

## **Autobiography Yitzhak Apeloig**

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I was born on September 1, 1944 in Bukhara, Uzbekistan, then part of the Soviet Union (USSR). My family is not native Jewish Bukharian – one of the oldest Jewish communities dating back some 2500 years. My parents were both Polish Jews who, after the German invasion of Poland in September 1939, fled separately to the Soviet Union occupied part of Poland. They were arrested and sent to enforced labour camps in north Russia and were released only in 1943. My parents met in Bukhara, got married and I was born there. The first three years of my life were spent mostly in trains, carriages and refuge camps in Europe. In 1947 we immigrated to Palestine, at that time under the British Mandate, and had to use false names and certificates to bypass the British “White Paper” which prevented Holocaust survivors from entering Palestine. A few months later in May 1948 the State of Israel was created.

I grew up in Ramat Gan – a suburb of Tel Aviv. Israel then had a population of only about 2 million people, it was very poor but it had a superb public education system. In high school I had outstanding teachers who stimulated my interest in the sciences, as well as in history and literature. I studied mathematics, physics and chemistry at the highest level – quite common at that time, but unfortunately very rare today. Chemistry was my favorite scientific subject and I had a small amateur laboratory in the basement of our apartment building, where I conducted a variety of experiments using chemicals that I could buy. One of my favorite experiments was preparing a variety of propellants and using them to fire “mini-rockets”. Only years later, I understood how dangerous these experiments were and how lucky I was not to get hurt! These experiments, and their unexpected outcomes in many cases, only increased my interest in learning chemistry and understanding more the rules that govern their properties and reactions.

In summer 1962, I graduated high school and successfully passed the matriculation certificate examinations. In Israel military service is obligatory, and I joined the army and served in paratroop unit.

In summer 1964, I received a three-month early release from the army in order not to miss the beginning of the 1964/5 academic year. I chose to study Chemistry and Physics at the Hebrew University of Jerusalem one of the two universities in Israel at that time. The first few months were very difficult since it was very challenging to return to high level university requirements after two years of army service, during which much of what I had learned in high school was forgotten. Nevertheless, after a period of adaptation I started enjoying my studies and especially the laboratories. In the last year of my BSc studies, I carried out a short research project with Prof. Zvi Rappoport, who had just joined the Chemistry Department. This short research experience in his laboratory convinced me that I wanted to continue my studies for a higher academic degree. In June 1967, my last semester of studies was disrupted by the Six-Day War, when I was drafted to my reserve paratroop unit and fought both in the Sinai Desert and the Golan Heights.

In the autumn of 1967, I received my BSc Degree in Chemistry and Physics and joined Prof. Zvi Rappoport’s group to study for an MSc Degree. Zvi had just returned

from a postdoctoral stay with Saul Winstein at the University of California in Los Angeles and established a modern school of physical organic chemistry in Israel. Zvi suggested that I study vinyl cations,  $R_2C=CR^+$ , that at that time chemists were debating whether they actually existed. Except for one paper by Grob that indicated that vinyl cations might be generated solvolytically, nothing was known about these species, their properties and their chemistry. I studied the stereochemistry in  $S_N1$  vinylic substitution and was the first to demonstrate experimentally that a vinyl cation had a linear geometry around the carbocationic center (*J. Am. Chem. Soc.*, **91**, 6734-6742 (1969)). This was my first paper, and as such, I have a special affection to it.

In spring 1969, I received my MSc Degree and decided to continue with Zvi Rappoport for a PhD Degree. In the same year I married my life partner Zipora (Tzipi) Zaltzberg.

In my PhD research I continued to study vinyl cations and concentrated on investigating the nature of the intermediate ion-pairs, (intimate, solvent-separated and free ions) in the solvolysis of vinyl halides and sulfonates. This work resulted in seven papers, four of them in the *Journal of the American Chemical Society* – very important for my future career. My thesis was awarded the Yashinski Prize for an outstanding PhD thesis.

In summer 1972, Prof. Paul von Ragué Schleyer (Princeton University) visited Jerusalem and presented three very exciting seminars about his research in solvolysis, adamantane chemistry and the use of force-field calculations to study reaction mechanisms. I was fascinated by these lectures and immediately decided that I wanted to work with him during my postdoctoral studies. When a few months later Schleyer offered me a postdoctoral position at Princeton University, I was delighted.

In the summer of 1973, I had to return to the army for three months to complete my military service which was postponed since 1964. Being already married and having a child, (Shai, 1971), I was assigned to an army office in Jerusalem. This was very convenient, as it allowed me to start writing my PhD thesis and my plan was to join Schleyer's group in November 1973. Events developed differently. On October 1973, Israel was attacked by Egypt and Syria and the Yom Kippur War erupted. I returned to my reserve paratroop unit. I fought first in the Golan Heights and then spent the next five months near the Suez Canal. In a tent in the desert between my various military duties, I wrote my PhD thesis, so that when I was finally released from the army in April 1974, I could submit it to the University Senate.

Paul Schleyer was very understanding and supportive and kept my postdoctoral fellowship throughout this time. When I was ready to join Schleyer in June 1974, Paul was already in Munich, Germany, for a six-month stay as a visiting professor in the Institute for Organic Chemistry of the Ludwig Maximilian University of Munich. Most of Schleyer's students (Jim Dill, Steve Godleski, Eluvathingal Jemmis and John Collins) joined him to Munich. Going to Princeton made no sense without initially planning to go to Germany. I therefore, joined Schleyer in Munich with my family. This proved to be an important academic experience. Our host in Munich was Prof. Rolf Huisgen. When I arrived in Munich, Paul Schleyer asked me whether I wished to work on an experimental or on a theoretical project. Knowing very little about theory at that time and not being excited about it, I chose an experimental problem and worked on the solvolysis of 2-norbornyl derivatives. This was at the peak of the period of the great debate between H.C.

Brown on the one hand, and Paul Schleyer and George Olah and others on the other hand whether the 2-norbornyl cation is “classical or non-classical”, In the 1960’s and 1970’s this question was one of the great intellectual challenges in organic chemistry and it was studied by numerous great chemists. I believed that I could make a contribution to this fascinating research problem. While in Munich, I collaborated on this project with Dr. Dieter Lenoir and this work resulted in several joint papers.

