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PREFACE

Preface

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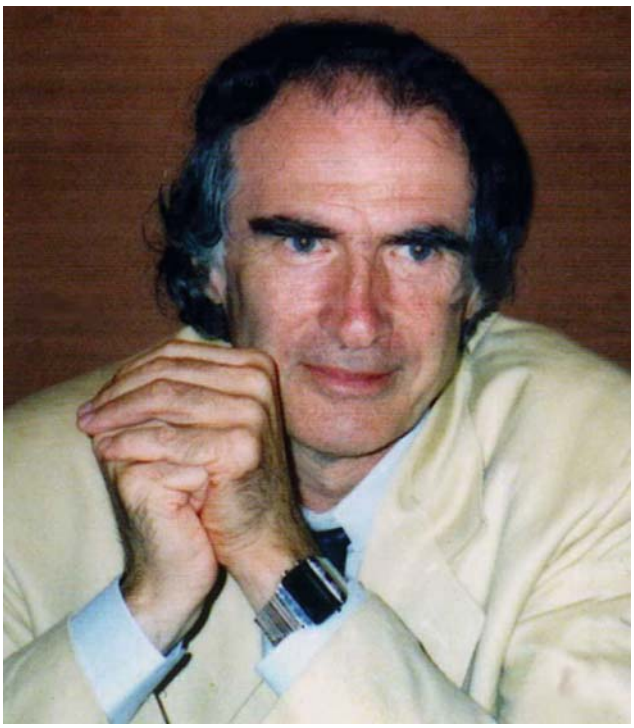

We were all saddened by Fernando Bernardi's untimely passing on February the 20th, 2006. With this special issue we honor his memory. Fernando was an esteemed colleague and a close friend of many of the contributors of this volume. We thank Don Truhlar and Chris Cramer for giving us the opportunity to edit this memorial issue. We also thank all Fernando's colleagues who contributed to this volume.

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Fernando Bernardi 1937–2006

Biographical notes

Michael A Robb

Forward

It seems appropriate to begin on a very personal note. I took the picture above when Fernando and Gemma came to visit us in the summer of 2005. I could not imagine it would be the last time we would meet. Fernando had been suffering from a degenerative disease for many years and this was the first time we had ever spoken openly about it. Apparently he had been responding to drug therapy very well. He was as happy and as optimistic about his future as he could be. So I was shocked to hear of Fernando's passing some six months later.

Early life, education and career

Fernando Bernardi was born in Verona in 1937, but his family moved to Bologna very shortly thereafter. Fernando's father was a senior officer on the Italian railway system. The war disrupted Fernando's elementary schooling (although he continued to study, despite of the war, with the help of a private elementary school teacher) and the family lived outside of Bologna intermittently near the end of the war in order to avoid the bombing. In Italy there are two main types of secondary school: a school devoted mainly to the arts and humanities (liceo classico) and the school devoted mainly to science (liceo scientifico). Not unusually for an Italian wishing to get a broader background in preparation for graduate studies, Fernando was educated at the liceo classico. The determination and drive that Fernando was to demonstrate in his research career became apparent on his entry in 1956 to Bologna University where he read chemistry in spite of having no science background. According to Gemma, he chose science rather than the humanities because "he wanted to leave something behind". (i.e., he wanted to give a contribution to the understanding and the improvement of scientific research.)

The Italian university degree at that time was usually five years where the last two years were involving a major project of scientific research. Fernando graduated in 1962 (magna cum lauda). Graduation carried with it the title Dottore. After graduation Fernando worked in the laboratory of a sugar factory in Bologna. However, he returned to academia a year later when his research career began.

