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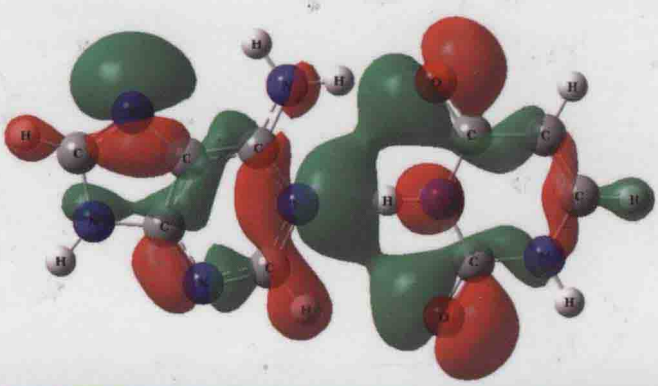
high resolution nmr spectroscopy:

understanding molecules and their electronic structures



Edited by
Rubén H. Contreras

High Resolution NMR Spectroscopy: Understanding Molecules and their Electronic Structures

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Rubén H. Contreras
Physics Department, Faculty of Exact and Natural Sciences
University of Buenos Aires and IFIBA
Argentina

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Contributors

Numbers in Parentheses indicate the pages on which the author's contributions begin.

Gustavo A. Aucar (9, 119), Physics Department, Natural and Exact Science Faculty, Northeastern University of Argentina and IMIT Institute, CONICET-UNNE, Corrientes, Argentina

Jochen Autschbach (69), Department of Chemistry, University at Buffalo, State University of New York, Buffalo, New York, USA

Rubén H. Contreras (1, 9, 245, 315), Physics Department, Faculty of Exact and Natural Sciences, University of Buenos Aires and IFIBA, Argentina

Lucas C. Ducati (245, 315), Chemistry Institute, University of Campinas, Campinas, Sao Paulo, Brazil

M.B. Ferraro (9), Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, and IFIBA, CONICET, Ciudad Universitaria, Pabellón 1 (C1428EHA), Buenos Aires, Argentina

J.M. García de la Vega (161), Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain

Claudia G. Giribet (119), Dpto. de Fisica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and IFIBA, CONICET, Buenos Aires, Argentina

Jean-Cyrille Hierso (285), Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB-UMR CNRS 6302), Université de Bourgogne, Dijon, and Institut Universitaire de France (IUF), France

Krystyna Kamieńska-Trela (347), Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka, Warsaw, Poland

P. Lazzeretti (209), Dipartimento di Chimica dell'Università degli Studi di Modena e Reggio Emilia, Modena, Italy

T. Llorente (315), Physics Department, Faculty of Exact and Natural Sciences, University of Buenos Aires and IFIBA, Argentina

Martin C. Ruiz de Azúa (9, 119), Dpto. de Fisica, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires and IFIBA, CONICET, Buenos Aires, Argentina

J. San Fabián (161), Departamento de Química Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, Madrid, Spain

Cláudio F. Tormena (245, 315), Chemistry Institute, University of Campinas, Campinas, Sao Paulo, Brazil

Juha Vaara (41), NMR Research Group, Department of Physics, University of Oulu, FIN-90014 Oulu, Finland

Jacek Wójcik (347), Institute of Biochemistry and Biophysics, Polish Academy of Sciences, Pawińskiego, Warsaw, Poland

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Chapter 1

Introduction

Rubén H. Contreras
Physics Department, Faculty of Exact and Natural Sciences, University of Buenos Aires and IFIBA, Argentina

During the past decades, there has been a very important progress in nuclear magnetic resonance spectroscopy (NMR). This progress took place both in experimental instrumentation and in theoretical approaches that help extracting invaluable molecular information from the spectral parameters commonly known as "high-resolution NMR parameters" (HR-NMR parameters). In this way, the scope of this spectroscopy for studying a large series of molecular problems has notably broadened. At first sight, this scenario could lead many people to wonder why a new book dealing with HR-NMR parameters is worthwhile when there are plenty of books dealing with related subjects. However, looking at that scenario from inside, it is noted that NMR spectroscopy has become a quite specialized field that requires of specialists if its potential is to be used at its best, which is the aim of this book. This is a notorious problem, and it is reflected in many scientific papers published in the current literature where this spectroscopy is only used on a routinely base. In several disciplines, where it could be used as a powerful tool to study many molecular problems, it is seldom used, narrowing notably its potential scope.

