

MIRJANA ECKERT-MAKSIĆ – *Biography and Contributions*

Mirjana was born in Banja Luka in the former Yugoslav Republic of Bosnia and Herzegovina on April 14, 1944. After graduating from high school, she enrolled in the Faculty of Chemical Technology at the University of Zagreb, where she initially majored in organic chemistry. In her third year of studies, she received a scholarship from the Ruđer Bošković Institute (RBI), where she gained insight into the trends in organic chemistry current at that time. She was particularly attracted to the mechanistic organic chemistry conducted by the research group of Professors Dionis Sunko and Stanko Borčić. Their work on the application of isotope effects in studying the mechanism of solvolytic reactions was highly recognized in the international scientific community. Consequently, the group hosted many leading physical organic chemists from all over the world, who delivered talks about their research or even spent some time working at the Institute. This contributed considerably to inspiring the working atmosphere and establishing firm and longstanding contacts between the laboratory members and leading physical organic groups. Mirjana was fortunate to have begun her scientific career in such an atmosphere. After receiving her B.Sc. degree (1967), she accepted the position of research assistant in the same laboratory and started work on her M.Sc. thesis in the field of solvolytic reactions.

It was then that she met her future husband, Zvonimir Maksić, who was finishing his Ph.D. in the quantum chemistry group at the Ruđer Bošković Institute. This was the beginning of their longstanding and highly successful collaboration, which resulted in a number of joint scientific papers published in respected journals and books. Their work ranged from the application of the simple Iterative Maximum Overlap Method (IMOM) to the qualitative and semiquantitative interpretation of C-H bond acidity,¹ the calculation of angular strain energies,² UV spectral transitions in highly strained hydrocarbons³ to sophisticated *ab initio* calculations of bond localization in the benzene moiety due to annelation with small strained ring(s) and its impact on reactivity toward electrophilic reagents⁴ and benchmark computations of bond-stretch isomerism using the Multireference Average Quadratic Coupled Cluster

(MR-AQCC) method.⁵ One of the notable episodes on this long scientific journey included the calculation of the electronic structure of vitamin C tautomers and radicals,⁶ which subsequently led to the preparation of various derivatives of ascorbic acid in Mirjana's group and the investigation of the biological activity of compounds formulated in this manner. The latter was accomplished in collaboration with Maja Osmak and Krešimir Pavelić at the RBI⁷ and Constance Tsao, senior researcher at the former Linus Pauling Institute of Science and Medicine in Palo Alto, California.⁸ Mirjana's strong inclination to combine quantum chemical methods with experimental studies would show up repeatedly in the various areas she investigated during her scientific career. She was always trying to transmit this attitude to her M.Sc. and Ph.D. students. At the same time, she gave them ample freedom to pursue their own ideas, encouraging them to develop their skills and creativity. After obtaining her Ph.D. from the University of Zagreb, Mirjana continued to work at the Ruđer Bošković Institute, where she was promoted first to senior research assistant (1972), and then to research associate (1975), senior research associate (1982) and senior scientist (1989). During that time, she was a visiting scientist at several universities abroad, including the Institute of Organic Chemistry, University of Heidelberg, Germany (1979–1981; 1983–1984; 1986, 1989, 2001, 2005); the Institute of Organic Chemistry, University of Münster, Germany (1991, 1992, 1993, 1994, 1996, 1998); the Institute of Organic Chemistry, University of Essen, Germany (1997), the University of Vienna, Austria, and the Autonomous University of Madrid, Spain. Part of her work in Heidelberg and Münster was sponsored by the Alexander von Humboldt Foundation. After her retirement in 2010, she was elected to the rank of RBI Scientist Emeritus and is still actively participating in the research projects carried out in her former laboratory.

SELECTED RESEARCH TOPICS

Mirjana's scientific interests are very broad. Her research has been mainly focused on computer design, the

laboratory preparation of organic and organometallic molecules with targeted properties, and the study of their electronic structure and reactivity using spectroscopic and quantum-chemical methods. More precisely, her scientific contributions are mainly in the field of acid/base chemistry,⁹ the investigation of the electronic structures of strained molecules by spectroscopic and computational methods² and the excited state deactivation of model compounds involving peptide bonds by applying rigorous multireference and multiconfigurational methods.¹⁰ With her coworkers, she has also contributed significantly to guanidine chemistry.¹¹ More recently, together with her former Ph.D. student and coworker V. Štrukil and one of the authors of this text, D. Margetić, she initiated an investigation of ecologically friendly mechanochemical approaches to organic synthesis in her laboratory, which led to successful collaboration with Professor Tomislav Friščić from McGill University in Montreal.¹² By applying both the neat and liquid-assisted grinding techniques, they prepared and fully characterized a number of substituted thioureas in excellent yields, providing firm evidence of the superiority of mechanochemistry to conventional solution-based methods.