Italy at the time had no Ph.D. programme. In order to pursue a specialist career in science which might lead a to an academic position, the usual approach involved work with a Professor in Italy, often followed by a period abroad. The prerequisite to an academic post was a "Libero Docente" (like a German habilitation), which Fernando obtained in 1970. At the time there were no textbooks in theoretical chemistry (i.e., quantum chemistry). One "learned ones trade" by attending one of the summer schools organized by Per-Olav Lowdin in Uppsala and Florida. I first met Fernando at the Uppsala School in 1968. A year later, Fernando went to work with SF Boys in Cambridge in 1969. (Boys was one of the first theoreticians who were trying to write computer programs to do calculations on molecules). Fernando married Gemma Monti in June 1969. It was a modest affair at the Cambridge Town Hall and their supporters were Professor Boys and one of his post docs. After leaving Cambridge in 1971, Fernando went to work with Carl Moser in Orsay. (Together with Raymond Daudel, Moser wrote the first book on the subject that we would now call quantum chemistry). It was here that Fernando collaborated with Warren Hehre (one of the authors of Gaussian who eventually set up the quantum chemistry package Spartan).

In spite of the fact that Fernando's early work in quantum chemistry was focussed on more fundamental methodology (e.g., the Boys-Bernardi counterpoise method and transcorrelated wavefunctions), when Fernando returned to Bologna in 1971 he began his collaboration with a senior organic chemist, A. Mangini, and, after an interlude in Orsay in 1972, became a professor in the organic chemistry Institute at the Chimica Industriale Faculty (the second big chemistry department in Bologna University). Fernando was one of the first people to do theoretical calculations that were aimed at providing useful information to physical organic chemists and synthetic organic chemists. He maintained his point of view throughout his entire research career. Since he had a background in fundamental theory, he was always ready to use the most advanced theoretical methods but was

determined to present the results of his computations in a way that it advanced organic chemistry. He believed that a major goal in quantum chemistry ought to be to enhance the interpretative models used in organic chemistry.

Cambridge with SF Boys

As noted above Fernando worked with Boys in Cambridge 1969. This was an exciting time for quantum chemistry. Calculations on molecules were just beginning, with Boys' group in Cambridge and in the group of Slater at MIT. However, there were many fundamental problems to be worked out. Fernando worked on two such problems with Boys: (a) the Function Counterpoise method (now associated with the Basis Set Superposition Error (BSSE) and (b) transcorrelated methods. The BSSE paper [1] is a citation classic with 5,846 citations. The reader is referred to the discussion of Handy [2] for a review of the importance of this paper. Fernando also published two papers on transcorrelated methods [3,4]. Transcorrelated methods used numerical methods to develop the solution of the Schrodinger equation for molecules. At the time it seemed these methods might replace matrix algebra methods in quantum chemistry. However, it proved difficult to get the required accuracy and to compute properties other than the energy.

Chimica Industriale, Istituto di Chimica Organica: colaborations with Mangini and other organic chemists

Fernando returned to the post of Professore Incaricato at Chimica Industriale in 1972 after a year in Orsay in the group of Moser. He remained at Chimica Industriale and held the post of Assistente Ordinario from 1974 to 1980. He worked in the Istituto di Chimica Organica that was directed by A. Mangini. Mangini stimulated Fernando to apply his theoretical skills to organic chemistry. (I met Mangini a few times. He was a benevolent dictator who would hold group meetings as part of a trip to hunt wild boar!). Fernando published many papers in the 1970s and early 1980s with collaborators who were organic chemists with an interest in theory such as I. G. Csizmadia, S. Wolfe, GF Pedulli and their students such as Berny Schlegel, M. H Wangbo and others.

As the discipline of ab initio computations on organic molecules began to mature, Fernando developed a collaboration with Nicholas Epiotis at the University of Washington and Saul Wolfe at Queens University in Kingston. This work was focussed on the idea that the results of ab intio computations ought to be analysed in terms of concepts from qualitative MO theory (QMOT) that can be used by the synthetic chemist to interpolate between theory and experiment. With Andrea Bottoni (a post-graduate at the time, now Dept. Head in Bologna) they developed the perturbed MO method that was a numerical implementation of the concepts in QMOT (see for example ref 5). This type of effort was to remain a central aspect of Fernando's work throughout his career. He believed passionately that, if quantum chemistry was to be important to organic mechanistic chemistry, it should have provided concepts as well as the very best numbers.