Taking into account comments made above, the main aim of this multiauthor book is intending to help reversing, at least in part, this trend, broadening notably the present scope for employing HR-NMR parameters to study a variety of molecular problems. For undertaking this task, it would be adequate to analyze first what are the main problems defining the mentioned situation. Perhaps the main reason is not difficult to be sorted out. To extract at its best possibilities electronic molecular information from HR-NMR parameters, it is required to have an interdisciplinary team of specialists to be able to (a) acquire the spectra using modern and sophisticated techniques. (b) After that comes the often not easy task of extracting and assigning HR-NMR parameters to atoms belonging to the molecular system under study. (c) From HR-NMR parameters thus found it is necessary to employ adequate approaches to extract, as much as possible, information on the electronic structure of the molecular system being studied. Without forgetting points (a) and (b), in this book are described few useful

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approaches to study aspects connected with point (c). The ability to extract in-depth electronic structure information from HR-NMR parameters requires of mathematical and physical backgrounds that are seldom acquired by undergraduate students in several disciplines. In fact, according to this editor's own experience, it is observed that for graduates in several disciplines to face either a rather involved equation or to deal with a tensor property is something similar to be confronted to a monster. For this reason, in this book, emphasis is placed on points like this: even complicated equations are rather easy to be "read physically" after a short and adequate training is acquired, which can easily be achieved even without having a sound background either in Mathematics or in Physics. Since it is expected that this book be adequate as a textbook for either advanced undergraduate or graduate student courses in disciplines like Biology, different branches of Chemistry, Physics, or Material Sciences, all authors were asked to explain ideas requiring complex concepts in the easiest possible way keeping at the same time, a sound background.

When organizing this book the following important point was also taken into account. In many laboratories where NMR spectroscopy is not an end in itself but just a powerful tool to investigate a large series of molecular problems, it is important to obtain insight on trends of HR-NMR parameters in terms of chemical interactions affecting them. Generally, in this type of laboratories that task is usually more important than just obtaining accurately calculated values that agree well with their experimental counterparts. That is the reason why in several parts of this book HR-NMR parameter trends are described employing either qualitative or approximate approaches. In other parts of this book, some other important concepts like that of the relationship between the transmission of the FC interaction and the Fermi hole (see Ref. [7] in Chapter 8) is used to rationalize several spin–spin coupling constant (SSCC) trends. On this line of thought, it is very easy to realize that any hyperconjugative interaction becomes a kind of "carrier" for the spin information associated with the FC term. In turn, this conclusion helps to identify, by just observing the general configuration of a molecular system, if the FC interaction of a given SSCC is transmitted through more than one pathway between two given isotopes. This physical understanding of the Fermi hole can also lead to an easy conceptual analysis on the sign of several types of couplings mainly transmitted by exchange interactions. One conspicuous case is that of *geminal* couplings where, for the same types of isotopes, it is experimentally known that in some cases, it is positive and in some other cases, negative. This task is notably achieved if discussions presented in Chapter 5 are followed in detail. From that chapter, it is easy to understand that in a given molecule the overlap between two adjacent bonds (or one bond and one nonbonding electron pair) is negative at the position of their common nucleus. This indicates that interactions favoring the corresponding positive electronic cloud algebraically increase the FC term of the *geminal* coupling under consideration and vice versa.

Several other FC contributions that can easily be rationalized on similar grounds are briefly cited here, like the phenomenon reported many years ago, about the FC transmission by an intermediate fragment; the long-range transmission of the FC term by sequences of concatenated hyperconjugative interactions and the different signs that can be observed in J_{FH} SSCCs mainly transmitted through space. A point that should be stressed when performing a qualitative analysis of this type is this one: in all cases when explaining concepts in easy terms, much care is taken in keeping all explanations on sound grounds.

