BIOGRAPHICAL MEMOIRS

Nicholas Turro

May 18, 1938–November 24, 2012
Elected to the NAS, 1981

A Biographical Memoir by Ronald G. Lawler and Vaidhyanathan Ramamurthy

Nick Turro was one of the most productive and innovative chemists of his generation. His genius lay in his ability to recognize new ways of bringing modern experimental techniques, usually involving photochemistry, to bear on problems in organic chemistry, biochemistry, and materials science. He was the author or co-author of more than 1,000 publications. He was a master in attracting other scientists to contribute their expertise and instrumentation to his research problems. In addition to mentoring more than 400 students and postdoctoral associates, he collaborated with at least 100 scientists from all over the world. One of his last publications had twenty-one co-authors from eight laboratories in five countries. He was the recipient of numerous awards, including the American Chemical Society Award in Pure Chemistry (1974), the Arthur C. Cope Award (2011), the E. O. Lawrence Award from the U.S. Department of Energy (1982), several awards for his contributions to photochemistry and photophysics, and a National Science Foundation (NSF) Director's Award for Distinguished Teaching Scholars (2002).

Early Life

Nicholas John Turro was born in Middletown, Connecticut, on May 18, 1938. His grandparents were Sicilian and Neapolitan immigrants whose families settled in Middletown in the early part of the previous century. After graduation from Middletown High, Nick entered Wesleyan University, at that time an all-male institution. His interest in science was sparked by his high school teachers, sustained by the Wesleyan chemistry faculty (including Gilbert Burford, Jose Gomez-Ibanez, John Sease, and Don Sebera), and enlivened by clandestine experiments with pyrotechnics. Summers were spent in a Connecticut Water Testing Laboratory working alongside his friend and mentor, the late Peter Leermakers, who graduated from Wesleyan two years before Nick. Nick graduated summa cum laude in June 1960 and followed Peter to the California Institute of Technology (Caltech). Within four years, he had obtained a Ph.D., completed a year's postdoctoral with P. D. Bartlett at Harvard University, and joined the faculty at Columbia University as an instructor. Thus began a career that lasted nearly five decades.

CAREER AS A CHEMIST

It is not often that a young scholar publishes the "bible" on a subject at the beginning of a career, but many of us who followed Nick Turro's contributions to several areas of chemistry considered that this characterization fit him perfectly. Shortly after starting at Columbia, Turro published *Molecular Photochemistry* in 1964.[1] The book made widely available to organic chemists the fundamentals of a rapidly developing new application of the methods of physical organic chemistry. To those of us beginning our own careers in physical organic chemistry at about that time, the book's impact resembled that of Robert B. Woodward's and Roald Hoffmann's *The Conservation of Orbital Symmetry*, published a few years later. *Molecular Photochemistry* was updated and expanded in new editions in 1978 and, with co-authors, in 2010.[2,3] In addition to his books, Turro left a legacy of numerous reviews of his work, including thirteen research summaries published in *Accounts of Chemical Research*, numerous invited perspectives on his research areas, and several short memoirs. In an essay in *Perspectives* published on the occasion of his receiving the Arthur C. Cope Award of the American Chemical Society in 2011, he outlined in some detail the highlights of his career and his approach to research and education.[4] His background and contributions have also been summarized in remarks by former students honoring or memorializing Nick.[5–8] Below we offer a condensed version of the trajectory of Nick's interests and career.