Her research has been supported by the Ministry of Science of Croatia, US Department of Energy, US National Science Foundation, the Volkswagen Foundation, and through a number of bilateral collaborations (in particular with Hans Lischka in Vienna, Paul Rademacher in Essen, Helmut Schwarz and Detlef Schroeder in Berlin) and, last but not least, the Alexander von Humboldt Foundation. She has collaborated with many colleagues from abroad, including H. Maskill, University of Newcastle upon Tyne; S. R. Kass, University of Minnesota; M. Yanez and O. Mo, the Autonomous University of Madrid; J. Elguero, Institute of Medical Chemistry Madrid; I. Koppel and I. Leito, University of Tartu; P. Naumov, New York State University in Abu Dhabi and many others.

Mirjana's first independent research was during her work on her Ph.D. thesis and concerned a low-temperature NMR study of the long-lived protonated phenols and phenylalkyl ethers in magic acid. She started to work on this topic at the University of Tennessee, Knoxville, in the group of John W. Larsen, where she spent one year (1970–1971). After returning to the Ruđer Bošković Institute, she successfully transferred this methodology to the group and defended her thesis in 1972. It should be mentioned that this was the first NMR study in Croatia on long-lived cations generated in magic acid. She continued her work by studying the protonation of aromatic thioethers, combining experimental work with semiempirical calculations of the electronic structure of the protonated species.¹³ However, due to severely limited instrumentation and without

access to an appropriate NMR spectrometer, she was not able to develop this investigation further. However, she returned to the use of very strong acids at a later stage, when she started a project on the ionic hydrogenations of organosulphur compounds, which was the topic of the M.Sc. thesis of D. Margetić.¹⁴ It is interesting to mention that this work was initiated during a search for an appropriate method for cleaving S–S and C–S bonds in the organosulphur compounds present in low-rank coals, which is known to be a critical step in processing sulphur-rich coals. She also continued to apply computational methods in exploring the effect of substituents on the protonation mode of various aromatic and heterocyclic species, particularly in the design of strong organic bases in years to come.

In 1979, she joined the group of Professor Rolf Gleiter at Ruprecht Karl University of Heidelberg, where she was involved in photoelectron spectroscopy studies of various organic and organometallic compounds. She spent two years in the group and continued to pay short visits there as an Alexander von Humboldt Foundation and G. Forster fellow for many years. She became particularly interested in exploring through bond and through space orbital interactions combining photoelectron spectroscopy and computational methods, as best illustrated by the papers on fused 7-oxanorbornenes published with her first Ph.D. student, Ljiljana Maksimović, and Davor Margetić.¹⁵ During that period, she began to investigate the electronic and molecular structure of polycyclic molecules with pyramidalized double bonds.¹⁶ Around 2000, Mirjana and her husband began a fruitful collaboration with Hans Lischka's group in Vienna on the modeling of organic and bioorganic compounds and processes in the ground and electronically excited states, employing highly accurate multiconfiguration and multireference computational methods, which resulted in a series of highly visible publications. Particularly valuable results were obtained by studying the phenomenon of bond-stretch isomerism in cyclobutadiene, [2.2.2]propellane and structurally related molecules.¹⁷ Another important direction of this work pertains to the photodissociation of model compounds containing peptide bonds, a project which combined state-of-the-art computational methods developed by the Vienna group (M. Barbatti and H. Lischka) and the dedicated work of Ivana Antol and Mario Vazdar from Mirjana's group. They performed dynamics simulations of the photodissociation processes of formamide and its O- and N-protonated forms, as well as its higher analogs acetamide and *N,N*-dimethylformamide in their low-lying singlet excited $n\sigma\pi^*$ and $\pi\pi^*$ states in the gas phase by employing the mixed quantum-classical direct trajectory method with surface hopping at the state-average complete active space self-consistent field SA-CASSCF(10,8)/6-31G(d) level. They explored the

photodeactivation of these model molecules in the gas phase, the argon matrix and polar and nonpolar solvents. Subsequently, the photodecomposition of higher formamide analogous acetamide and *N,N*-dimethylformamide was explored. An overview of these results is presented in two recently published books.¹⁸

