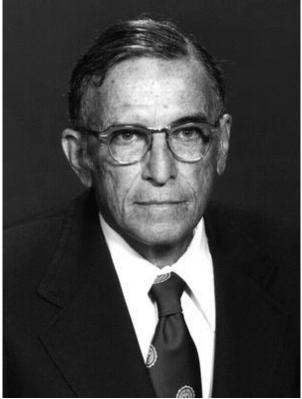


BIOGRAPHICAL MEMOIRS



M. J. herma

Melvin Spencer Newman March 10, 1908 — May 30, 1993 By Leo A. Paquette and Milton Orchin

Courtesy of the Ohio State University

EVERY UNDERGRADUATE STUDENT ENROLLED in a course dealing with organic chemistry is quickly made familiar with the Newman Projection, named after Melvin Newman, because this method of representing the geometry of organic molecules appears in practically every text of organic chemistry. As originally suggested by Newman in 1952, this technique involves looking down the bond between two connected (sp $^3$ -hybridized) carbon atoms and projecting the three-dimensional structure around this bond onto a plane surface. For example, the simple two-carbon compound ethane is represented in a line formula by CH<sub>3</sub>-CH<sub>3</sub> and

conventionally by the side-on perspective (sawhorse) formula (see A below). The arms of the Y and the inverted Y are understood to represent the six hydrogen atoms, the points at the intersection of the arms represent the carbon atoms, and the diagonal line connecting the Y's represents the carbon-carbon bond. In the Newman projection (see B below) the view of the molecule is not from the side but rather down the C-C bond axis so that the front carbon eclipses the rear carbon. Then to bring the formula onto the plane of the paper as shown, one imagines that the two Y's of (A) are squashed together, that is, the front inverted Y (CH $_2$ ) is

projected backward and the rear Y (CH<sub>3</sub>) is projected forward to the plane of the paper to give the plane projection formula (B),

the Newman Projection. Here the front carbon is represented by the intersection of the three arms of the front Y and the rear carbon, which is eclipsed by the front one imagined to be at the center of the rear circle. Hence the spatial relation between the two carbons (which is in front and which is in back) is defined and thus a major problem with plane projections is finessed. The Newman projection is not only admirably suited for assessing steric effects but is also useful for analyzing symmetry properties. Thus the formula (B) readily reveals that the (inferred) carbon-carbon bond axis in ethane is not only a three-fold rotational axis but more importantly is a six-fold alternating axis ( $S_6$ -in symmetry notation) as well, thus accounting for the equivalency of all six

hydrogen atoms and the fact that only one mono-substitution product of ethane is possible.



Melvin S. Newman, a member of the National Academy of Sciences since 1956, died on May 30, 1993, in Columbus, Ohio, at the age of eighty-five. Thus ended the long and productive career of an enthusiastic and inspiring teacher and an outstanding pioneer in the fundamental development of organic chemistry for more than five decades. His lasting contributions to research and to Ohio State University with which he was associated for fifty-seven years were instrumental in maintaining excellence at his adopted institution. Mel's enormous impact was prominently recognized by naming the most recent building addition to the chemistry department the Newman-Wolfrom Laboratory.

Melvin Spencer Newman was born on March 10, 1908, in New York City, the fourth and last child of Jacob Kiefer Newman and Mae Polack Newman. His father made a specialty of reorganizing companies in financial difficulty to satisfy the claims of different stock and bond holders. Shortly after Mel's birth, the family moved to New Orleans, Louisiana. There he attended the Isadore Newman Manual Training Academy, a school founded by his paternal grandfather. Mel's chief interest as a child was in sports, except for membership in a short-lived chemistry club, where his chief activity, as he put it, "was to mix gun powder and deposit same in envelopes on street car tracks."

When he was fourteen years old, his family moved back to New York City where he missed his friends and street play. For his high school education, he attended Riverdale County School. Recognizing Mel's precocity, his parents secured a private chemistry tutor for him who did much to stimulate Mel's interest in the field. After graduating from Riverdale in 1925, he enrolled at Yale University and received his B.S. degree magna cum laude in 1929. He excelled in mathematics and chemistry, and particularly enjoyed a semester reading and studying Shakespeare. During this time, he developed an absorbing interest in music both classical and jazz. He was particularly fond of New Orleans jazz and a great admirer of Louis (Satchmo) Armstrong, with whom he became very friendly later in his career. His early life in New Orleans left indelible impressions, including an accent and way of speaking associated with that fascinating city.

