

**Professor Ion GROSU** 

## ACADEMIA ROMÂNĂ



Revue Roumaine de Chimie http://web.icf.ro/rrch/

*Rev. Roum. Chim.*, **2020**, *65*(6), 513-515

## PROFESSOR ION GROSU – MASTERING ORGANIC CHEMISTRY

The Roumanian research community has the privilege and honor to celebrate the 65<sup>th</sup> anniversary of Dr. Ion Grosu, Professor of Organic Chemistry at Babeş-Bolyai University (UBB) Cluj-Napoca, Corresponding Member of the Roumanian Academy and Director of Chemical Doctoral School Cluj-Napoca.

Professor Ion Grosu was born in 1955 in Cluj-Napoca where he completed his basic education and continued his academic qualification: B. Sc. (1979), M.Sc. (1980) at Faculty of Chemistry and Chemical Engineering, UBB, Cluj-Napoca.

After graduation he activated as chemistry teacher (1980–1990) at High School for Informatics in Cluj-Napoca, meanwhile conducting research in the laboratory of Professor Sorin Mager at the Faculty of Chemistry and Chemical Engineering, UBB, Cluj-Napoca. In 1993, he defended his PhD thesis in chemistry at UBB, Cluj-Napoca under direction of Prof. Sorin Mager.

Since 1990, he successively held positions of Lecturer (1990–1995), Associate Professor (1995–1997) and Professor (1997 – present) within Department of Chemistry, Faculty of Chemistry and Chemical Engineering, Babeş-Bolyai University, Cluj-Napoca. During 1994 and 1995 he was a postdoctoral researcher at Instituto de Quimica de la UNAM (Mexico DF, Mexico).

Since 1999, he has been a PhD supervisor, mentor to more than 30 PhD students (26 finalized doctoral thesis); and led the research activity of 10 postdoctoral researchers in his laboratories.

Since 2010, he has been Co-director of the *Supramolecular Organic and Organometallic Chemistry Center* (SOOMCC) and head of the Organic and Supramolecular Chemistry Group, part of SOOMCC. He has been Vice-president of the National Chemistry Olympiad Committee (11<sup>th</sup> grade) for 15 years. He is a member of the Romanian Chemical Society and of the American Chemical Society.

Since 2011, Professor Ion Grosu is member of Chemistry Department of the National Council for Attesting Titles, Diplomas and Certificates (CNATDCU) and was a member of the National Council of Scientific Research (CNCS, 2011–2013).

Starting with 2012, Prof. Ion Grosu has become the Director of Chemical Doctoral School at UBB. He is currently member of the Editorial Board for *Open Journal of Organic Chemistry* (Bentham SP), *Studia Universitatis Babeş-Bolyai, Chemistry* (Cluj University Press) and Revue Roumaine de Chimie and reviewer for high impact journals such as: *Organic Letters, Journal of Organic Chemistry, Organometallics, Tetrahedron, Journal of Molecular Structure, Journal of Magnetic Resonance, Australian Journal of Chemistry etc.* 

Prof. Ion Grosu is a researcher with an outstanding academic activity (over 150 publications in mainstream journals, 4 books and numerous invited lectures at prestigious universities or at international congresses). He established collaborations with top scientists from over 15 universities worldwide and visited, as Invited Professor, prestigious European universities such as: University of Montpellier II (France), University of Angers (France), Humboldt University (Berlin, Germany) and University of Rouen (France).

Professor Grosu is the founder and leader of a dynamic research group at Babeş-Bolyai University Cluj-Napoca, which is one of the very few "excellence islands" in Roumania. As recognition of his research activity, Prof. Grosu was awarded C. D. Nenițescu Prize of the Romanian Academy (1994) for his original research in the field of conformational analysis of saturated heterocycles and the prizes "Excellence in Scientific Research" (2004 and 2005) as well as "The Best Book Published Abroad" (1999) by UBB. In 2014 he was appointed as Corresponding Member of the Roumanian Academy.

Undoubtedly, Professor Grosu is the most influent organic chemist that Roumania produced since Prof. Nenițescu. He had important contributions in two strongly interrelated cutting-edge fields of organic chemistry, namely stereochemistry and organic supramolecular chemistry.