Turro was a master at introducing what was common knowledge in one area of science to a new audience in another. An excellent example, mentioned by him as early as 2004 in an interview, was the existence of the *ortho* and *para* nuclear spin isomers of hydrogen, a phenomenon known to physicists for three-quarters of a century, but, aside from recent applications to studies of catalytic hydrogenation and related reactions via intensity effects in nuclear magnetic resonance, largely ignored by organic chemists.[9] His appreciation of this effect, and the mechanism of conversion between the two forms, was a natural extension of many decades spent studying the singlet and triplet states of organic molecules and the rates of interconversion between them. Shortly thereafter, he and his co-workers began studies of *ortho-para* conversion of hydrogen and eventually water, incorporated in fullerenes, characterizing the environment sensed by encapsulated molecules and the extent to which they communicate with the outside world. [Figure 1]

The distinguishing feature of Nick's preeminent position in the field of photochemistry is that it does not rest upon a single line of inquiry pursued over an extended period of time. Rather it is based on multiple experimental and conceptual contributions—one or two per decade—integrated over time. Nick's scholarly interests were in nine main areas, listed in a rough order of when he began research and publication in each:

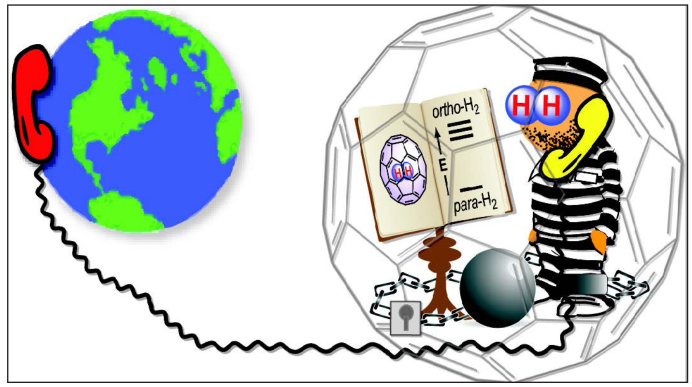

Figure 1 Encapsulated hydrogen communicating with the outside world. (Turro, N.J. et. al, 2010, *Acc. Chem. Res.* 43:335-345; Credit: Judy Chen.)

- Mechanistic photochemistry and photophysics (1960)
- Synthesis and reactions of energy-rich molecules (1965)
- Surface crossings in organic photoreactions (1970)
- Supramolecular photochemistry (1972)
- Magnetic effects and spin chemistry (1978, 1990)
- Chemistry of reactive intermediates (1980)
- DNA as a wire (1985)
- Endofullerene chemistry and physics (2008)
- Philosophy of science and science education (1986)

The theme uniting most of these areas is molecular photochemistry and its associated techniques and theory. Presented below is a brief summary of Turro's contributions in each area. We have attempted to describe the chronological and intellectual progression as he moved from one area to another. A more detailed analysis and chronology was presented by Turro himself in 2011.[10]

MECHANISTIC PHOTOCHEMISTRY AND PHOTOPHYSICS (1960)

In 1960, the year that Nick entered graduate school at Caltech, the field of organic photochemistry had been dominated for decades by the discovery and use of photoreactions as, in effect, another reagent in the toolbox of synthetic organic chemists.[11] With few exceptions, determining the details of photochemical reaction pathways was left to physical chemists and the study of reactions in the gas phase. One of the exceptions was the work of George Hammond, who had recently moved from Iowa State University to Caltech.

On the advice of his friend and fellow Wesleyan student Peter Leermakers, who was already at Caltech, Nick decided to work with Hammond on problems in mechanistic photochemistry. Nick and Peter did the first experiments on triplet-sensitized organic photoreactions, which helped Hammond to establish the concept of triplet sensitization that remains popular and valuable today.[12] This led to a decade of publications by Nick on carbonyl photochemistry under the title *Molecular Photochemistry* that was finally phased out in 1977 after 121 publications.[13] By then, Nick's photochemical research had expanded in too many directions to receive a single label. His work had undergone excursions into the theory of excited states,[14] surface and supramolecular chemistry,[15] and the intersection of inorganic photochemistry and DNA.[16]

SYNTHESIS AND REACTION OF ENERGY-RICH MOLECULES (1965)

During his doctoral research at Caltech, Nick became aware of the potential for using photochemistry to prepare high energy organic molecules, notably those with strained rings. As he later recalled, after joining the faculty at Columbia University he used the study of strained rings as an opportunity to broaden his research interests and establish a research group that included an area less directly related to his thesis work. This led to his preparation and study of cyclopropanone, the smallest cyclic ketone, which until then had only been proposed as a reactive intermediate.[17] The research resulted in nineteen publications in five years.[18] This work also was instrumental in earning him promotion from instructor to full professor at Columbia in five years.

