewar on the other. A controversial standoff emerged as to whether the rearrangements were all concerted (path a, Ingold and Hughes) or were stepwise reactions involving π-complexes (**2**, path b, Dewar). That controversy was settled only in the 1980s in Shine's labs at Texas Tech where, with nitrogen and carbon kinetic isotope effects, it was shown that benzidine rearrangements, both acid-catalyzed and thermal, were sigmatropic, controlled by the dictates of orbital symmetry.[6,14]



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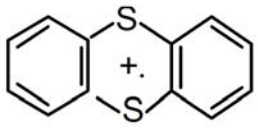
That is, some are indeed concerted, whereas others, such as the ortho-semidine rearrangement, are not. The successful application of heavy-atom kinetic isotope effects to the benzidine rearrangements led to their use in other rearrangements and reactions, such as the nitramine, photo-Wallach, photo-Fries, Smiles, quinamine, and Claisen rearrangements,[15] and the Diels-Alder reaction.[16]

His interest in the rearrangement of hydrazobenzene was also the cause of Shine's entry into organosulfur and cation radical chemistry. Soon after beginning at Texas Tech, he began asking if diphenyl disulfide, the sulfur analogue of hydrazobenzene would undergo acid catalyzed rearrangement.[17] That quest proved to be fruitless in itself, but led by serendipity to the thianthrene cation radical and many years of cation radical studies, studies which are still going on today.

When diphenyl disulfide dissolves in concentrated sulfuric acid, the acid that was used to promote the rearrangement, a deep purple solution is formed. Shine set out to find why the solution was purple, a quest that took several years and a venture into epr spectroscopy. The purple colour was that of the thianthrene cation radical. In concentrated sulfuric acid, diphenyl disulfide is converted in part into thianthrene that is subsequently oxidized by the acid to its cation radical. This was deduced by Shine in 1960, but proved only with the help of epr spectroscopy with Lawrence Piette at Varian Associates in Palo Alto, Calif.[18]



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The story of the discovery of the thianthrene cation radical has been written for the 50th anniversary of the discovery of epr spectroscopy.[19] From that beginning have come more than 90 publications in ion radical and related chemistry. The early work concentrated on epr spectroscopy, to characterize the new cation radicals of substituted thianthrenes, after which studies of the reactions of thianthrene and other aromatic cation radicals with a large variety of reactants followed.[20] They continue until the present time.[21].

After joining Texas Tech as Assistant Professor in 1954, Shine was promoted to Associate Professor (1957) and Professor (1960). He served as Chairman of the Department of Chemistry (1969-1975). In 1968, he was designated Paul Whitfield Horn Professor, the highest recognition afforded a faculty member by Texas Tech University.

At Texas Tech University, Shine has received the Faculty Research Award (1982), the Texas Tech Dads Association Distinguished Faculty Research Award (1983), the President's Academic Achievement Award (1991), and the Texas Tech Dads and Moms Association Faculty Distinguished Leadership Award (1994). He received a Senior Distinguished U. S. Scientist Award from the Alexander von Humboldt Foundation in 1986. His research work has been supported by the Research Corporation and the Petroleum Research Fund and, for many years, by the National Science Foundation, the Air Force Office of Scientific Research, and the Robert A. Welch Foundation. From The Welch Foundation, Shine has received support continuously since 1955. From this research has come nearly 200 publications and the book "Aromatic Rearrangements" Elsevier, 1967.

Shine began half-time teaching in the fall of 1996 and retired from his teaching position fully in 1999. He was then designated Paul Whitfield Horn Professor Emeritus and Research Professor at Texas Tech, continuing his research in cation radical chemistry.

Shine married Sellie Schneider in New York City on June 14, 1953, and lived happily ever after. The Shines have two children, Stephanie, who, with husband Hamid and two children, Naomi and Leah, lives in Lubbock, and Trevor, who, with wife Melanie and daughter, India, lives in England.

On a personal note, it was Henry Shine who hired me into the Department of Chemistry at Texas Tech University in 1974. Since then I have enjoyed his chemistry and friendship. It is my pleasure to serve as Facilitator for the Henry J. Shine Commemorative Issue of *ARKIVOC*.

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