One of Mel's loves while at Yale was golf, a sport at which he was notably skillful, having once played in the National Intercollegiate Tournament. Although discouraged from continuing his graduate work at Yale, he insisted on advancing his studies there, one reason being that no other university that he considered going to had a golf course. He even offered to pay his own tuition at Yale rather than receive a fellowship, an offer he soon rescinded after learning that his father had lost his money in the Wall Street crash of 1929 and could no longer support him.

Mel Newman completed his graduate studies in three years and received his Ph.D. degree at Yale in 1932 (Fleischman fellow, 1930-32) for research conducted on the chemistry of lipids under the direction of Professor Rudolph J. Anderson. Thereafter he accepted three postdoctoral fellowships in sequence. The first, supported by the National Tuberculosis Association was held at Yale (1932-33). He then joined Columbia University as a National Research Council fellow (1932-33) and then Harvard University as an Eli Lilly fellow (1934-36). This last position, spent in the laboratories of Professor Louis Fieser, initiated Mel's long-lasting interest in the field of polycyclic aromatic hydrocarbons.

His independent academic career began in the fall of 1936 as an instructor at Ohio State University, where he remained during his entire professional career. In 1940 he became an assistant professor and in 1944, in an unprecedented promotion, was awarded full professorship status.

Melvin Newman was married on June 30, 1933, to Beatrice Naomi Crystal of New Rochelle, New York, the daughter of a very successful retail merchant of women's fashion wear. Bea's reputation as a most gracious hostess caused the Newman home to be a popular meeting place for visiting scientists, faculty, and students. The Newmans had four children: Anthony Kiefer, Susan Crystal, Beth Clair (deceased), and Robert Melvin.

# PROFESSIONAL HISTORY

Newman's interest in steric effects and what he called "overcrowded" molecules was a central theme during his entire research career and resulted in many seminal contributions to the elucidation of reaction mechanisms and an appreciation of the chiral properties of various types of molecules. The book *Steric Effects in Organic Chemistry*, which he edited in 1956, integrated a great variety of phenomena whose understanding was facilitated by the consideration of steric effects and was thus of great service to the chemical community.

One of the most enduring of Newman's research interests involved the synthesis and properties of substituted 1,2benzanthracenes and related compounds. His very first publication from Ohio State University (1937) was entitled "The Synthesis of 1,2-Benzanthracene Derivatives Related to 3,4-Benzpyrene." One of the last of his many papers written approximately half a century later (1986) was a contribution in the same series entitled "An Unusual Synthesis of 5-Methoxy-7,12-dimethyl-1,2benzanthracene." His interest in polynuclear aromatic compounds was sustained by the practical importance of these substances to the understanding of their carcinogenic activity, as well as by the scientific drive to understand the profound influence of steric interactions on structure and properties.

Newman's interests were not confined to the carcinogenic properties of the polycyclic hydrocarbons. Such compounds also provided a venue for some of his most impressive work on steric effects. One of the early triumphs of Mel's work was the synthesis of 4,5-dimethylchrysene. Predictions had been made that this hydrocarbon would not be amenable to synthesis because of the extreme overcrowding of the methyl groups and the necessity that the four benzene rings remain coplanar because of pi electron delocalization. Mel proceeded to demonstrate that the rings in this and related compounds were indeed bent and furthermore that such structures should be chiral.

The developments to follow attracted international acclaim. In 1955 Newman demonstrated the capacity to sustain optical activity by synthesizing and resolving hexa-helicene. The absence of functionality on this structurally unusual hydrocarbon required that resolution be accomplished in a novel manner. Through charge transfer complexation with a tetranitrofluorenyl derivative,

diastereomeric complexes were generated and then successfully separated. The enantiomers proved to have unusually high specific rotation ([a] > 3700°). Hexahelicene became the first member of a new class of aromatic hydrocarbons that coil to form a helix.

Once it became clear that the metabolic dihydrodihydroxy epoxides of the aromatic polynuclears rather than the hydrocarbon precursors themselves were the carcinogens, and that the activity was associated with certain regions of these hydrocarbons, Mel was stimulated to synthesize 7,11,12-trimethyl-1,2-benzanthracene. This specifically targeted compound proved to be one of the most potent hydrocarbon precursors to carcinogenic activity ever synthesized.

