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Special Issue Preface

Autobiography of Josef Michl

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I was born in Prague, the capital of Czechoslovakia, three days before Hitler's army occupied it in mid-March of 1939. My parents were Czech, only a few generations from strictly agricultural life in a region downslope from the Eagle Mountains, a range of hills at the Polish border. Father was a judge at the highest court of appeals and Mother was a busy housewife with four children, of which I was the oldest. They both loved nature, especially mountains, and instilled this feeling in us children. Life was not easy during the war, when we almost perished in an air raid, nor under the communists, when Father was demoted to a notary public and banished from Prague for years because he refused to join the Party. Mother found a job sorting mushrooms and I earned a little money tutoring weaker pupils. I was a sickly child and had eight surgeries on my feet by the time I was 14.

I was incredibly fortunate in having wonderful parents and a series of outstanding teachers. In grade school, Mother started to teach me English, and when scarlet fever forced me to spend the whole summer vacation after fourth grade in total isolation, Father supplied me daily with graph paper and functions of a single variable to plot. I was also given one cowboy story book that I read 106 times, and I have had a weakness for the American West ever since.

One of my grade-school teachers, Ms. Matoušová, is responsible for my becoming a chemist. She showed her class how embers burst into flames when inserted into a test tube in whose bottom a little $KMnO_4$ is heated, and I decided at the age of ten that this is exactly what I wanted to do all my life. Well before my high school chemistry teacher, Ms. Havlínová, had an opportunity to teach me much, I already had a small room in my parents' apartment filled with chemicals, performed reactions such as Na + H_2O and FeS + HCl/H_2O, and, surprisingly, survived. My parents were amazingly tolerant, but I must confess that Mother cried when she discovered that I dissolved one of her precious silver spoons in acid because I was in desperate need of $AgNO_3$, and both frowned when all upholstery in our apartment smelled strongly of bitter almonds for weeks after I nitrated benzene in the kitchen.

My streak of good luck with superb mentors continued after I became an undergraduate at the Charles University. I decided to become an organic chemist while working part-time in a Research Institute of Pharmacy and Biochemistry as an assistant to Jan Kopecký, who synthesized new sulfonamides. His after-hours ambition was to perform a total synthesis of colchicine, an alkaloid containing a tropolone ring, derived from $C_7H_7^+$. He infected me with his interest in its nonbenzenoid aromaticity and advised me to learn about quantum chemistry, nearly unknown in the country at the time.

I earned my MS degree at the Charles University under the very beneficial joint supervision by a physical organic chemist, Václav Horák, and an electrochemist, Petr Zuman. The project dealt with a reaction mechanism, and the kinetics were followed by polarography. My PhD supervisor, working at the Physical Chemistry Institute of the Academy of Sciences, was another outstanding individual, Rudolf Zahradník, who collaborated with a theoretical physicist, Jaroslav Koutecký, to build the first quantum chemistry group in Czechoslovakia. He supported my desire to work simultaneously on the theory, electronic spectroscopy, and synthesis of nonalternant π-electron systems, and became my idol and role model. In those days, theory for organic molecules was at the level of the Hückel and Pariser−Parr−Pople models. A hand PPP calculation for the nonalternant hydrocarbon, fluoranthene ($C_{16}H_{10}$), was my top achievement.

I was similarly fortunate with my postdoctoral supervisors. The first was Ralph Becker at the University of Houston. In his laboratory I learned about photophysics and developed my life-long interest in photochemistry. After a few months with Andy Albrecht at Cornell, where I learned more photophysics, I prepared fluorofluoranthenes and measured their ^{19}F NMR spectra in the laboratory of Michael Dewar at the University of Texas, Austin. I traveled all over the American West and fell more deeply in love with it and its inhabitants, especially with Sara Allensworth, then a student at Berkeley, whom I had met some years earlier in Prague. Nevertheless, I returned to Prague, feeling that I owed it to my family and country of origin. I rejoined Zahradník's group at the Institute of Physical Chemistry. I was told to work on anything I wanted, and I chose magnetic circular dichroism (MCD) of π-electron chromophores, because I was intrigued by a student seminar in Dewar's group that described a Hammett-type correlation for the intensity of the MCD effect of the first transition in substituted benzenes, with no explanation of its origin. Very few other MCD measurements on organic compounds had

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been reported. They yielded an apparently random set of positive and negative signs for various electronic transitions. Unfortunately, my attempt to build an MCD spectrometer was an abject failure. I was unable to secure the necessary optical, electrical, and mechanical components domestically, and purchases abroad were impossible.