Saul Wolfe (now Emeritus Professor at Simon Frazer University in Canada) first met Fernando in 1972. At the time, Professor Mangini was interested in Wolfe's theories *d*-orbital conjugation, and Fernando was asked to be involved in computations on the CDC 6600 computer of the Universita di Bologna. The collaboration also involved M. Whannbo, and Berny Schlegel and used Pople's Gaussian 70 programme. Berny Schlegel was a Ph.D. student at the time with S. Wolfe in Kingston Canada. Fernando and Berny, as well the other collaborators, were amongst the first people to do mechanistic studies in organic chemistry with full geometry optimization. Thus the objective of carrying out high level quantum chemistry computations on organic mechanistic chemistry as well as producing a post-computation analysis of the results became a reality during this period.

Dipartimento di Chimica "G. Ciamician"

Fernando became Professore Ordinario (Full Professor) in Theoretical Organic Chemistry, at the Department of Chemistry "G. Ciamician" of Bologna University, 1st November 1980, although he retained strong links, as well as a lab, at the Chimica Industriale Faculty for several years.

In Italy, the appointment as a Professor was associated with the teaching of a particular course. Thus, few comments on "Fernando as a Professor" (drawn mainly from the recollections of Marco Garavelli) seem appropriate. The Theoretical Organic Chemistry course held by Fernando was feared but respected by the students. For most students, it forced them to change the way in which they perceived chemistry and chemical reactivity. Fernando was hard task-master: his classes, held in his office, were more like a constant examination, he was constantly asking questions to the participants and forcing them to "think on their feet". Often glacial silence was the result, while waiting for an answer from the selected victim. But students rose to this challenge rather than risk humiliation. Thus his classes were seen as a milestone on path to becoming an organic chemist who could see reaction mechanisms using modern theoretical ideas.

In Italy, the final two years of the undergraduate degree were devoted to a research project. You needed to be strongly motivated to work with him on a thesis project, which was always very demanding. (Until recently Italy did not have a Ph.D. so this project was the entry into research and similar to the early years of a PhD in the USA. Indeed, Europe has

now adopted the Bologna model: 3 y. B.sc, 2 y M.sc and 3 yr. Ph.D.). As a project supervisor, he was demanding. He took a close personal interest and wanted to be informed of progress on a daily basis. However, Fernando also took an almost fatherly interest in all the students he supervised. He made great efforts to ensure that the young people who worked for him obtained a placement on the next stage of their scientific career. Several of his students (Andrea Bottoni, Massimo Olivucci, Marco Garavelli, Alessandro Venturini) now hold permanent positions in academic or research structures in Italy.

This seems like a suitable point more personal digression about our long term collaboration. Although we had met many times before, I first came to collaborate with Fernando in 1982 when I was on sabbatical. Our collaboration continued until his death with 112 joint publications including some 47 papers in JACS.

I arrived at the gates of Bologna just before Christmas in 1981 with my wife and a two-year-old child, having just driven from London. Fernando met me in his flashy green Alpha Romeo coupe and we went in convoy around the inner ring road of Bologna where I was to live for 8 months. Our scientific objective was to apply our MCSCF codes to forbidden cycloadditions and to find ways of understanding the concepts of forbidden and allowed reactivity in terms of an analytical method that was compatible with high level computations. In fact, this topic kept us both very busy for more than 10 years.

But it was not all hard work! Post 1982, I was a regular visitor to Bologna. My visit often began at a restaurant "da Guido" which had a speciality of capra (goat) and was washed down with '*refosco dal pedunculo rosso,* (*the refosco with the red stalk*) a great wine from Friuli. Fernando was an expert on the wines of Emilia-Romagna. He got his wine directly from the farmer and had a huge cellar. Fernando also had a summer home in the Gargano peninsula in Puglia. With my family, I spent many vacations in a villa in a nearby village that Fernando had found for us. My lasting memory is many meals of cozze (mussels) and the wonderful fish of the south Mediterranean, as well as the "black wine" of Puglia.