During the course of developing required synthetic methodology, Newman encountered some unusual esterification behavior of *o*benzoylbenzoic acids and their analogs. He found that normal acid-catalyzed esterification gave cyclic esters. About this time, L. P. Hammett published his seminal book *Physical Organic Chemistry*. Stimulated by some of the results described therein involving 100%  $H_2SO_4$ , Mel undertook a series of studies in which a variety of oxygen-containing structures were dissolved in this solvent

and the number and kind of various ionic species present were deduced from the cryoscopic behavior. With characteristic enthusiasm, he addressed the question of how this information could be usefully applied to synthetic problems with the result that anyone wishing to esterify highly hindered acids, which are resistant to normal esterification, now uses his methodology of dissolution in 100%  $H_2SO_4$  followed by quenching with the alcohol of choice.

Newman was among the first to propose the existence of vinyl carbocations, as he was seeking to rationalize the course of reactions of oxazolidinones with base. When Jack Hine suggested that the results could also be explained by the intermediacy of unsaturated carbenes, the end products of vinyl carbocation deprotonation, Mel proceeded to show that Hine was correct by preparing such intermediates and demonstrating their utility.

Melvin Newman had a long and productive career. His articles are concise, clear, and direct. His writing and lectures were the embodiment of Albert Einstein's admonition: "Everything should be made as simple as possible but not simpler." As a consequence, he was a popular and much sought-after lecturer and gave hundreds of invited seminars in the United States and around the world. For his scientific contributions, Mel received many high honors, including the American Chemical Society Award for Creative Work in Synthetic Organic Chemistry (1961), the Morley Medal of the Cleveland Section of the American Chemical Society (1969), the Wilbur Lucius Cross Medal of Yale University (1975), an honorary doctor of science from the University of New Orleans (1975), the Columbus Section American Chemical Society Award (1976), and the Sullivant Medal, the highest award bestowed by Ohio State University (1976).

## **REMINI SCENCES**

Mel was known and respected for his warm openness, his infectious enthusiasm, and his complete integrity. In addition to his passion for golf and chemistry (he often remarked how fortunate he was to be paid for something that he loved to do), Newman took very special interest in family, students, music, food, and humor. His beloved children vividly recall the pungent chemical odors that they detected coming from his ties and accordingly his Hawaiian shirts were never viewed by them as smelling of exotic flowers. Mel always encouraged his children to hard work and implanted in them a strong pursuit of their personal interests without being intrusive.

He was held in great affection by his many students, and deservedly so because he cared deeply about them both professionally and personally. Mel had a fervent love for hands-on laboratory work, at which he was very proficient, and he inspired his associates along these lines. He would take great delight in watching his students mature. Sometimes he took over at the bench with his own hands with phrases such as "If I were running that reaction, I'd do it this way." At other times, he could be heard saying "The crystals are great, but what about the yield?" He was fascinated by crystals and continued work in the laboratory to the very end.

The sounds that came from his study were either classical or jazz-oriented. His order of preference was Louis Armstrong, Prokofiev, and Bach; the Newman collection of Armstrong recordings was unrivaled. In mid-1953 Armstrong was playing in Columbus, the date overlapping with a visit by Robert Woodward to Ohio State to give a lecture series on the tetracyclines. Mel made certain that Woodward and Ian Scott, a postdoctoral in the Newman group at the time, attended an engagement, after which they were escorted backstage for a personal encounter with Satchmo. The next day, Mel in his introduction to Woodward's final lecture described the encounter:

Mel: "Louis - I'd like you to meet Professor Woodward from Harvard. He is to chemistry what you are to jazz."

Louis: "Gee! Mr. Newman - this cat must really be something!"

Newman loved good jokes, and he remembered many. He particularly delighted with clever twists of words. His laugh was especially memorable.

Over the years, he developed a laboratory course for advanced students and incorporated the series of recommended experiments in a book (1972). Among the dedications was one to his beloved wife Bea, "who can always control my reactions."

THE AUTHORS ARE VERY grateful to Beatrice Newman, Kiefer Newman, Susan Crystal Newman Katz, and Professor A. I. Scott for providing relevant background material for this biography.

# SELECTED BIBLIOGRAPHY

## 1937

The synthesis of 1,2-benzanthracene derivatives related to 3,4-benzpyrene. *J. Am. Chem. Soc.* 59:1003.