In each chapter is included a "References" section, which includes some seminal works, some basic references and others that could satisfy highly motivated readers. However, an important point that should be taken into account when reading this book is this: quoted references by no means cover exhaustively the current literature corresponding to each chapter. The reason is that each chapter does not constitute a kind of a review article; in all cases, all authors intended to cover didactic aspects of each chapter contents instead of citing exhaustively the corresponding current literature. It is stressed that a huge amount of articles were not quoted not because they were considered "second rate," but simply because those which were quoted referred adequately to the subject under consideration. Besides, all in all, special care was taken for the length of each chapter, not to exceed reasonable limits.

Each chapter includes an exercise section that could help understanding different concepts. Additionally, such section will be particularly useful if this book is adopted as a textbook in a course either for advanced undergraduate or for graduate students. It is important to note that the levels of those exercises are not uniform. It is expected that, when using this book as a textbook, the advice of each tutor or professor will be of particular relevance when addressing such exercises and in using them in the most appropriate way.

It is remarked that no chapter of this book deals with NMR parameters for compounds measured in anisotropic phase. This does not mean that this field is not adequately appreciated as a very valuable one whose importance is expected to continue increasing notably during the next few years. Similar advice can be made about NMR relaxation times. Also, it is important to remark that no chapter is devoted neither to describe nor to compare theoretical approaches for calculating HR-NMR parameters. Such apparent omission originates in these three important reasons: (a) the goal of avoiding significant overlap of the contents of this book with any other book dealing with HR-NMR parameters; (b) the fact that in the current literature there are excellent books and review articles dealing with this subject suggested that their adequate citations in several chapters of this book would be the best way to proceed; (c) the constraint on the length of the whole book to be kept within reasonable limits.

Chapters are written by different well-known specialists that use different methodologies and approaches in their everyday scientific works. Each

chapter is divided into sections helping in this way the part of the readership that could be interested only on some basic aspects of a given subject. In such case, they could skip some sections and concentrate in those parts that the reader considers more appealing for her/his studies. On the other hand, interest can arise in going further on several other parts of the subject being read. In that case, interested readers could resort to the basic literature quoted at the end of the respective chapter. Finally, a few cross-references between chapters are marked alongside the book.

Besides comments made above, in this introductory chapter, succinct descriptions of aims and contents for different chapters are given. However, such comments do not necessarily follow the chapters' ordering. Hence, this outlook is expected to highlight notably the coherence and the unity of the whole book, while remarking some generalized interesting conclusions. Whenever considered convenient, some relevant comments are included describing in simple terms how chemical shifts and coupling constants can be powerful indicators of some chemical interactions being present in the molecular system under consideration.

As mentioned above, all authors took care of presenting each subject taking into account didactic aspects. In this editor's opinion, the goal has been successfully achieved. As a complementary point, most authors agreed with the editor about the usefulness of opening adequate channels for asking questions related to this book. The suggested e-mail contact is contrera@df.uba.ar.

First, Chapter 2 starts describing some basic aspects of electron–nucleus magnetic interactions originating the HR-NMR parameters known as nuclear magnetic shielding constants, $\sigma(A)$, and indirect spin–spin coupling constants, J_{AB}. Only aspects of these parameters corresponding to "light atoms" are considered in that chapter. Besides, it is assumed that the molecular system under study corresponds to a "closed shell" one. Furthermore, only the case where these parameters are measured in an isotropic phase is taken into account.

The expression "light atoms" is used here to denote atoms whose parameters are described correctly within the framework of nonrelativistic quantum chemistry. A very didactic introduction to relativistic quantum chemistry is presented in Chapter 4. This also includes its application to HR-NMR parameters. It is highly recommended for students dealing with organometallic compounds to study Chapter 4 carefully.

Although nowadays most HR-NMR spectroscopy applications correspond to closed-shell molecular systems, it is expected that in the near future this spectroscopy will also be applied to study, in an extensive way, paramagnetic compounds. For this reason, when planning the organization of this book, it was considered important to include Chapter 3, entitled "Chemical Shift in Paramagnetic Systems," which is dubbed as pNMR. This is a very clearly written chapter, where an interesting set of references is given. It is noted that this subject is seldom described in the current