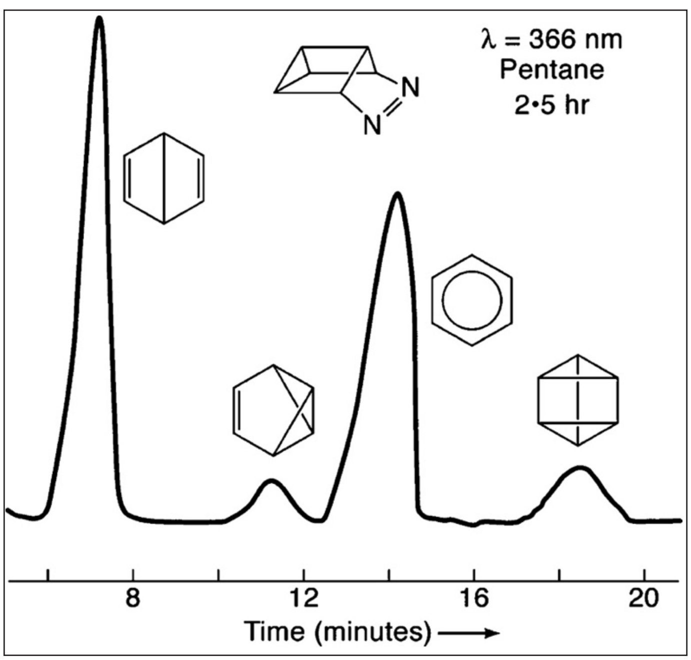

Figure 2 Benzene isomers separated on a GC column at room temperature upon photolysis of a bicyclic azoalkane (Turro, N. J. and V. Ramamurthy, *Rec. Trav. Chim*. 1979, 98:173–178).

Following the success with cyclopropanones, Nick proceeded to synthesize and investigate the chemistry of energy-rich isomers of benzene and dioxetanes. Recognizing the value of collaboration, Nick took the help of Ronald C. D. Breslow and Thomas J. Katz, colleagues in the department, and established the adiabatic photochemistry of isomers of Dewar benzene, benzvalene, and prismane. Elegant studies on dioxetanes established their decomposition to ketones to be a chemiluminescent process, and thermolysis generates products in their excited states. The concepts of upconversion, infrared-induced chemical reaction, and spin-forbidden thermal reactions resulted from the studies on dioxetanes. [Figure 2]

SURFACE CROSSINGS IN ORGANIC PHOTOREACTIONS (1970)

By the 1970s, the number of known photoreactions had begun to expand rapidly. Conditions were ripe for a better answer to questions about how excited molecules give up their energies to yield ground state products. Questions included "At what point along the reaction co-ordinate does electron demotion occur?", "Why do nπ* and ππ* excited states give specific, and often different, products?", and "'What decides whether a photoreaction occurs by diabatic or adiabatic movement on potential energy surfaces?" Nick and Bill Dauben, with the driving force provided by Lionel Salem, developed a classification of photoreactions based on crossings of ground- and excited-state surfaces.[19] In Nick's words: "Both Bill (Dauben) and I were extremely fortunate to take part in a very special intellectual and scientific adventure and collaboration (with Lionel Salem), …"[20] The Salem diagrams (as Turro named them) are meant to be applied to photochemical reactions in the same manner that Woodward-Hoffman correlation diagrams illuminated the pathways of pericyclic reactions.