The field in which Mirjana and her coworkers (primarily Zoran Glasovac and Vjekoslav Štrukil) have most recently performed significant work is guanidine chemistry. The main objective of their study was to examine the impact of intramolecular hydrogen bonding and the increase of the guanidine core on the basicity of this class of compounds, with the aim of extending the basicity scale and developing strongly basic organic catalysts. This project nicely illustrates Mirjana's approach of combining various experimental and theoretical methods in solving complex problems. Within the project, a number of new derivatives of guanidine substituted with heteroalkyl groups capable of forming intramolecular hydrogen bonds were synthesized and characterized by spectroscopic methods available at the institute. They were then used to measure proton affinities¹⁹ (in collaboration with D. Schroder and H. Schwarz) and pK_a values²⁰ (in collaboration with I. Koppel and I. Leito) in the gas phase and acetonitrile, respectively. Subsequently, the catalytic activity of the most basic representatives was explored in transesterification reactions, with promising results.²¹ Another direction of this work, which is still in progress, encompasses the successful preparation of higher guanidine derivatives, substituted triguanides and tetraguanides, the efficient synthesis of which has not been previously reported.²² This represents only a fraction of Mirjana's actual work and, therefore, we provide a complete list of her publications.

During her career, Mirjana participated in many domestic and international conferences with communications as a plenary or invited lecturer, or a section chairperson. For her scientific contributions, she received the Ruđer Bošković Award of the Republic of Croatia for Scientific Achievements (1993), the City of Zagreb Award for Scientific Accomplishments (2004), and the Annual Award of the Ruđer Bošković Institute (2010 and 2012).

SERVING THE SCIENTIFIC COMMUNITY

In addition to her scientific contributions, Mirjana served the scientific community for many years through activities at the Ruđer Bošković Institute and elsewhere, both in Croatia and at the international level. In the scope of her activities at the Ruđer Bošković Institute, she established her own research group within the former Laboratory for Physical and Synthetic Organic Chemistry (1983). In 1990, it became the core of the newly founded Laboratory for Physical Organic Chem-

istry, which she headed until her retirement in 2010. She also chaired the Division of Organic Chemistry and Biochemistry at the Ruđer Bošković Institute (2005–2008) and was the vice president of the Scientific Council of the Institute (1999–2004) and a member of the Board of Governors (2010–2013). Mirjana was a member of the Managing Board of the Croatian Science Foundation and is currently the coordinator of the Permanent Committee for Natural Science of the Foundation. From 2004 until 2006, she served as a member of the National Scientific Council of the Republic of Croatia, and from 2005 to 2007 as the president of the Council for the Natural Sciences of the Ministry of Science, Education and Sports of Croatia. She is a member of the Croatian Chemical Society and served as the president (1998–2002) and vice president (2002–2004). As president she presented the activities of the society to the public, fostered connections with related international societies and strove to attract young chemists to research by, among other things, establishing the annual Leopold Ružička Award for the Most Successful Young Chemist, which was approved by the General Assembly of the Society in 2003. At the international level, she has been a member of the International Organizing Committee of the European Symposium on Organic Reactivity (ESOR) since 1999 and was the chairperson of the ESOR meeting held in the serene city of Cavtat in 2001, the first international meeting of organic chemists in Croatia after the country declared independence. She also serves as a member of the Subcommittee on Structural and Mechanistic Chemistry of the International Union of Pure and Applied Chemistry (IUPAC). She was active in the COST Chemistry Actions D10 and D30 and served as the representative of Croatia on the Management Board of the former.

Finally, we mention her editorial work. She has been an associate editor of the *Journal of Physical Organic Chemistry* (since the beginning of 2006) and the editor for physical-organic chemistry of *Central European Journal of Chemistry (Open Chemistry)* as of this year since it was launched in 2003. Prior to that, she was a member of the Editorial Board of *Croatica Chemica Acta*, in which she served as an assistant editor from 1977 to 1979. She also was co-editor (with Z. B. Maksić) of the book *Molecules in Natural Science and Medicine. An Encomium for Linus Pauling*, Ellis Horwood Ltd, 1991, and several special issues of *Croatica Chemica Acta* (1989, 1991 and 1992) and *Journal of Physical Organic Chemistry* (2002). In addition to her editorial work, she has been engaged as a referee by several scientific journals in the areas of organic and theoretical chemistry and also as a reviewer by several granting agencies.

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