The scientific highlight of my stay in Munich was a course taught by Prof. Schleyer on qualitative molecular orbital theory, using the illuminating orbital drawings in the book “Organic Chemist’s Book of Orbitals” by W. L. Jorgensen and L. Salem published just a year earlier in 1973. This was a fascinating course that opened for me an entire new world. For the first time I started thinking about molecules and their reactions in terms of molecular orbitals! Slowly, I became interested in performing calculations myself in order to obtain the molecular orbitals of molecules in which I was interested. Only very small molecules could be computed at that time and each calculation required a walk with heavy boxes of punched computer cards to the central computer center of the university. As the university was located in the center of Munich, this was a pleasant and an enjoyable walk, (except when it was raining – and it was often raining!) and sometimes it ended with a visit to the Alte Pinakoteck or one of the other outstanding art museums around the university. This is how I became involved with theory and the world of computational chemistry. As the time passed, I became more and more involved in this endeavour which only a few months earlier seemed to me to be very remote from chemistry.

During my stay in Munich I regularly participated in the group meetings of Prof. Rolf Huisgen, which were held on the weekends and ran according to the best traditions of the German Chemistry School. After all, Rolf Huisgen was holding the Chemistry Chair of giants and Nobel Prize Laureates like Heinrich Wieland, Adolf von Bayer and Richard Willstätter who worked in the same university before him. The group meetings were very formal: very different from what we had in Jerusalem. I learned a lot from them, in particular the responsibility of a professor for every fact and every small experimental detail that was reported in a thesis or a scientific paper.

Of course, one can not be in Munich without enjoying its cultural scene: the museums; the opera and concerts; the famous October Fest; and its proximity to the beautiful Bavarian Alps. So, overall, my stay in Munich was very fruitful scientifically and enjoyable.

In December 1974, Paul Schleyer’s stay in Munich ended, and I (and other group members) moved to Princeton, New Jersey. Princeton is a lovely small university-town dominated by its world-leading university. We rented a beautiful two-floor flat in the university’s Hibben Apartments overlooking a beautiful small lake surrounded by woods, where Princeton University canoeing team used to practice. After living in the very formal Germany and in a small dark apartment in Munich, Princeton was a wonderful change. Schleyer’s laboratories in the Frick Chemistry Building overlooked the nice Woodrow Wilson Building and the small pool and fountain in front of it. Soon after we arrived in Princeton, Tim Clark from Ireland joined the group. The atmosphere within the group was great, with many stimulating group meetings (in many cases together with Kurt Mislow’s group) and many social activities, such as group picnics in Paul Schleyer’s farm outside of Princeton overlooking the Delaware River.

On December 15, 1975 my daughter Noa was born in the Princeton University Hospital and thus I have a permanent “souvenir” from Princeton!

The Chemistry Department in Princeton was a very stimulating place with many leading chemists coming to present seminars and many vivid discussions. I continued my experimental work on 2-norbornyl cation. The differences, between the way the administrative issues were handled in Princeton and in Munich, were striking. It became immediately clear to me why it was so much more effective (or so it was then) to do an experiment in Princeton rather than in Munich. For example, while in Munich, the stockroom would be open for only two hours a day and you needed at least five signatures to receive a chemical, in Princeton, you would simply go to the stockroom any time of the day and purchase the chemicals as if you were in a supermarket and simply sign your name on the slip of purchase. The only item for which I needed Paul's signature was 100% ethanol (to avoid people using it for making whiskey!) which I needed for the solvolysis studies. Tim Clark, Steve Godleski and I were doing mostly experimental work, while the rest of the group concentrated on theoretical work and calculations.

Prof. John Pople, then at Carnegie Mellon University in Pittsburgh, used to come to Princeton for a few days every several weeks. Meeting John Pople had a major influence on my career. From Pople I learned the idea of developing systematic mathematical models which then create an entire “chemistry” at a particular level of theory. By studying this “chemistry” systematically across many elements and comparing it with the experiment, one learns how to improve the model and how to extrapolate from the model to the experiment, allowing one to make reliable predictions. The potential to be able to make reliable predictions and to direct the experiment is what attracted me to start doing calculations.

One of the topics that fascinated Schleyer's group at that time was the question: how to “break” the conventional rules that control the structures of carbon compounds? For example: how to force tetra-coordinate carbon to be planar (rather than tetrahedral), or an olefin to have a perpendicular (rather than planar) geometry and so forth. While studying these questions, we discovered the unique effect of lithium, an element that continues to fascinate me with its uniqueness until today. This research led to the publication of three joint papers with Schleyer and Pople on the stabilization of planar tetra-coordinate carbon; stabilization of perpendicular olefins, and on the cyclic structure of monomeric dilithioacetylene. These papers attracted considerable interest but also raised intensive debate as at that time most chemists did not trust the results of molecular orbital calculations. Actually, most of the organic chemists were puzzled by the fact that Paul Schleyer, one of the leading experimental organic chemists, was moving away from experiment and concentrating on calculations, which many regarded as an absolute waste of time!

John Pople was developing at that time the landmark Gaussian 70 series of programs for *ab-initio* quantum mechanical calculations – a program that we have now realized marked a new area in computational and theoretical chemistry. We were the first group outside Pittsburgh to use it. Gaussian 70, which was very user-friendly, certainly relative to other *ab-initio* packages of that time and opened for me many new opportunities. I started applying calculations to a variety of reactive organic intermediates, especially carbocations, since I believed that here theory can be especially

enlightening because there was essentially no experimental structural information available due to their short life times. We published papers on the effect of  $\alpha$ - and  $\beta$ -substituents on ethyl and vinyl cations, as well as on silicenium ions.