Our initial applications, with Fernando, of MCSCF theory to organic chemistry in 1982 also involved Berny Schlegel, Glauco Tonachini. With Berny the gradients were added to MCSCF and Glauco produced a mechanistic results on sigmatropic shifts in propene [6]. A method for VB analysis [7,8] was also produced at this time. In subsequent years, many applications followed to classic multibond reactions in organic chemistry. We shared many co-workers during this period (Andrea Bottoni and Alessandro Venturini from Italy, and Joe Mcdouall and Slav Paleolog from England).

Both Fernando and I began to change the focus of our collaboration in early 1990s. This eventually led to the emergence of rather new ideas and to the most productive time of our collaboration. Under Fernando's supervision and following his inspiration, Massimo Olivucci (now professor in Siena and in Bowling Green Ohio) completed his Ph.D. in Bologna (1988) on a project that was focussed on the analysis of ground and excited states using Heitler–London Valence bond theory.

Qualitative valence bond theory was central to Fernando's scientific thinking at that time. Epiotis, Pross and Shaik had successfully used such schemes for the decomposition of an adiabatic reaction potential energy profile into diabatic components [8]. One had an individual diabatic describing the bonding features of the reactants and products of a reaction. The crossing between diabatics was then associated with the position of transition states. Thus reactivity could be rationalized via a change in slope or stability of such diabatic curves. At this time, we took this idea to its next level by setting up a diabatic decomposition scheme that could yield a quantitative (rather than qualitative) decomposition of the MCSCF reaction energy profile. As documented in several papers, the use of effective Hamiltonian theory, together with the simple Heitler–London valence bond formalism, were keys to success and the method was applied to allowed and forbidden pericyclic reactions [9].

Remarkably, this same scientific approach also lead to theories of excited state reactivity. In photochemistry, certain diabatic crossings corresponded to "real" crossings of excited and ground state potential energy surfaces. Such ideas provided the first seeds of a new approach to photochemistry (that we would now call 'Computational Photochemistry') that we developed jointly following Fernando's principle of *doing the most accurate computation possible but producing new concepts that could be understood by the experimental chemist.* After many applications, a few years later, these developments were recognized by the Italian organic chemistry community, who awarded Fernando the prestigious "A. Mangini medal" during the 1999 annual meeting of the Organic Chemistry Division. Further, in 2001 Olivucci, Robb and Bernardi were selected as finalists of the European Community René Descartes Prizes for the excellence in research.

In the latter part of his career, Fernando (together with Marco Garavelli and Massimo Olivucci) recognized the importance of using the theoretical approach to photochemistry and applying it to photobiology. Under his supervision, Marco Garavelli (now Professor in Bologna) completed his Ph.D. project (1997) on the modelling of photophysical and photochemical properties of biological chromophores such as retinals, using the highest ab initio methods available. Since then, many fundamental new concepts emerged [10–12] and this topic was the principle focus of Fernando's science until his death.

In conclusion, Fernando was a theoretical chemist with his *feet on ground*. He was one of the initiators of a new focus on physical organic chemistry, which now use theoretical

computations to yield concepts that could be used to interpolate between experiments. This was in contrast to traditional methods that were based upon linear free energy relationships that were focussed only on the properties of the reactants.

Acknowledgements It is a pleasure to acknowledge many discussions how to present such biographical notes. Also, my thanks are due to many who responded to my requests for recollections but in particular to Gemma who helped me remember many happy times.

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Personal recollections

This section collects memories from some close friends and colleagues of Fernando Bernardi. We think these writings, which are all very tender and nice, do represent a unique opportunity for seeing Nando both as an Academic and as a man.

We would like to warmly thank Prof. Francesco A. Gianturco, Prof. Lodovico Lunazzi and Prof. Andrea Bottoni for their very personal contributions.

Reminiscences of 50 years: by Francesco A. Gianturco

Nando and I met at undergraduate classes just fifty years ago, in the winter of 1956, when we started our studies in chemistry at the University of Bologna, in Italy. We were both keen students and eager to get on with our work, so quickly found ourselves part of small group within our large class (those days a lot of young Italians wanted to study chemistry!) made up of like-minded fellows (no girls in those days!) who wanted to pass as many courses as feasible and, if at all possible, at the top of the class!