SUPRAMOLECULAR PHOTOCHEMISTRY (1972)

In the early 1970s, Nick became interested in the possibility of using photoprobes to study the structure and dynamics of micelles and related supramolecular systems. This was an outgrowth of the increasing instrumental capabilities of his lab, including time-correlated fluorescence methods,[21] time-resolved optical excitation-detection techniques, and electron spin resonance. His lab became a center for probing the environment of organized structures as reported by suitably placed probe molecules. This naturally led to exploring supramolecular assemblies as reaction vessels. Photoreactions within micro/nano reaction vessels became an active area of research in Turro group beginning in 1978. Dibenzyl ketone (DBK) became a key molecule, the "cage effect" the key concept, and *paradigm* the key word for Nick's research in this area, which expanded over the next decades to include micelles, zeolites, silica surfaces, polymers, dendrimers, and colloids, among others, as micro/nano reaction vessels.

Spin Chemistry and Magnetic Effects (1978)

In the late 1960s, the phenomenon of chemically induced dynamic polarization was discovered during the study of fast, high-energy reactions using electron spin resonance and nuclear magnetic resonance, termed CIDEP and CIDNP, respectively.[22,23,24] Within a few years, it became clear that the majority of these effects could be explained by a mechanism involving the influence of internal and external magnetic fields, including those from magnetic nuclei, on the electron-spin dependence of the reactivity of pairs of free radicals.[25,26] Interestingly, George Hammond was one of the first organic chemists to explore experimentally the influence of electron spin on free radical yields via "cage effects" of the sort invoked in the radical pair mechanism.[27]An important new direction in supramolecular photochemistry came to fruition when Nick realized that nuclear spins may strongly influence the rate and efficiency of a chemical reaction. Indeed, Turro and Bernhard Kräutler soon demonstrated such a magnetic isotope effect (MIE) via the considerable enrichment of dibenzyl ketone with a ^{13}C-labelled carbonyl group during photolysis of an aqueous micellar solution of the ketone at room temperature, a phenomenon strongly influenced by the application of an external magnetic field. This finding triggered a range of important and fundamental studies in the Turro lab, in which magnetic isotope and magnetic field effects were analyzed more deeply. In the next decade, Nick's laboratory pioneered the application of magnetic polarization and magnetic field effects to infer the environment of radical pairs in supramolecular and solid matrices.

Nick's entry into the field was influenced by his association with Anatoly Buchachenko, whom he called his "spin doctor." The collaboration began in 1990 and resulted in more than two decades of collaboration that helped define and expand the field of spin chemistry. In the opinion of the two authors of this memoir, the work on photo-initiated spin chemistry using time-resolved EPR and the MIE is one of Nick's crowning achievements.

Chemistry of Reactive Intermediates (1980)

In 1980, Nick constructed, for the first time, a single laboratory with nanosecond systems capable of employing analysis of transients produced by pulsed lasers by a complete range of spectroscopic methods including UV/VIS absorption or emission, resonance Raman spectroscopy, IR, NMR, and ESR (including CIDNP and CIDEP). Using these powerful techniques, he pioneered systematic investigations of reactive intermediates such as carbenes, biradicals, ylides, radical pairs, and singlet oxygen generated in homogeneous solutions and in supramolecular assemblies. During this time, he moved into previously unexplored areas for which the methodology of physical organic chemistry proved to be of enormous potential: the development of a systematic approach to structure-reactivity relations in reactions in homogeneous solution and supramolecular systems.

DNA as a Wire (1985)

Nick's interest in electron transfer and supramolecular chemistry including polymers led him to explore DNA as a medium for electron transfer. The presence of Jacqueline K. Barton in the department at Columbia led to a vibrant collaborative program that prompted them to conclude "DNA is a wire." As Jackie recalled,

> "We began to study DNA-mediated electron transfer. At first neither of us thought that the charge transport was going through the DNA helix, but we did more and more experiments on faster and faster timescales to learn that indeed the reaction was DNA mediated. As the chemistry was getting more interesting, I moved to Caltech. But the collaboration continued. As the work became more interesting, it also became quite controversial. What we were seeing was quite different than had been seen with electron transfer in proteins, both with respect to the distance over which the electron was transported, and the time scale. But the controversy didn't bother Nick at all. He just concentrated on the data and doing more experiments with faster and more sensitive instrumentation. At one point, he suggested we write a paper entitled "Paradigms, Supermolecules, Electron Transfer and Chemistry at a Distance. What's the Problem? The Science or the Paradigm?" Nick wrote the title and asked me to write the full paper. But the title really reflected how Nick felt."[28]