Once I discovered the power of *ab-initio* calculations, there were hundreds of fascinating species that I wished to study! The only limiting factor was the time available for the group on the central computer of Princeton University. Actually, it was not lack of CPU time as the computer was actually idle most of the time. The issue was the cost charged per CPU time by the university which was extremely high and at that time grant agencies did not provide for computer time – the scientific world had not yet recognized this new research need of chemists. Paul Schleyer was furious about the university policy and this finally led to the fact that in early 1976 he announced that he would be leaving Princeton to move to the University of Erlangen-Nürnberg, Germany, where he was offered a Chair and essentially unlimited computer time. This move of a leading chemist from a top American university to a German university shocked the community of chemists. To me it was an example of a “blinded” university administration that inflicted significant damage to Princeton’s Chemistry Department by not understanding the needs of a new emerging discipline – the discipline of computational sciences! (This was a lesson I remembered when I attained later administrative positions). After this announcement, the Schleyer group in Princeton started disintegrating and Tim Clark, Steve Godleski and I, were the last ones to stay during the summer of 1976.

In 1975 Schleyer received an invitation to lecture in a special American Chemical Society symposium within the National ACS meeting in Chicago. Paul could not attend the meeting and thus suggested to the organizers that I should replace him – the organizers agreed. The topic of the symposium was carbocations – my PhD thesis topic. I immediately started working computationally on a variety of vinyl cations and reached many interesting insights into their structures and energies. This symposium was my first lecture to an international symposium and it gave me the opportunity to demonstrate to my experimental physical organic chemistry colleagues - many of whom I knew personally from my PhD work - the power of molecular orbital calculations. In this symposium, I also met Prof. Peter Stang – then a young Assistant Professor at the University of Utah, who after listening to my lecture became enthusiastic about the potential of calculations, creating the background for a fruitful future collaboration and a life-long personal friendship.

At the end of 1975, I started looking for a position in Israel. This was the time of a global recession after the hiking of the oil prices in 1973-4. In Israel there were no academic position openings and although I received several job offers in the USA, I was determined to return home. Consequently I started looking into gaining a position in the Israeli chemical industry. My friends in Princeton did not really understand why I chose to go back to war-torn Israel, especially as the salaries in Israel were, by a factor of three, lower than in the USA! This was difficult to explain using rational arguments!

Luckily, in the middle of 1976, a position opened up unexpectedly at the Technion – Israel Institute of Technology in Haifa and I grabbed the opportunity. I returned to Israel in August 1976. At the Technion I received a small laboratory and a \$1500 “start-up package” to purchase a conductance bridge for solvolysis rate measurements. Now, as Technion President, when I regularly authorize “start-up packages” of \$1/2 million to \$1 million to new faculty members, I often remember the

small grant that I received for starting my career. This demonstrates how dramatically the needs of modern science in general, and of chemistry in particular, have changed during the last 30 years.

I joined the Department of Chemistry at the Technion at the lowest point in its then 25 years history. For reasons that I will not go into here, there was a national-wide decline in the interest of youngsters in the natural sciences in general and in chemistry in particular. The number of students enrolling in chemistry was very low and around 1980 had reached the lowest point ever of only 10 new students. Similarly, the number of new enrolments for graduate degree studies was very small. Under these circumstances, it was very difficult to create a sizable research group. I was therefore fortunate that in 1978 a talented student Dorit Arad (Technion graduate) and a year later Amnon Stanger who graduated the Hebrew University in Jerusalem, joined my group. They both chose experimental projects; Dorit continued to work in the field of 2-norbornyl solvolysis, and later on attempted to generate solvolytically the unknown phenyl cation, while Amnon worked on the substituent effect of silyl groups on carbocations and on attempts to generate solvolytically the unknown silicenium ion,  $R_3Si^+$ .

I obtained a copy of Gaussian 70 from John Pople and started to perform *ab-initio* calculations. On the educational level, I taught a course in physical and mechanistic organic chemistry and a course in molecular orbital theory which I developed – which included a “hand-on” experience in performing calculations. At that time this course was one of the first of its kind in the world and the first to be taught in Israel. While my experimental efforts were favorably accepted by my Technion senior colleagues, my theoretical efforts were accepted with much skepticism, reluctance and were often ridiculed. I was advised many times by my senior colleagues to stop the theoretical activity and to concentrate on experiment. This was the attitude not only at the Technion and in Israel, but also worldwide and many of the pioneers of computational chemistry, such as Paul Schleyer, suffered from it too. I was at the beginning of my career, and therefore was naturally more vulnerable to such criticism. I remember vividly a case when a respected senior organic chemist of my department came into my office one day, all agitated and angry, shouting: “How dare you publish a paper in which you claim that an experimental measurement is wrong because it does not fit your stupid calculations?! You are shaming our department!” He was referring to my paper “On the Experimental-theoretical Discrepancy Regarding the Silicon-Carbon Double Bond Length”, *J. Chem. Soc., Chem. Comm.*, **768**, (1984). This incident was typical of the period and I had heard similar comments many times following lectures and seminars I presented in Israel and abroad. Luckily, the reaction of the students who were taking my course in computational chemistry was very different. They loved the course and doing calculations. Moreover, the Technion Student Association survey ranked me several times as an “outstanding teacher”.

Slowly my group grew and the practice of many would be to have an experimental project at the same time as carrying out calculations, either related to their own project (if applicable) or work computationally on other projects. In 1980, Dr. Miri Karni, who finished her PhD with Prof. Asher Mandelbaum – a mass spectrometrists in my department, joined my research group for a year, but as it turned out, she is still with us today. From the very beginning Miri devoted herself to theoretical computational work

which she learned by herself from scratch— and she was and continues to be an extremely important part of the research effort of my group.

In those years my main interest was still mostly in reactive intermediates, in particular carbenium ions, and our efforts in the field were both experimental and computational. We published on the solvolysis of 2-norbornyl derivatives, adding yet another strong evidence to support the non-classical nature of this ion. We also looked computationally into the structures, energetics and electronic nature of many other carbocations. A concept that fascinated me in these years was hyperconjugation and in a series of papers together with Zvi Rappoport I used this interesting stereoelectronic phenomenon to explain the preferred retention of stereochemistry in nucleophilic vinylic substitution reactions - a question that puzzled many chemists, - and to understand the anomeric effect in a variety of molecules.