We then started to meet with this small group of 5–6 people to study and discuss together, making the rounds of all our respective homes or digs (some of us come from outside Bologna) for many fiery encounters and energetic discussions which went on well into the night. Nando was always one who was a stickler for details and wanted to make sure that no dark corners were left in our understanding of whatever it was that we were studying that day. This capacity to concentrate, and to demand to himself and to others the necessary efforts, served his well all his life and guided his attitude to both research and teaching.

We separated a bit later on along the curriculum since I wanted to be a theorist from the very beginning while Nando tried different pastures before choosing theory as his main interest: here again, the man wanted to know better, and more certainly, details of the various options!

I went on to do my military service (it was compulsory in Italy then) for nearly two years while Nando managed to avoid it.

However, we met again in England, where I was doing my D.Phil. with the late Charles Coulson in Oxford and Nando was in Cambridge with Frank Boys: once more we started discussing what we were doing and comparing our research interests with the same eagerness of our earlier students' days. Nando was very enthusiastic and as careful as always about getting right the various tricks of the computational trade!

We moved then to different research fields, and therefore did not meet anymore at Conferences or at Summer Schools as in the earlier days, nor were we in close by Universities.

However, I kept hearing of his scientific success and of his work, which he kept pursuing with the same keenness and the same attention to detail as when we were students, ever ready for a good discussion or for comparing notes on current scientific topics.

He was an example for all of his students and a stimulus to their work: he will be sorely missed by all of them and by his colleagues, including the very early ones like myself, for his enthusiasm and conscientiousness.

A personal recollection: by Lodovico Lunazzi

I first met Nando (nobody called him with his full name Fernando) in 1963 when I was preparing my dissertation: at that time he, slightly older than I, had already obtained his degree. We subsequently used to share the same office, together with a number of other young people doing research in the then Institute of Physical Chemistry, directed by the late Carlo Zauli. Nando was already involved in his studies of theoretical chemistry and, in addition, was teaching mathematics to the students of the Faculty of Industrial Chemistry.

At that time my research on NMR spectroscopy required frequent use of mathematical tools for analyzing spectra without the benefit of modern computers, so quite often Nando helped me in solving my mathematical difficulties.

We lost contact for a while when I was post-doctoring in Canada whereas he was post-doctoring in Cambridge with the late S. F. Boys.

When Nando returned to Italy, the late Professor Angelo Mangini encouraged him to apply his broad knowledge of theoretical methods to organic chemistry. So I had the opportunity to take advantage of his capability in approaching theoretical problems in order to achieve a more profound insight of my experimental data. This eventually resulted in a quite interesting joint paper (*J. Am. Chem. Soc*. 1977, 99, 4573) dealing with the stereodynamics and conformation of a fundamental hydrocarbon as studied by experimental and theoretical methods: even nowadays this work is still widely quoted both in research articles and books.

When in 1985 he was co-editor (with Mangini and Csizmadia) of the book "Organic Sulphur Chemistry: theoretical and experimental advances" I was asked to contribute an article and I was happy to oblige.

Nando was really a believer in the power of theory in order to unravel the secrets of nature. Once I was discussing with him which kind of experiment I should make to prove a certain hypothesis. His straightforward answer was: "why do not you rather make a calculation?". I was left almost shocked by his reply since, in my opinion, calculations were not as trustworthy as Nando seemed to believe. Evidently, even at that time, he knew how powerful were already the modern techniques he mastered so well. Indeed his statement can be linked to what anticipated in 1953 by the great physicist J. R. Oppenheimer: "The high speed computer ……is a sort of a substitute for experiment" (in A. Pais: J. Robert Oppenheimer, a life. Oxford University Press, 2006, p.119). After that I began to trust more the results of calculations judiciously performed and used them as an useful guide to conceive appropriate experiments.

