NMR in Supramolecular Chemistry

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edited by

M. Pons

Departament de Química Orgànica,
Universitat de Barcelona, Spain

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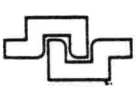

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FOREWORD

The challenge of developing large but well characterized discrete systems for technological or other applications is being met by exploiting non-covalent interactions between smaller subunits to form unique supramolecular structures. The weakness of the forces involved in the stabilization of the desired structures make them inherently dynamic and the desired uniqueness has to be built in during the design of the subunits. Careful experimental characterization of the final equilibrium structure is mandatory.

The power of NMR as a tool for the structural determination of complex systems has been proven in the field of biomolecules. In addition, NMR has a unique capability for the study of dynamics in different time scales that is being extensively exploited at present in the field of molecular biology. The strong interaction between NMR specialists and structural and molecular biologists has been crucial for the success of NMR in this field : it has guided the development of new NMR techniques needed for specific problems but has also led to the development of labeling techniques that have expanded the range of feasible NMR experiments.

Supramolecular systems have obvious connections with biomolecules. Most processes inside a living organisms are based on non-covalent interactions between different macromolecules and many designed supramolecular systems have been inspired by natural models. On the other hand, the range of possible supramolecular systems extends well beyond the biological models. The Advanced Research Workshop "Applications of NMR to the study of structure and dynamics of supramolecular systems" was conceived as a way of stimulating the interaction between Supramolecular Chemists and NMR specialists, including biomolecular NMR experts.

This idea was encouraged by the steering committee of the NATO Supramolecular Chemistry Program and benefitted from the advice and suggestions of the colleagues, and friends, that accepted invitations to sit on the international organizing committee. Additional financial support was provided by the Ministerio de Educación y Cultura and the Generalitat de Catalunya. The meeting was held in Sitges, near Barcelona (Spain) from the 4th to the 9th of May, 1998.

The presentations could be broadly classified under three general categories: the first class illustrated the state of the art in the design of supramolecular systems and included examples of different classes of supramolecular complexes: catenanes, rotaxanes, hydrogen-bonded rosettes, tubes, capsules, dendrimers, and metal-containing hosts. A second class comprised contributions to NMR methods that can be applied to address the main structural problems that arise in supramolecular chemistry. The third class included biological supramolecular systems studied by state of the art NMR techniques.

Specific structural problems in supramolecular chemistry were identified. These include determining the conformation of a bound molecule in equilibrium with a free state; avoiding the degeneracy problems that complicate the study of symmetrical molecules; avoiding the spin-diffusion problems arising from chemical exchange; coping with ensembles of different conformations in fast exchange; characterizing the dynamics of the systems at different time scales or determining the size or aggregation state of the system.

In addition to the traditional NMR techniques already used extensively, the meeting highlighted some special NMR methods that are not exploited very often in "ordinary" chemistry but that may find increased applications in supramolecular systems: the use of paramagnetic ions, the creation of coherence due to the special properties of quadrupolar nuclei in anisotropic environments, the exploitation of the interference between different relaxation mechanisms, the use of optical pumping to increase NMR sensitivity or the combination of multiple-quantum filtration with diffusion measurements.

The true interdisciplinary atmosphere that developed during the Sitges meeting is difficult to reflect in the pages of a book but browsing through the titles of the contributions may provide a hint. If some of the readers of this volume are encouraged to walk out of their labs and talk to the colleagues in the Department next door, the main purpose of this book of Proceedings and of the Advanced Research Workshop itself will have been achieved.

Miquel Pons

LIST OF PARTICIPANTS

KEY SPEAKERS

Feng Ni
Biotechnology Research Institute
6100 Royalmount Ave
Montreal Quebec H4P 2R2 Canada

Geoffrey Bodenhausen
Ecole Normale Supérieure
24 rue Lhormond
75231 Paris cedex 05, France

Guy Lippens
Institute Pasteur Lille
1, Rue Calmette
59019-Lille CEDEX, France

Volker Böhmer
Institut für Organische Chemie, Johannes Guttenberg Universität Mainz
J.J. Becher-Weg 18-20
D-55099 Mainz, Germany

Horst Kessler
Institute für Organische Chemie und Biochemie II
T. U. München
Lichtenbergstrasse, 4
85747 Garching, Germany