In the summer of 1982, I was invited for the first time to lecture at a conference in Japan – the first KISPOC symposium held in Fukuoka, Kyushu in which Nobel Prize Laureates H.C. Brown and K. Fukui participated. The meeting was organized by Prof. Hiroshi Taniguchi, one of the leaders in the study of vinyl cations and Prof. Yuho Tsuno, a leader in physical organic chemistry. This meeting proved to be my “door-opener” to the Japanese physical organic chemistry community, and the first of many KISPOC meetings that I would attend and two longer three-month JSPS stays in Japan (1991 and 1999) that would follow. The KISPOC meetings were an excellent avenue to try to convince the physical organic chemistry community, especially those studying solvolysis about the value of *ab-initio* molecular orbital calculations for their experimental work. Many collaborations and personal friendships developed during these meetings and I was overwhelmed by the Japanese unique culture and wonderful hospitality. In the summer of 1991, I returned to Fukuoka for three months as a JSPS fellow and during this time lectured extensively across Japan. The idea of using *ab-initio* calculations to understand, expand and predict new experiments was accepted very politely, with respect but with great skepticism. Nevertheless, wherever I went, the hospitality was fantastic.

One of the great pleasures of computational chemistry was that it called for collaboration with experimentalists who required theoretical insight into the results of their experiments. This suited my character very well. I love working and collaborating with other people and enjoy both the scientific exchange as well as the personal contacts. Indeed, through such collaborations I gained many personal relationships and some of them became life-long friendships which soon enough also involved our families. In these early years, I collaborated extensively with Paul Schleyer, John Pople, Peter Stang and Zvi Rappoport. Many more collaborations would develop in later years as can be seen from my list of collaborators.

The Chemistry Department at the Technion was always a great place to meet leading chemists, and was probably even more so in the late 1970's and early 1980's. Numerous world leading chemists from all disciplines and from around the world visited the Technion, some for short visits and some stayed for one or two months. Here are a few names of the visitors who stayed for a longer period: Dulio Arigoni, Allen Battersby, Frank Cotton, Ernest Davidson, Jack Dunitz, Albert Eschnmoser, Léon Ghosez, Harry Gray, Rolf Huisgen, Antony Kirby, Armin de Meijere, Josef Michl, Robert Parr, John Pople, Benton Rabinovitch, Paul Schleyer, Peter Stang, Emmanuel Vogel. There were many many more. I enjoyed interacting with these great chemists, to discover their

unique chemistries and also to take them on trips around the North of Israel and share with them the special landscape and history of this land, so important to humanity and to the Jewish people. Only in retrospect can I appreciate the importance of these visits to my own career and to the career of my students.

At the Technion, the late Prof. David Ginsburg served as my “philosophical mentor”. David was one of the leading Israeli scientists and a world-renowned organic chemist with a magnetic personality. From him I learned much about “science politics” and about the value and personal rewards of scientific connections. He was a mentor in the best sense of the word – not imposing and very helpful in opening doors and making connections with his many scientific friends. I enjoyed tremendously our daily, over a cup of coffee, discussions on chemistry and other topics, ranging from food and wine to art, literature and history.

In 1982 a young German faculty member, Helmut Schwarz, from Berlin visited the Technion. This visit resulted in a very fruitful collaboration leading eventually to many joint papers and a life-long friendship. The collaboration with Schwarz’ group was “natural” because he carried out sophisticated experiments in the gas-phase studying molecular fragmentation mechanisms and complex rearrangements and calculations were essential for understanding the experimental results. Gas phase experiments were ideal for calculations because experiments were not complicated by solvent effects which were (and still are) difficult to calculate accurately. I started traveling often to Berlin, where I had the pleasure to interact and work with Schwartz’s outstanding students and collaborators. In addition, I enjoyed Helmut’s outstanding hospitality and the wonderful musical and cultural scene of Western Berlin, a city at that time still divided. I collaborated with Gernot Frenking and Wolfram Koch, then in Schwarz’ group and later to become independent researchers, and with Detlef Schröder, who could solve any mass-spectroscopic experimental problem that was brought to him. As I had seen earlier in my career in Huisgen’s group I again saw German chemistry at its best, albeit in a completely different personal style,. Helmut Schwarz also visited Israel and the Technion very often and also stayed at the Technion for long periods as a visiting Professor.

As I mentioned above, Paul Schleyer moved to Erlangen, Germany and Tim Clark joined him there. Erlangen soon became the center for organic and inorganic chemists interested in theory and in quantum mechanical calculations. I used to spend a few weeks in Erlangen every summer and these stays were always extremely exciting scientifically, with many visitors and excellent lectures and great exchanges of ideas. Paul and Inga Schleyer rented a large house in the center of the city (which everyone called the “Wagner Villa”, because the conductor of the Bayreuth Wagner opera festivals previously lived there) and they were extremely generous and hospitable, allowing many of their visitors to stay in the house. I remember one summer when some 15 people lived in the house at the same time including John Pople, Eluvathingal Jemmis, Jeremiah Chandrasheker, Martin Saunders, several others and me, Tzipi my wife, and our two children! The atmosphere in the evenings around the dinner table was marvelous and the discussions and ideas floating around were extremely exciting. The opportunities opened by the new computational methods that Pople and his group developed were endless and new exciting discoveries and insights were made every day using these new techniques. A new field of “*chemistry in silico*” was emerging. The experiences of these summers were very rewarding both scientifically and personally. In 1983, Robert West visited the

Technion and gave an exciting seminar on his recent work in organosilicon chemistry. I was especially fascinated by his synthesis and isolation of the first stable disilene, a compound with a Si=Si double bond. West's lecture attracted my attention because for many years, compounds with multiple bonds to silicon were believed to be non-existent. Furthermore, because essentially nothing was known on the physical or chemical properties of these compounds, I saw here a vast potential for computational chemistry. In contrast to organic chemistry, where much was already known about the properties of many small molecules amenable to calculations, in silicon chemistry almost nothing was known and calculations could lead experiment by making predictions. Thus, calculations could be used to predict the basic properties of unknown organosilicon molecules, such as their structures, **before** they are actually synthesized! I thought that if we can come up with several such predictions that later will be verified by experiment, this will convince the experimental chemists' community, which at that time was still very skeptical, about the value of quantum mechanical calculations to their laboratory work. In short, I believed that silicon chemistry was – and still is – a wonderful “playground” for computational chemistry.