Endofullerene Chemistry and Physics (2008)

As mentioned above, in about 2004 Nick became interested in the analogy between excited-state intersystem crossing, the radical-pair mechanism of spin chemistry, and the interconversion of the *ortho* and *para* spin states of hydrogen and other small molecules. He was fascinated to discover Adalbert Farkas's 1935 book *Orthohydrogen, Parahydrogen and Heavy Hydrogen* and was quick to remember that Werner Heisenberg's Nobel Prize citation included the statement "… for the creation of quantum mechanics, the application of which has, *inter alia*, led to the discovery of the allotropic forms of hydrogen."

A perfect opportunity to test a completely new environment for interconversion of the hydrogen allotropes presented itself when Koichi Komatsu and Yasujiro Murata reported a rational synthesis of the fullerene $H_2@C_{60}$.[29] In typical Turro fashion, Nick almost immediately contacted Komatsu, whom he had already met at a meeting, for a sample of the endofullerene. His request initiated a collaboration that continued for the rest of Nick's life and beyond, eventually involving contributions from students and other colleagues in at least five countries. Under Nick's leadership, the project expanded to include the study of a wide range of properties of small molecules caged in C_{60} and its derivatives and related fullerenes.[30]

Philosophy of Science and Science Education (1986)

In talking science with Nick the conversation often came around to the intellectual history of the topic at hand. He loved the word "paradigm" in the Kuhnian sense and even wrote a paper titled "Paradigms Lost and Paradigms Found: Examples of Science Extraordinary and Science Pathological—and How to Tell the Difference."[31] This tendency to look at the big picture also drove Nick to publish a steady stream of reviews of the current state and future directions of the fields to which he was contributing. He may have set a record for the number of short reviews he published with co-workers in *Accounts of Chemical Research*.

Nick's love of teaching was evident by the time he published his first book on photochemistry. The book itself was an outgrowth of a lecture series that he presented at Dupont during his postdoctoral work at Harvard. Less well known is his development of web-based resources for chemical education at Columbia University in the late 1990s. His work was recognized in 2002 by an NSF Director's Award for Distinguished Teaching Scholars.[32] In 2006, he was one of the distinguished invitees to an NSF workshop entitled "Reconsidering the Textbook."[33] Nick was also aware of both the promises and perils of online instruction, publishing a review of the website *Online Ethics*.[34] [Figure 3]