Fritz Vögtle
Institute für Organische Chemie und Biochemie
Rheinischen Friedrich-Wilhelms Universität Bonn
Gerhard-Domagk Str. 1
53121 Bonn, Germany

Rolf Boelens
Department of Chemistry
University of Utrecht
Padualaan 8,
3584 CH Utrecht, The Netherlands

David N. Reinhoudt
Faculty of Chemical Technology
University of Twente
P.O Box 217
7500 AE Enschede, The Netherlands

Carlos Geraldes
Departamento de Bioquimica
Universidade de Coimbra
Apartado 3126,
3000-Coimbra, Portugal

Ernest. Giralt
Departament de Química Orgànica
Universitat de Barcelona
Marti i Franques, 1
08028-Barcelona, Spain

Jesus Jimenez-Barbero
Instituto de Química Orgánica, CSIC
Juan de la Cierva, 3
28006 Madrid, Spain

Javier de Mendoza
Departamento de Quimica Organica
Universidad Autonoma de Madrid
Cantoblanco
28049-Madrid, Spain

Miquel Pons
Departament de Química Orgànica
Universitat de Barcelona
Marti i Franques, 1
08028-Barcelona, Spain

James Feeney
Division of Molecular Structure
National Institute for Medical Research
The Ridgeway, Mill-Hill
London NW7 1AA, United Kingdom

Jeremy Sanders
Department of Chemistry
University of Cambridge
Lensfield Road,
Cambridge CB2 1EW, United Kingdom

Art Palmer
Department of Biochemistry and Molecular Biophysics
Columbia University
630 W. 168th St.
New York, NY 10032, USA

Alex Pines
Department of Chemistry
University of California at Berkeley
CA 94720, USA

B.D. Nageswara Rao
Department of Physics, IUPUI
402 N. Blackford Street
Indianapolis, IN 46202-3273, USA

J Fraser Stoddart
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue,
Los Angeles, CA 90095-1569, USA

Gerhard Wagner
Department of Biological Chemistry and Molecular Pharmacology, Harvard Medical School
240 Longwood Ave,
Boston, MA 02115, USA

Jacob Anglister
Department of Structural Biology
Weizmann Institute of Science
76100 Rehovot, Israel

Gil Navon
School of Chemistry, Tel Aviv University
Tel Aviv 69978, Israel

Anil Kumar
Department of Physics and Sophisticated Instruments Facility
Indian Institute of Science
Bangalore-560012
India

OTHER PARTICIPANTS

Pascale Delangle
CEA-Grenoble
/DRFMC/SCIB/Reconnaissance Ionique
17 avenue des martyrs
38054 Grenoble cedex 9, France

Andreas Doelle
Institute of Physical Chemistry, RWTH Aachen
52056 Aachen, Germany

Margit Gruner
Institute of Organic Chemistry of the TU Dresden
Mommsenstrasse 13
01062 Dresden, Germany

Tanja Kortemme
European Molecular Biology Laboratory
Meyerhofstr. 1
69117 Heidelberg, Germany

Alessandro Casnati
Dept. of Organic and Industrial Chemistry
Viale delle Scienze 78
43100 Parma, Italy

Enrico Redenti
Chiesi Farmaceutici
Via S. Leonardo 96
43100 Parma, Italy

Gert Jan Boender
University of Nijmegen
Toernooiveld 1
6525 ED, Nijmegen, The Netherlands

Willem Verboom
Laboratory of Suparmolecular Chemistry and Technology
University of Twente
P.O.Box 217
7500 AE Enschede, The Netherlands

Juan Espinosa
Instituto de Química Orgánica
Juan de la Cierva 3
28006 Madrid, Spain

Juan Granja
Departamento de Química
Universidad de Santiago
Santiago de Compostela, Spain

Mª Antonia Molins
University of Barcelona
Martí i Franqués 1
08028 Barcelona, Spain

Pedro Nieto
Instituto de Investigaciones Químicas
c/ Américo Vespucio s/n
41092 Isla de la Cartuja
Sevilla, Spain

Eduardo Rubio
Universidad de Oviedo
Dept. Química Orgànica e Inorgànica
Facultad de Química
33071 Oviedo, Spain

Francesc Sánchez-Ferrando
Universitat de Barcelona
Departament de Química
08193 Bellaterra, Spain