## 1940

The synthesis of 5-methylchrysene and related compounds. J. Am. Chem. Soc. 62:870.

## 1941

A new method for the esterification of certain sterically hindered acids. *J. Am. Chem. Soc.* 63:2431.

# 1945

With H. G. Kuivila and A. B. Garrett. Normal and complex ionization of organic molecules in solvent sulfuric acid. (I). Methyl 2,4,6-trimethyl-benzoate; <u>o</u>-benzoylbenzoic acid and its normal and pseudo methyl esters. *J. Am. Chem. Soc.* 67:704.

### 1947

With A. S. Hussey. Optical activity from a new type of steric hindrance. *J. Am. Chem. Soc.* 69:978.

## 1948

With W. B. Wheatley. Optical activity of the 4,5-phenanthrene type: 4-(1-methylbenzo[<u>c</u>] phenanthylacetic acid and 1-methylbenzo[<u>c</u>] phenanthrene. *J. Am. Chem. Soc.* 70:1913.

### 1949

With R. A. Craig and A. B. Garrett. The behavior of oxygenated compounds in acid media. *J. Am. Chem. Soc.* 71:869.

### 1950

With H. K. Connor. Steric hindrance: Some reactions of mesitylacetylene. *J. Am. Chem. Soc.* 72:4002.

### 1951

With N. C. Deno. Aryl carbonium ions in sulfuric acid. J. Am. Chem. Soc. 73:3644.

# 1952

A useful notation for visualizing certain stereospecific reactions. Rec. chem. prog. 13:111.

# 1953

With H. V. Anderson and K. H. Takemura. The synthesis of polynuclear aromatic hydrocarbons. II. Methylbenzo[c]phenanthrenes. *J. Am. Chem. Soc.* 75:347.

### 1954

With W. M. Edwards. New reactions involving alkaline treatment of 3-nitroso-2-oxazolidones. II. J. Am. Chem. Soc. 76:1840.

## 1955

With W. B. Lutz and D. Lednicer. A new reagent for resolution by complex formation: The resolution of phenanthro[3,4,<u>c]</u> phenanthrene. *J. Am. Chem. Soc.* 77:3420.

## 1956

With others. Synthesis of hydroaromatic compounds containing angular methyl groups. V. Equilenin series. *J. Am. Chem. Soc.* 76:2331.

With W. B. Lutz. α-(2,4,5,7-Tetranitro-9-fluorenylidine aminoxy)-propionic acid. A new reagent for resolution by complex formation. *J. Am. Chem. Soc.* 78:2469.

With D. Lednicer. The synthesis and resolution of hexahelicene. J. Am. Chem. Soc. 78:4765.

## 1957

With A. W. Weinberg. Pyrolysis of 3-nitroso-5,5-disubstituted-2-oxazolidones. *J. Am. Chem. Soc.* 79:2814.

### 1958

With R. J. Harper, Jr. Kinetic and equilibrium studies of cyclic ketal formation and drolysis. *J. Am. Chem. Soc.* 80:6350.

## 1962

With D. Pawellek and S. Ramachandran. Synthesis and reactions of 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone. *J. Am. Chem. Soc.* 84:995.

### 1964

With J. Blum. The synthesis and ionization constants of the six aminobenzo[c]phenanthrenes. *J. Am. Chem. Soc.* 86:1835.

### 1966

With C. Courduvelis. Reactions proceeding by the [3.2.1] bicyclic path. *J. Am. Chem. Soc.* 88:781.

### 1968

With others. Synthesis and polarographic reduction of strained phenanthrenequinones. The buttressing effect. *J. Am. Chem. Soc.* 90:458.

### 1974

With D. R. Olson. A new hypothesis concerning the reactive species in carcinogenesis by 7,12dimethylbenz[a]anthracene. The 5-hydroxy-7,12-dimethylbenz[a]anthracene-7,12dimethylbenz[a] anthracene-5(6<u>H</u>)-one equilibrium. *J. Am. Chem. Soc.* 96:6207.

### 1979

With V. K. Khanna and K. A. Kanakarajan. A novel synthesis of 7-fluorobenzo[a]pyrene involving two new molecular rearrangements. *J. Am. Chem. Soc.* 101:6788.

With A. Kumar. An unusual synthesis of 5-methoxy-7,12-dimethylbenz[a] anthracene. J. Org. Chem. 51:2379

**Biographical Memoirs** 

National Academy of Sciences