His achievements in the field of organic compounds' stereochemistry had a great impact, in particular for a deeper understanding of the structure and dynamics of synthetic and natural compounds and,

consequently, for the design and synthesis of new useful molecules. Just to mention a few of these achievements – elaboration of the rational nomenclature for helical chirality and *syn-anti* isomerism of spiro compounds, report of the first example of cyclic geometric enantiomers, identification and introduction of stereochemical descriptors for the tricoordinated virtual chiral center of 1,3-oxathianes. Rewardingly, the measure of the perceived importance of Prof. Grosu's work, can be illustrated by the fact that the *syn-anti* isomerism and the helical chirality of the spiro compounds as well as the NMR investigations of the ring-chain tautomerism of 1,3-oxathianes were cited in the 6<sup>th</sup>–8<sup>th</sup> Editions of March's Advanced Organic Chemistry, Wiley, New-York, **2007** (p. 104, 150).

Prof. Grosu's early work in the field of stereochemistry involved pioneering studies on the conformational analysis of saturated heterocyclic compounds (i.e. 1,3-dioxane, 1,3-dithiane, 1,3-oxathiane and 1,3-perhydrooxazine derivatives). The most important results stem from the synthesis and investigation of a plethora of six-membered-ring, saturated heterocycles with two identical or different heteroatoms. These studies allowed: characterization of the conformational behavior of compounds with anancomeric, flexible or semiflexible structures together with understanding the preference of various functional groups for the axial or equatorial position (Tetrahedron, 2008, 7295; Heterocycles, 2003, 1477; Acta Chem. Scand., 1998, 366; Tetrahedron, 1998, 2905; Liebigs Annalen/Recueil, 1997, 2371); determination of the energy barriers required for "flipping" in various six-membered rings (Curr. Org. Chem., 2005, 1287; Heterocycles, 2003, 1477); achievement of diastereoselective bromination of 2,2-disubstituted-1,3-dioxanes and elucidation of the reaction mechanism (J. Chem. Soc. Perkin Trans. 1, 2000, 3635); development of an EI-MS method for discrimination between cis and trans diastereoisomers (Rapid Commun. Mass Spectrom., 2005, 19, 1644); highlighting the cis-trans and like-unlike equilibria and demonstration of ring-chain tautomerism for 1,3-oxathiane derivatives (Heterocycles, 2003, 1477; Tetrahedron, 2001, 8751; Tetrahedron Lett., 2000, 1967); discovery of helical chirality and syn-anti isomerism for spiro compounds with six-membered rings as well as elaboration of the rational nomenclature and the algorithm that allows description of the spiranic stereoisomers, regardless of the number of spirane units. (Tetrahedron Lett., 2000, 1967; Curr. Org. Chem., **2005**, 1287; Tetrahedron, **2004**, 3173; J. Chem. Soc. Perkin Trans. 1, **2001**, 2413; Acta Chem. Scand., **1998**, 366; Liebigs Annalen/Recueil, 1997, 2371; Tetrahedron, 1996, 12783; J. Chem. Soc. Chem. Commun., 1995, 167); introduction of the stereochemical descriptors associated to the unsubstituted alkylidene-cycloalkanes axial chirality as well as for similar compounds such as cyclohexanone oxime (J. Org. Chem., 2009, 3944); recognition of the tri-coordinated virtual chiral center of 1,3-oxathianes and introduction of the stereochemical descriptors thereof (Chirality, 1996, 311); report of the first example of cyclic geometric enantiomers (Chirality, 2011, 23, 167); first time measurement of the energy barriers for the racemization of chiral dienes (J. Org. Chem., 2009, 74, 9062), synthesis and characterization of "Geländer" macrocycles (Tetrahedron Lett., 2019, 335).

Moreover, his contribution to supramolecular chemistry led to the development of efficient construction of a large number of host molecules (macrocycles, cyclophanes, cryptands), molecular machines and self-assembled structures that found various applications. Many of these compounds are very interesting structures for the development of new materials such as self-assembled arrays, metal-organic and covalent-organic frameworks (MOFs and COFs).

Briefly, chiral macrocycles with spiro-1,3-dioxane units, *syn* and *anti* dispiro-1,3-dioxanes as well as macrocycles bearing thiophene, bithiophene, terthiophene, phenothiazine or triazine units are just a few examples to mention. Study of their complexation abilities towards metal-ions and neutral molecules (using ESI-MS, cyclic voltammetry or NMR) resulted in the construction of K<sup>+</sup> selective chemosensors. Moreover, electropolymerization of bithiophene- and terthiophene-based macrocycles afforded new materials with interesting conductive properties. In addition, some of these macrocycles showed remarkable selectivity for complexation of Li<sup>+</sup> and Pb<sup>2+</sup>. (*J. Incl. Phenom. Macrocycl. Chem.*, **2008**, 227; *J. Org. Chem.*, **2007**, 5285; *Electrochem. Commun.*, **2007**, 1587; *Tetrahedron*, **2004**, 4789; *J. Org. Chem.*, **2003**, 3153).