Cristina Vicent
Instituto de Química Orgánica, CSIC
c/ Juan de la Cierva 3
28006 Madrid, Spain

Anton Vidal
Dept. Química Orgánica
Universitat de Barcelona
Martí i Franquès 1
08028 Barcelona, Spain

Erk Çakil
Istanbul Technical University
Maslak
80626 Istanbul, Turkey

Nick Bampos
Department of Chemistry
University of Cambridge
Lensfield Road
CB2 1EW Cambridge, United Kingdom

Eric Brouwer
Department of Chemistry
University of Durham
Science Laboratories, South Road
DH1 3LE Durham, United Kingdom

Gianni Chessari
University of Sheffield
Chemistry Department, Brook Hill
S3 7HF Sheffield, United Kingdom

Stefan Freund
Centre for Protein Engeneering
Chemical Laboratories, Lensfield Road
CB4 3PP Cambridge, United Kingdom

Phil Douglas
School of Chemistry
University of Birmingham
Edgbaston
Birmingham B15 2TT, United Kingdom

Nuria Assa-Munt
Structural Biology Program
NMR Facility Faculty Supervisor
The Burnham Institute
10901 North Torrey Pines Road
La Jolla, CA 92037, U.S.A.

Brian J. Stockman
Structural, Analytical and Medicinal
Chemistry
Pharmacioa & Upjohn
301 Henrietta St.
Kalamazoo, MI 49001, U.S.A.

Gyula Batta
L. Kossuth University
Egyetem ter 1
4010 Debrecen, Hungary

Yoram Cohen
Tel Aviv University
Ramat-Aviv
69978 Tel-Aviv, Israel

Konstantin Pervouchine
Institut für Molekularbiologie und
Biophysik
Eidgenossische Technische Hochshule
Hoggerberg
8093 Zurich, Switzerland

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S.J. CANTRILL, M.C.T. FYFE, F.M. RAYMO, J.F. STODDART
Department of Chemistry and Biochemistry
University of California, Los Angeles
405 Hilgard Avenue, Los Angeles, CA 90095-1569, USA

1. NMR Spectroscopy in Supramolecular Chemistry

One of the major challenges in supramolecular chemistry [1] is the characterization of the (super)structural properties of the (supra)molecular species resulting from self-assembly [2,3] processes. Although the stereoelectronic properties of the supramolecular synthons are responsible for determining the geometries of the final self-assembled (super)strucures, in most instances the experimental conditions (*e.g.*, solvent, temperature, pressure, and stoichiometry) play a dominant role. As a result, the prediction of the geometries of supramolecular entities is difficult and, more often than not, impossible even by means of computational methods [4]. Experimental techniques that are able to establish the (super)structural properties of (supra)molecular species unequivocably are much in demand. X-Ray crystallography has played a major role in determining the superstructures of supermolecules and supramolecular arrays, as well as the structures of large and complex molecular assemblies, in the solid state [5]. The characterization of self-assembled monolayers at the air/water interface — and on solid supports — has been achieved employing sophisticated microscopic techniques {*e.g.*, Brewster angle microscopy [6], scanning and transmission electron microscopies (SEM and TEM) [7], atomic force microscopy (AFM) [8] and scanning tunneling microscopy (STM) [9]}. The combination of absorption and emission spectroscopies [10], along with electrochemical techniques [11], has permitted the characterization of self-assembled products in solution. Chromatographic methods {*e.g.*, high performance liquid chromatography (HPLC) [12] and gel permeation chromatography (GPC) [13]}, often coupled with mass spectrometric techniques {*e.g.*, fast atom bombardment and liquid secondary ion mass spectrometries (FABMS and LSIMS) [14], electrospray mass spectrometry (ESMS) [15], and matrix-assisted laser desorption ionization time-of-flight mass spectometry (MALDI–TOF–MS) [16]}, are becoming more and more powerful analytical methods for the characterization of (supra)molecular species. However, the most informative and widely used analytical method employed for the study of such species in solution is nuclear magnetic resonance (NMR) spectroscopy [17]. By relying on the evaluation of simple parameters (*e.g.*, chemical shifts, relative signal intensities, and spin–spin couplings) inter-component interactions, thermodynamic (*e.g.*,

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