Following West's visit my group embarked on an extensive theoretical study of organosilicon molecules, mainly low-valent silicon compounds. These computational studies later developed also into an extensive experimental programme. Many of our studies were conducted as a joint experimental-theoretical endeavour, some carried out entirely in my group and some conducted in collaboration with other groups, especially Bob West's group at the University of Wisconsin in Madison (USA).

In the summer of 1983, I left with my family for a one-year sabbatical with Prof. Roald Hoffmann at Cornell University in Ithaca, New York (USA). This was a wonderful year scientifically as well as in many other aspects. Attending Roald Hoffmann's group meetings, which included a blend of chemistry, art, literature and cultural topics, was a unique experience which I will always treasure. At Cornell University for the first time, I was exposed to surface and solid state chemistry and the exciting challenges that exist in this field of research. I published with Roald Hoffmann and Chong Zheng a very long paper (25 pages) on the “Bonding and Coupling of C<sub>1</sub> Fragments on Metal Surfaces” (modeling the Fischer-Tropsch process), of which I am very proud (*J. Am. Chem. Soc.*, **119**, 749-774 (1988)). Although I did not continue to do research in solid-state chemistry, this year played an important role in my career as it taught me the vast insights that can be gained by qualitative analysis and by examining carefully molecular orbitals, their shapes and similarities or differences, compared to other molecules (e.g., the “isolobal analogy”.)

Upstate New York and the Finger-lakes region where Ithaca is located, is a wonderful one and we enjoyed many weekends traveling through this beautiful land – extremely green to the eyes of someone coming from Israel. Ithaca also gave me the opportunity to learn down-hill skiing which I continue to enjoy to this day.

In the 1980's my research group shifted slowly from physical organic chemistry to organosilicon chemistry. Most of our studies included a combination of theory and experiment, and in many cases the same students were doing both the molecular orbital calculations and the experiments. We became one of the first groups in the world to practice both theory and experiment, and this became our “trademark”. Today, there are a

significant number of groups who combine experiment and theory, but it is still not a sufficiently common practice.

At the beginning of our shift to silicon chemistry we were still interested mainly in reactive intermediates. A typical example is our interest in the effect of silyl substitution on carbocation stability. Calculations showed surprisingly that although silicon is more electropositive than carbon  $\alpha$ -silyl substitution destabilizes a carbocation, contrary to simple qualitative expectation. Amnon Stanger, one of my first PhD students and now a faculty member at the Technion, calculated this theoretical prediction and then demonstrated it experimentally by solvolysis of a 2-adamantyl derivative (*J. Am. Chem. Soc.*, **107**, 2806-2807 (1985)). Amnon's study, again following a theoretical prediction that a silicenium ion is more stable than an  $\alpha$ -silyl carbenium ion, led also to the first experimental demonstration of a solvolytic generation a silicenium ion,  $R_3Si^+$  (*J. Am. Chem. Soc.*, **109**, 272-273 (1987)). We also studied the unusual effect of  $\alpha$ - and  $\beta$ - silyl substitution on a variety of other species such as vinyl and phenyl cations, leading to the first observation by NMR of the first stable vinyl cation (with Uli Siehl).

In these years there were a growing number of experimental organic chemists who began to realize the value of quantum mechanical calculations and many approached me asking to collaborate. I was happy to do so whenever I thought that the experimental problem was amenable to a reliable theoretical analysis or prediction. I saw these collaborations as being extremely important in convincing the experimental community to use calculations routinely, similarly to the way they use NMR or mass-spectrometry, to do their research.

In these years our collaborations with several groups intensified. With Helmut Schwarz (Berlin) we studied a variety of problems related to gas-phase reaction mechanisms, fragmentations, dissociation and rearrangement pathways, etc. With Peter Stang (Utah) we studied alkylidenecarbenes and their reactions with olefins, alkynyl sulfonates and carboxylic ethers, dication ethers, etc. With Zvi Rappoport (Jerusalem) we studied substituent effects on keto-enol equilibria, and the role of hyperconjugation on nucleophilic vinylic substitution. With Brian Halton (New Zealand) and Peter Stang we also studied highly strained molecules such as cyclopropabenzene, cyclopropabenzynes, and alkylidene cyclopropabenzene. The names of my other research partners with whom I had the pleasure to interact are given in the list of collaborators.

In August 1990, I organized the 10<sup>th</sup> IUPAC Conference on Physical Organic Chemistry at the Technion in Haifa. A day before the conference started, Iraq invaded Kuwait and the tension in the region rose to unprecedented heights. Nevertheless, as most people were already on their way to Israel, there were very few cancellations. The first three days of the conference were very tense but then the USA announced that it gave Iraq six months to withdraw and life returned to normal. More than 300 participants from around the world came, including many scientists from the former USSR and the Eastern Europe, who were allowed to travel to Israel for the first time following the collapse of the Communist regime. This provided a wonderful opportunity to Israeli students to be exposed to world-leading chemists and for the strong Israeli physical organic chemistry groups (many created by previous PhD students of Zvi Rappoport) to present their research. Anyone who has organized a conference knows how much work and time is spent in the organization, but at the end this is very worthwhile and rewarding, especially in a small country which is quite remote from the major scientific centers. Therefore, I

always encouraged my colleagues to take upon themselves such a commitment when the opportunity arose.

As pointed out above, in the 1980's our interest in silicon chemistry grew, and at the beginning it centered on the effect of silyl substitution on organic molecules. Later we turned our attention to multiply-bonded silicon compounds, of which at that time only two compounds were known – a silene ( $R_2Si=CR_2$ ) and a disilene ( $R_2Si=SiR_2$ ). In 1984, Miri Karni and I published a theoretical study on the effects of substituents on the carbon-silicon double bond (*J. Am. Chem. Soc.*, **106**, 6676-6682, (1984)) which played a very important role in our future work as well as in the work of other researchers in the field. In this paper we predicted that silyl substitution at the silicon atom of the C=Si bond would stabilize the silene electronically by reducing its high inherent polarity. This theoretical discovery motivated us to try and demonstrate in the laboratory that this computational prediction is indeed correct. It will take another 10 years until this was finally achieved experimentally (see below).