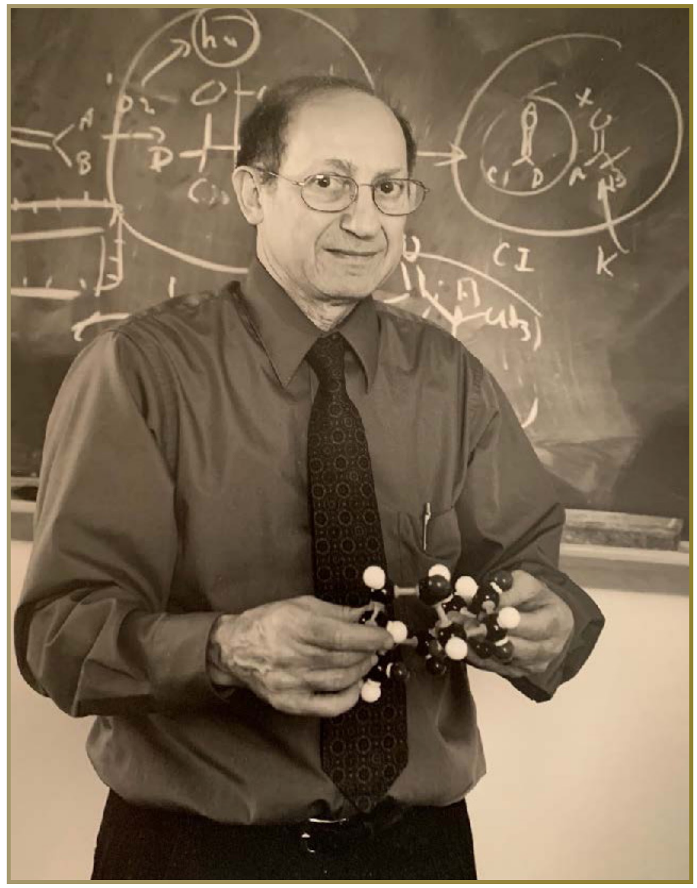

Figure 3 Nick Turro the teacher, discussing dioxetane chemistry with his students, circa early 1970s.

Turro the Researcher

Underlying Nick's extraordinary productivity was his knowledge of the literature in the areas to which he contributed. He believed that with mastery of the literature, one can move rapidly in research because one knows how to mine the existing data and find out the important information without having to waste time in the lab discovering how not to run an experiment or rediscovering artifacts, which every technique has hidden from the novice. He had the practice of going to the library every Saturday, going through about forty or fifty journals by hand. He was a strong proponent of students' being familiar with the literature. This becomes evident in a 2004 interview in which he says, "I really value students who understand the effort required to go into the literature and get the information they need. Students I like are those who really like to dig and take the extra effort to move forward."

Nick preferred simple models to complex equations. At conferences, he called on his physical and theoretical colleagues to provide simple models, such as Kasha's rule, El-Sayed's rule, the Woodward–Hoffman rules, and vector representations of spin dynamics. Much like a child, he did not hesitate to repeat the questions until he could visualize the concepts. As per Jackie Barton, "he was humble, interested, and wanted to learn new things. He had marvelous energy and an attitude that was just so refreshing. He was so interested in learning new science … and without any politics."

In the same manner, Turro had uncanny ability to explain complex photochemical concepts to anyone, eloquently using intuitive physical models in non-mathematical terms. He deeply believed discussions enhance one's ability to understand new science and solve problems. This led to weekly group meetings that lasted more than three or four hours at which he would talk more than the speaker. In later years, the meetings would often include remote internet participation by members of his international group of collaborators and former students. Often the weekly meetings would shift to Kuhn's ideas on scientific revolutions and paradigms, Rene Thom's "catastrophe theory," Langmuir's pathological science, and others. He was enthusiastic about learning new technology and using it innovatively to communicate. His genuine interest to motivate and educate students independent of their background and location was evident in such meetings.

As the research director, Nick made several short trips to the laboratory over the course of a day and enquired in a friendly manner "what's new." His response to either positive or negative answers was always encouraging, so rarely the group felt pressured. Each visit came with a new suggestion beginning, "Why don't you…?" These suggestions could lead a fellow researcher to juggle between half a dozen different research projects at any time. During these visits, his respect for the literature often came to light, as stated by C. V. Kumar: "When any of us reported new results, so we thought, he would immediately ask us to look up papers that were published already."

Turro the Mentor, Colleague, and Friend

Over the course of a career lasting nearly five decades, Nick sponsored approximately eighty graduate students, 150 postdoctoral fellows, more than 200 undergraduate students, and more than 100 visitors from other institutions who came to Columbia to use his photochemical and magnetic resonance facilities. For those of us fortunate enough to fall into one or more of those categories, working with Nick was like being welcomed into a large, lively, happy family. He was a friendly competitor (except, according to some, on the handball or tennis court), always quick to acknowledge anyone who contributed to a project and never shying away from sharing his latest research with anyone who might be interested or whom he thought might be able to contribute to the effort. To members of his group, he was "Boss," and for good reason: He recruited them, pointed them in promising directions, tried to make sure they had enough resources to get the job done, and kept the projects moving. A favorite expression he used to motivate lagging progress was, "Without time, everything happens at once. Without deadlines, nothing ever happens." [Figure 4]