Although our scientific cooperation was not very intense (we only published four papers together) we had a quite close personal relationship that also involved his dear wife Gemma and my late wife Anna. We enjoyed often quite agreeable dinners on the occasion of the visit of our common friends both from Italy and abroad. He also remained very fond of the late Prof. A. Mangini, that had helped him so much in indicating such a fruitful path of research, and often we took him out to dinner (together with the late Prof. Maccagnani). Inevitably the discussion, after the meal, turned to science and in particular to computational chemistry, with Nando trying to explain to the old professor the complicated aspects of the new available theoretical approaches. It was typical of Nando to start talking science quite seriously, even on the occasion of social gatherings.

I still remember the last time I met Nando: despite his serious sickness he was still discussing planes for future works, completely oblivious of his difficult personal situation. We, that have been colleagues of Nando for so many years, have lost a friend but the University of Bologna has been deprived not only by one of its best chemists but, indeed, by one of its most renown scientists that has honoured worldwide the name of our institution.

From the funeral oration: by Andrea Bottoni

I was one of the first Fernando's graduate students (may be the first) and we had together the chance of being witness to the incredible evolution of Computational Chemistry during the last three decades. Now I like to remember a few moments of Fernando's academic life.

I knew Fernando Bernardi in 1974. At that time I was a young student looking for a Ph.D. thesis and I was hooked on Theoretical Chemistry when many experimental chemists were still looking at this discipline perplexedly and suspiciously. As a matter of fact they were not entirely wrong, since during the first seventies, we could use Quantum Chemistry to describe only very simple systems and these systems were much different from the complex molecules experimentalists were handling every day. However, beyond all doubt I wanted a thesis project in this field and Fernando, a young assistant professor at that time, gave me the chance to start my discovery of the Quantum Chemistry world.

Fernando was back from a long period (three years) spent in Cambridge in the group of Prof. Boys. During that period

he had already understood the importance of Boys' theoretical work and its potential for future applications in chemistry.

At the time computers were slow and expensive and the idea of practical applications of theoretical methods required the capability of imaging beyond the big problems that we had to overcome in that period to find computing facilities and carry out some theoretical work. I must say that Fernando owned this capability of foreseeing the future of Quantum Chemistry. Following his belief he defined (or, in some way, "invented"), a new research field, which was then almost unknown. I mean the field of Theoretical and Computational Organic Chemistry, i.e., the investigation of structure and reactivity of organic molecules using computational methods. Fernando gave a big contribution to make this field more and more important in the understanding of chemistry and become accepted by many scientists, still much skeptical that chemistry problems could be "solved in silicon".

After those years of pioneering work, when we were always desperately looking for some place where computers were available for new computations (possibly free), we saw, as Fernando had predicted, the unbelievably fast evolution of computer technology. Faster and faster (and cheaper and cheaper) computing machines became available. A simultaneous development of theoretical chemistry "software" came along with the increasing "hardware" power. The collaboration with the group of Mike Robb at the London King's College begun, new people entered the research group in Bologna, all attracted by the enthusiasm Fernando was able to arouse. As a result the "new science" became stronger and was accepted. People understood that the computational approach represented a new way for gathering important and valuable chemical information. At the end the "new science" became officially part of Organic Chemistry. Nowadays lectures in Computational Organic Chemistry are usually given in many universities at the same level as other important techniques of Organic Chemistry are explained. These results led to Fernando and his coworkers many important awards at both the national and international level.

During the last years our research interests became more and more different. This is, of course, the natural evolution of a teacher-student relation. However, I must say that many problems I started to investigate stem from initial Fernando's ideas and from his belief that the Theoretical Chemistry approach could show the way to the understanding of more and more complex systems, including the huge molecules involved in the life processes. Even if recently our collaborations had become occasional, Fernando was always interested in the projects I was developing. He liked to discuss them in details since he could see in these new applications the fulfillment of dreams and intuitions he had many years ago.

I am firmly convinced of the extremely important contribution Fernando gave to the chemical research and I know that many of us must be grateful for what he has done.