As my interest in silicon compounds grew, I embarked together with Paul Schleyer and John Pople and coworkers on an extensive systematic study on singly bonded (*J. Am. Chem. Soc.*, **108**, 206-269 (1986)) and of unsaturated or multi-bonded and divalent silicon compounds (*J. Am. Chem. Soc.* **108**, 750-756 (1986)) and compared them to their carbon analogues. These two papers included many predictions because most of the species calculated were not known experimentally. In the following years many of these predictions would be verified by experiment. These two papers played an important role in establishing quantum mechanical calculations as a useful technique for studying silicon compounds.

The calculations revealed vast differences between silicon molecules and analogous carbon compounds, in terms of both their structures and energies. For example, the basic structural motifs for carbon and silicon were found to be very different. Thus, olefins are planar while disilenes ( $R_2Si=SiR_2$ ) were calculated to have a trans-bent structure; acetylene is linear while disilyne ( $RSi\equiv SiR$ ) is calculated to be strongly trans-bent. Furthermore, the energy differences between various isomers (e.g.,  $RE\equiv ER$  vs.  $R_2E=E$ ,  $E=C,Si$ ) were found to be much smaller for silicon than for carbon and in some cases the more stable isomer in carbon chemistry is different than in the analogous silicon compound. For example,  $R_2Si=Si$  is more stable than  $RSi\equiv SiR$  while the opposite is true for  $C_2R_2$  where  $R_2C=C$  has a very high energy relative to  $RC\equiv CR$ . Many of these surprising theoretical predictions were later verified experimentally. *So in many cases in silicon chemistry theory preceded and lead experiment into new discoveries, fulfilling the promise of computational chemistry.*

The unusual structures and properties of low-coordination silicon compounds continued to fascinate my research group for the years to come. For example, we looked into the functional nature of  $RFSi=SiRF$  and showed that it has a doubly-F-bridged structure in contrast to a previous interpretation of an experimental NMR. Again, later it was shown that theory was correct. We also studied amino-substituted disilenes and their equilibrium with aminosilylenes and this led to an interesting collaboration with the group of Mitsuo Kira at Thokou University, Japan.

For many years I was quite scientifically isolated in Israel as I was the only one who was carrying out research in computational chemistry on relatively large molecules. There were in Israel groups working in the field of quantum chemistry, but the work of

these groups was “hard core” theoretical in nature and very remote from my own research. The only colleague with whom I had a joint theoretical interest was Sason Shaik, who was then starting his career at Ben Gurion University in Beer Sheva. Sason was using at that time mostly qualitative valence bond theory and curve crossing diagram to develop his beautiful and insightful work on the  $S_N2$  reaction, electron-transfer and other processes and did not use calculations. However, as time passed he realized that reliable quantitative data which can be obtained from *ab-initio* MO calculations can make an important contribution to his research.

In 1994, after Sason moved to the Hebrew University of Jerusalem, we started discussing the need to create a “computational quantum chemistry community” in Israel in order to raise the awareness of the experimental community to what such calculations offer, in order to educate a new generation of students who would feel comfortable with theory as they did with experiment and to create financial resources to purchase modern computers and to support the researchers, especially PhD students who wished to do computational work. The fund resources available in Israel for achieving such a goal did not exist and we searched for external sources. As I already had very strong scientific collaborations in Germany, we thought that Minerva Foundation – a German foundation that supports scientific collaborations between Germany and Israel, was a possible choice. We knew that the chances for success were low because about 30 applications in all fields of science and the humanities would be competing for only two yearly grants, and because the value of computational chemistry was still under discussion. Sason and I invested a lot of time in preparing the application which was submitted in March 1995. A year later we were informed that our application to establish a Minerva Center for Computational Quantum Chemistry was approved. This was an important achievement as the Center’s endowment provided a long-term basis for our research in computational chemistry. We named the Center in honour of Lise Meitner – the great Jewish-German scientist who discovered the splitting of the atom together with Otto Hahn in the early 1930’s and had to escape Nazi Germany in 1938 to save her life. The creation of the Lise Meitner-Minerva Center was an important point in the development of computational chemistry in Israel because it allowed us to interest many chemists, especially the young ones, in this activity; to invite to Israel world-renowned quantum chemists; to hold a yearly conference; and to spread the word of computational chemistry in Israel. Looking back now, 13 years later, it is clear that our expectations were fully met and the Lise Meitner-Minerva Center is now a thriving place which includes members, mostly young, from four Israeli universities: the Technion, Hebrew University of Jerusalem, Weizmann Institute of Science and Bar-Ilan University. The research topics in the center have broadened significantly and encompass organic and inorganic chemistry, material and nano science, biological molecules, as well as the development of new computational methods.

In summer 1996, I organized in Jerusalem (together with Amiram Goldblum from the Hebrew University) the 5<sup>th</sup> International Conference of the World Association of Theoretically Oriented Chemists (WATOC). This was very important for the still small computational chemistry community in Israel and was instrumental in raising the interest of experimentalists and attracting students to the field. While organizing this conference, we faced unprecedented challenges when in early 1996 the Palestinian Intifada erupted with many terror attacks within Israel’s cities, including the blowing up of public buses

by suicide terrorists. Despite this wave of terror, I was amazed that not even one of the plenary and the invited lecturers many of whom are world-leading scientists like J. Pople, P. v. R. Schleyer, L. Radem and others, cancelled their participation – indeed remarkable! Despite the tension preceding it, the conference was a great success and especially fulfilled my expectations that it would raise awareness in Israel to computational chemistry.

In 2002 I was awarded the Israel Chemical Society Prize “For the unique implementation of experimental and computational methods in exploring highly reactive intermediates and in new organosilicon chemistry”. For me this signified the acceptance of computational chemistry as a legitimate integral part of chemistry practice and methodology. The 25 year-long struggle for the legitimacy of computational chemistry was over!