Prof. Grosu's research played an important role in the development and characterization of cyclophanes. For example, he has conducted extensive research to describe series of [7.7] and [4.4]cyclophanes, monomers and oligomers {[7.7.7.7] or [7.7.7.7.7]cyclophanes} bearing 1,3-dioxanes units either in bridges or as substituents. The substrate pre-organization enabled achievement of remarkable macrocyclization reaction yields, while the 1,3-dioxane units were used to monitor the structural changes in the cyclophanes structures. Some of these compounds were characterized as molecular devices (*i.e.* "rocking")

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chair", "wringer", "rudder" or "amusement ride") and some of the oligomers display very interesting solid-state structures that were described as triangles, rhombuses or pentagons. (J. Org. Chem., 2008, 5831; Tetrahedron Lett., 2008, 5204; Eur. J. Org. Chem., 2007, 4674; Org. Lett., 2006, 2619; J. Org. Chem., 2004, 69, 1337). Although initially seen as chemical curiosities, these molecular devices may be interesting building blocks in the context of the emergence of functional units that rely on controlled movement at the molecular scale.

Last, but not least, Prof. Grosu brought an important contribution to the synthesis and investigation of supramolecular properties of new cryptands based on 1,3,5-tris-(1,3-dioxan-2-yl)benzene, 1,3,5-triphenyl-triazine, 1,3,5-triphenyl-benzene or 1,1,1-trithiophenyletane as central units and various connecting linkers as arms (*J. Org. Chem.*, **2013**, 78, 8722; *Tetrahedron*, **2015**, 6888; *Tetrahedron*, 68, **2012**, 8581; *Tetrahedron Lett.* **2013**, 6133, *Beilstein J. Org. Chem.* **2018**, 1370).

Recent research of Prof. Grosu focuses on the synthesis of self-assembled structures. For example, achiral *syn* or chiral *anti* isomers of bicyclo[3.3.1]nonane dioximes constitute building blocks for the construction of a supramolecular wheel or homochiral dimers through H-bonding self-assembly (*J. Org. Chem.*, **2009**, 3944); the formation of H-bonding self-assembled structures with hexameric hydrophilic or hydrophobic channels (*CrystEngComm*, **2012**, 632) and solid-state networks of tetrahedral building blocks self-assembled exclusively via hydrophobic interactions (*Org. Lett.* **2015**, 3494); formation of supramolecular architectures *via* cooperative C(sp³)–H·anion interactions (*Chem. Commun.*, **2016**, 12322); supramolecular macrocycles formed by charge-assisted hydrogen bonding (*Cryst. Growth Des.*, **2016**, 327); synthesis of coordination polymers based on tetrahedral or tetragonal ligands (*CrystEngComm*, **2017**, 27; *Eur. J. Inorg. Chem.*, **2019**, 5025); halogen-bond–induced supramolecular architectures (*Cryst. Growth Des.*, **2020**).

In addition to all this, he has very recently set up, in collaboration with Professor Jean Roncali, an Organic Solar Cells (OSCs) Laboratory at UBB. The first results on dyads with arylamine-based push-pull systems as donor block and  $C_{60}$  fullerene as acceptor connected by a flexible insulating linker showed their potential as active layer in single-material organic solar cells (*Dyes Pigm.* **2019**, 107748).

Professor Ion Grosu is an outstanding researcher and a very devoted professor. His passion for science resulted in important advances in organic chemistry knowledge and markedly influenced the professional development of a large number of young researchers who have embraced either academic positions (in top Universities or Research Institutes from Roumania, France, Switzerland, Germany, United Kingdom, Singapore, US) or industrial careers (*i.e.* GlaxoSmithKline, UK and Arbutus Biopharma Corporation) etc.

His dedication to science, kindness, sense of humor, enthusiasm and honesty was the source of motivation for those of us who were lucky enough to work with him or under his guidance.

The Editorial Board of *Revue Roumaine de Chimie* and the Roumanian scientific community are very pleased to send their best wishes to Prof. Ion Grosu on the occasion of his 65<sup>th</sup> anniversary and look forward to many more years of collaboration.

The Editorial Board