According to Harry Gray, "Turro was truly a spectacular teacher-scholar who made everyone he worked with better. Turro devoted enormous amounts of time and energy to training students of all ages." He led his students to think on their own and analyze data critically. Although outwardly he seemed to accept any suggestions and interpretations,

Figure 4 The Turro group, with Sandy, in 2011.

he had an instinct for distinguishing right from wrong interpretations and conclusions. Through discussions without criticism, he led the students to recognize their strengths and weaknesses. Through passive encouragement, he made them better. In his presence no one felt intimidated. As per Matt Zimmt, "He constantly promoted cross-fertilization of ideas (paradigms), technologies and discoveries among students and projects." As Steffen Jockusch points out, "Turro's ability to expose multiple interdisciplinary fields to the group coupled with his guidance and genuine interest in the advancement of co-workers has helped his graduate students and postdocs to develop into mature scientists."

Turro did not shirk from departmental responsibilities while climbing Mount Everest in science. He was the chair of Columbia's Department of Chemistry from 1981 to 1983 and cochaired the Department of Chemical Engineering with George W. Flynn from 1997 to 2000. Jackie Barton, whom Turro hired while chair, states that "Turro was generous and very supportive of his young colleague, and he wanted me to succeed."

Turro had a lovely and happy personal life that he cherished. He married Sandy in 1960, and they had two daughters and five grandchildren. He never forgot that science is only a part of life. In addition to biological daughters and grandchildren, Nick and Sandy treated all of those who passed through their domain on the seventh floor of Chandler Hall as members of their extended chemical family. The Turros treated every human being with respect and love and were genuinely interested in the well-being of their family, students, friends and colleagues [Figure 5]. In a reciprocal gesture his students and colleagues instituted in 2017 an award in his name, the Nicholas J. Turro Award, to be handled by the Inter-American Photochemical Society.

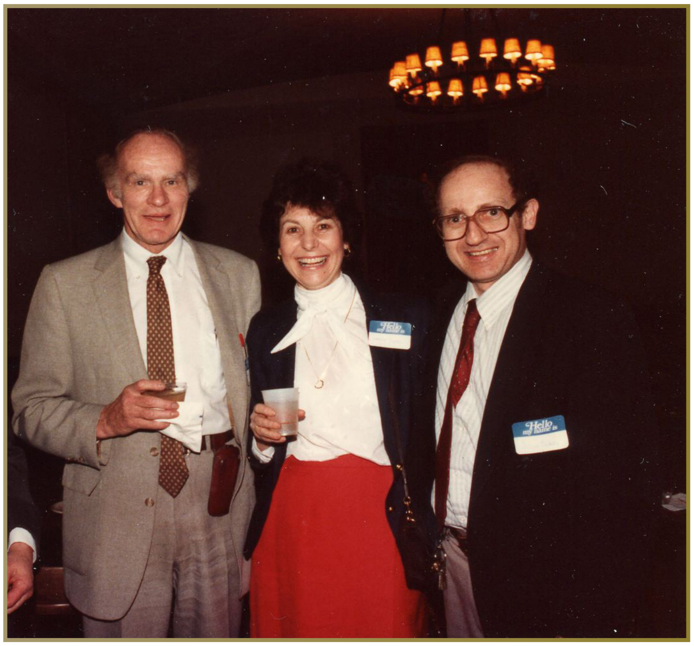

Figure 5 Nick and Sandy Turro with George Hammond, circa 1998.

Acknowledgments

We are grateful for messages about Nick and his contributions sent by several of his former students and colleagues and comments made at a memorial celebration in May 2013. The information about Nick's early life came from Sandy Turro and via remarks published by Fred Lewis on the occasion of Nick's award of the 1991 Award in Photochemistry of the Inter-American Photochemical Society.

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