Until the late 1990’s our work in silicon chemistry was mostly theoretical. In 1989 the Soviet Union started to collapse. After 70 years of almost complete isolation the Russian Jewish community was finally allowed to practice its religion and most importantly to leave the Soviet Union. A massive Jewish immigration from the Soviet Union started and within the years 1990-1995 nearly one million immigrants came to Israel, with a population at that time of some five million people. Many of these new immigrants were scientists and engineers and this made a significant contribution to the scientific activity in Israel. I was fortunate that Dr. Dmitry Bravo-Zhivotovskii joined my group in the summer of 1990. Dmitry came from the Irkutsk Institute of Organic Chemistry of the Siberian Branch of the Academy of Sciences of the USSR headed by M. Voronok – a leading group in organosilicon chemistry. Dmitry brought to my group very valuable experimental experience in organosilicon chemistry, in particular in the preparation of metallosilyl reagents. This experience proved to be extremely useful to our research.

With Dmitry in my group, we decided to try following experimentally our theoretical discovery that silyl substitution at the silicon atom stabilizes kinetically the C=Si bond, and we embarked on the synthesis of silenes of the type  $(R_3Si)_2Si=CR_2$ . We chose to synthesize them using a sila-analogue of the Peterson olefination reaction (which we named the sila-olefination reaction). After some unsuccessful attempts that revealed how complex is this reaction, we found the right reaction conditions by reacting [is this the right word?]  $(Me_3Si)_3SiLi \cdot 3THF$  with 2-adamantanone in hydrocarbon solvents yielding a new persistent silene,  $(Me_3Si)_2Si=2-Ad$  that under the reaction conditions dimerized to the corresponding 1,2-disilacyclobutane. The presence of the silene could be demonstrated by its trapping by methanol, butadiene and other reagents (*Organometallics*, **11**, 2326-2328 (1992)). This method led later to the synthesis by our group of stable silenes that could be isolated and analyzed by X-ray crystallography (*J. Am. Chem. Soc.*, **118**, 12228-12229 (1996)); two of these novel silenes are shown on the cover page. The sila-olefination reaction required metallosilyl reagents and we found that, like in so many other fields of silicon chemistry, knowledge was very limited and the number of metalosililanes (e.g., silyl lithiums) available was very small. We therefore, embarked on an extensive research program that led to the development of a new synthetic route to silyl lithium reagents via the corresponding silyl mercury compounds and lead to the preparation, isolation and X-ray structural characterization of many new silyl lithium reagents (see, for example papers 109, 144, 171 in my list of

publications; one of these novel reagents is shown on the cover page) opening new synthetic opportunities in organosilicon chemistry.

During 1994-1999 I spent a total period of 12 months at the Technische Universität Berlin with the group of Helmut Schwarz, as an Alexander von Humboldt research Awardee. This was a very enjoyable, productive and stimulating period. Helmut's group included outstanding experimental researchers like Detlef Schröder and brilliant PhD students. One of my goals for this visit was to demonstrate experimentally that compounds with a triple bond to silicon – one of the remaining “Holy Grails” of silicon chemistry, are capable of existence. We studied this question extensively theoretically, especially for silynes  $\text{RSi}\equiv\text{CR}'$ . The major challenge in obtaining silynes was that  $\text{RSi}\equiv\text{CR}'$  are in general thermodynamically less stable than the isomeric silylidene  $\text{R}'\text{RC}=\text{Si}$ : and that the energy barrier for the  $\text{RC}\equiv\text{SiR}'\rightarrow\text{R}'\text{RC}=\text{Si}$  rearrangement is very low. We suggested two strategies to stabilize silynes so that they can be observed. One is to use large bulky substituents that will destabilize  $\text{RR}'\text{C}=\text{Si}$ : relative to  $\text{RC}=\text{SiR}'$  and the second is to stabilize  $\text{RC}\equiv\text{SiR}'$  electronically. We predicted that  $\text{RC}\equiv\text{SiX}$  ( $\text{X}=\text{F}, \text{Cl}$ ) should be stable enough to be observed, (*Organometallics*, **16**, 310-392 (1997)). I discussed this prediction with Helmut Schwarz and Detlef Schröder and they devised an ingenious sophisticated tandem mass-spectroscopic experiment that for the first time demonstrated the existence of a silyne and have thus verified the theoretical prediction (*Angew. Chem. Int. Ed. Engl.* **38**, 331-335 (1999)). I regard this as one of the convincing examples demonstrating how synergism between theory and experiment can benefit and expand our chemical knowledge. Another important theoretical prediction (with Max Holthausen and W. Koch) that developed during my stay in Berlin was how to stabilize a triplet silylene (*J. Am. Chem. Soc.*, **121**, 2622-2623 (1999)), a prediction later verified experimentally.

My Humboldt stay in Germany provided me also with the opportunity to strengthen and expand my many theoretical-experimental collaborations with German groups, such as those of Armin de Meijere, Uli Siehl, Gerhard Mass, Norbert Auner, Roland Böese and many more. It also allowed me to enjoy the wonderful musical life of Berlin and the hospitality of Helmut Schwarz.

In January 1995, I was nominated to Dean of the Department of Chemistry – a position which I held for four years. This naturally burdened my schedule and limited the time that I could devote to chemistry but at the same time taught me that, if determined, one can combine academic administration duties and research. During this period, I learned the importance of a leadership administrative position in the academic arena, providing one with the opportunity to influence the development and the future of a department.

During these years I edited jointly with Zvi Rapoport four books (covering nearly 4000 pages) on “The Chemistry of Organic Silicon Compounds”, to which all the leaders in the field contributed chapters which reviewed all aspects of silicon chemistry. The amount of work involved in this endeavour was tremendous, but it was certainly worthwhile because by reading and editing all these chapters I learned everything that was known in silicon chemistry, including very remote topics from my personal research interests. These four volumes demonstrated the vast progress that had been made in organosilicon chemistry over the previous 20 years and they became the main reference books for researchers in the field.

In the spring of 1999, I went for three months to Tohoku University in Sendai, Japan as a Japan Society for the Promotion of Science (JSPS) visiting professor. My host was Prof. Mitsuo Kira. Once again, this stay emphasized a joint theoretical-experimental collaboration. In particular, we studied jointly the fascinating and complex equilibria between diaminodisilenes, their doubly-bridged 4-membered ring isomer and their diaminosilylenes precursors. I also traveled extensively all over Japan and this time visited mostly the many excellent Japanese groups studying organosilicon chemistry. There is no doubt that the large number and high quality of research groups makes Japan the world-leading country in organosilicon chemistry. I enjoyed tremendously my stay in this culturally fascinating country and the wonderful hospitality of my Japanese colleagues wherever I visited.

In October 2001 I began a new phase in my life when I was appointed President of the Technion – Israel Institute of Technology. The responsibility of leading a major research university is enormous; this duty is even more pronounced for the Technion because it is the major technological university in Israel providing the country with 70% of its engineers and technological man-power. Of course, the challenges that this position presents are tremendous, but so is the opportunity to influence and determine the future of the university. I will not discuss here what I have achieved as President of the Technion – this is to be judged by others. I would only like to state that my career as a scientist was an essential prerequisite to be successful as a university President. One has to have a deep understanding of the academic world in order to lead a university.

The appointment as President of the Technion presented a new challenge to my scientific activity. Most people I have consulted told me that I would have to quit my scientific activity. However, after serious consideration, I made a decision to continue my research work. My wife, who would have to pay a heavy price in terms of our time together, fully supported this decision. This support was crucial for making the decision.

In general, I devoted Fridays, when Technion administration does not work, to hold group meetings and meet with my research group and students. Papers and great applications were written mostly late at night, on the weekends and on the long flights to the USA that I made several times a year to raise funds for the Technion. I have even continued to teach one course a year. It may sound as an easy solution, but it was not – it required a lot of effort and determination! There were also important benefits to these efforts. My time with the group and the hours which I devoted to science were my “meditation hours” during which I forgot the burdens of my presidential duties, and when I returned to the President duties I felt energized.

The continuation of my scientific activity would not have been possible without the dedication and the academic excellence of my research group. In particular, my senior coworkers: Dr. Dmitry Bravo-Zhivotovskii who leads the experimental effort and Dr. Miri Karni who leads the theoretical effort. The independence that my students showed was impressive and due to their talent and dedication our group continued to publish high quality research results and remained a leading research group in the field of organosilicon chemistry during the eight years of my two four-year presidential terms. In 2007, I was awarded the Wacker Silicone Award – one of the two most important awards in the field of silicon chemistry and I owe it first and foremost to my research group.

During these eight years we concentrated our efforts, both synthetic and computational, on multiply-bonded silicon compounds, including the synthesis and

isolation of the first bis-silene, which also is the first metallo-substituted silene. Much effort was devoted to the synthesis of metallocsilanes and dimetallocsilanes, and to low-coordination silicon reactive intermediates such as silylenes, silylenoids and silyl radicals. The cover page of this special issue shows some of these novel molecules.

In a month, on October 1, 2009 I will step down from my present position as President of the Technion and will return full time to research and teaching and to my research group. I am looking forward very much to this moment. Leading a major university like the Technion is a great challenge and an extremely important service to the scientific community and to one's country, but the excitement of a scientific discovery and the pleasure of working with brilliant colleagues and talented students competes favorably.

### **A personal note**

First, I wish to thank the three guest editors: Dr. Miri Karni, Prof. Ilan Marek and Prof. Sason Shaik, all of whom are long-time friends and collaborators, who took the initiative to gather and edit this special volume of Chemistry – A European Journal, marking my 65<sup>th</sup> birthday. Secondly, I wish to thank all the authors of the excellent papers that comprise this volume. I am humbled and honored by this impressive parade of excellent science covering a wide range of topics dedicated to me. I have known and collaborated with many of the authors for more than 30 years and have benefited from their wisdom and friendship. I could not have imagined a more precious birthday present!

This volume also provides me with the opportunity to thank my teachers and colleagues who have strongly influenced my carrier; great scientists from whom I have learned so much. Here, due to space limitations, I can mention only a few.

From Prof. Zvi Rappoport, my Masters and doctoral thesis supervisor, I have absorbed the love for understanding reaction mechanisms and learned the importance of accuracy and reliability of experiments and in reporting results. He taught me how to critically analyze experimental results avoiding “wishful thinking” interpretations. Zvi is also the legendary editor of the “The Chemistry of the Functional Groups” series who convinced me at a later stage of my career to join him in editing four volumes in the series on “The Chemistry of Organic Silicon Compounds.”

Prof. Paul Schleyer, my postdoctoral mentor at Princeton University, introduced me to the magical world of computational quantum chemistry and its vast potential. He also taught me that “chemistry is one” and that the borders between organic chemistry and inorganic chemistry are entirely artificial. I was, and still am, amazed by Paul's enthusiasm about chemistry, the constant flow of new ideas and his unbelievable productivity.

Prof. John Pople introduced me to the beauty of his mathematical quantum mechanical models and the miracles of the Gaussian series of programs that for the first time allowed experimental chemists, like myself, to enter the “holy playground” of theoretical chemists and carry out by myself accurate and reliable quantum mechanical calculations, which until then was the sole territory of theoretical chemists.

When I joined the Technion in 1976 as a young faculty member, Prof. David Ginsburg's guidance in the complex roads of "science politics" was extremely valuable to me and I learned a lot from his wisdom.

My sabbatical year at Cornell University with Prof. Roald Hoffmann was one of the most enjoyable years in my career. Roald Hoffmann's group meetings, lasting several hours each, covering topics from chemistry to arts and literature, were an extremely stimulating intellectual experience.

My sabbatical year with Prof. Helmut Schwarz in Berlin was yet another unique experience. The combination of an excellent research group with enthusiastic students, a city undergoing a dramatic transformation due to its reunification, and of Helmut Schwarz' wonderful hospitality, created a truly unique experience, which I will always treasure. From Helmut I have learned the fascinating rich world of experiments that one can do by sophisticated mass-spectroscopy and how to "hunt" for non-existent molecules and this way expand our basic knowledge of nature.

In my autobiography, I have already thanked my research group and in particular my long-time collaborators: Dr. Dmitry Bravo-Zhivotovskii and Dr. Miri Karni, who made such a crucial contribution to my research effort.

And finally I wish to thank my life-long supporter and partner – my wife Tzipi without whose devotion and support none of what I described above would have been possible.