This was the year of the Prague Spring. The hitherto very oppressive communist regime began to acquire a less inhumane face, the future started to look rosier, and I became involved in politics. The dream was terminated abruptly by a Russian invasion in August 1968, which launched an even worse wave of oppression for two more decades. At the time of the attack, I was attending the Löwdin summer school of quantum chemistry in Norway and after a period of hesitation decided not to return home. I was invited by one of Löwdin's lecturers, a theoretical physicist Jan Linderberg, to join his group in Aarhus, Denmark, and spent a splendid year working out the rules for circular dichroism of disulfides. I disliked the Danish weather but adored the people. I made life-long friends, in particular Erik Thulstrup, a student of Jürgen Eggers, who introduced me to the use of stretched polymers as media for polarization electronic spectroscopy, but also Mark Ratner, an American postdoc. However, I missed mountains and dreamed of the American West. In 1969 I married my American sweetheart Sara, whom I had left in the USA when I returned to Prague, and subsequently spent a half century of bliss with her until she recently succumbed to a cerebral hemorrhage. Two of our three children died of cancer and the third one is an architect in southern California. His son just celebrated his fifth birthday. Sara had an indomitable spirit and was a wonderful life companion. Our honeymoon was a two-week cross-country ski trek across Finnish Lapland from one of a series of uninhabited huts to the next (after nearly missing our wedding ceremony because we had been busy shopping for a hatchet, which was not needed for the ceremony but was essential for cutting dead trees for firewood in the huts). Later, Sara suspected that she was pregnant with our first child when we climbed the 6000 m tall Mt. Kilimanjaro in Tanzania, but she did not tell me since she worried that I might cancel the climb. At various times, we survived a car crash in Sumatran mountains, a collision of small boats on a river in Malaya that sent ours to the bottom, and a cholera epidemic on the Niger river in Mali. We walked from Argentina to Chile across the Andes. She lost most of the skin off one of her shins in Isfahan, Iran. On her first kayak trip, she made it to the other side of a barbed wire fence stretched across the San Rafael river in Utah involuntarily turned upside down and climbing out later. At the end of a two-month stay in Kyoto, hosted by an incredibly kind Japanese theoretician, Hiroshi Nakatsuji, where she had spent 7 days a week visiting temples, gardens, museums, and the like while I was at work except during weekends, I reminded her that the next day we are returning home. She protested vehemently, claiming that we cannot leave yet, because she had not seen everything there was to visit. When she broke her shoulder skiing too fast in a fog at Wolf Creek Pass and I asked why she chose the steepest ski run, the excuse was "the devil made me do it". I could continue. When I wondered whether she was reckless, her response was, of course not, just adventuresome. Thereafter, I never admitted that I was stubborn, just principled.

After a year in Aarhus, I accepted a postdoctoral position in the Physics Department at the University of Utah with another of the Löwdin summer-school teachers, Frank Harris. Now, I was in the American West and I was able to hike, kayak, and cross-country ski all over it! At Goblin Valley, one of Utah's State Parks, I even ran into the navigator who had thrown bombs at me during the air raid on Prague in February 1945 and nearly killed me. He told me that his squadron got lost and thought that they were bombing nearby Dresden in Germany. With Harris, I learned about *ab initio* calculations and worked out the electronic spectroscopy of many aromatic compounds containing adjacent boron and nitrogen. Sara and I realized that we found a wonderful home in Utah and when Harris arranged a seminar for me in the Chemistry Department and I was offered a research faculty position by the then chairman David Grant, I accepted without hesitation. This started my independent career as a scientist. To celebrate, Sara and I went on our first trip around the world, associated with conferences in Switzerland and Japan. In Davos, I first encountered the community of organic photochemists that became my home base, with long-term friends like Jack Saltiel, Fred Lewis, Dick Caldwell, Pete Wagner, and many others. At the first ISNA conference on nonbenzenoid aromatics in Sendai, I had to think of Jan Kopecký when I encountered the legendary tropolone chemist, Tetsuo Nozoe. There, I also met the three Roberts who became lifelong friends: Bergman (then at Caltech), Miller (at IBM San Jose), and West (at Madison). At Utah, I had an excellent unofficial faculty mentor in Pete Gardner, an organic chemist. I learned more about NMR and many other matters from David Grant, met the living legend, Henry Eyring, made additional life-long friends like Peter Stang and Dale Poulter, and benefitted from other great colleagues. I had much continued contact with both Stang and Poulter later when we all served as editors of ACS journals, and my 31 years as editor-in-chief of *Chemical Reviews* were particularly rewarding.

In 1975 I became a naturalized US citizen and automatically lost my Czechoslovak citizenship. I went through the faculty ranks at Utah and served as chairman for five years. Sara, a political scientist, discovered that, for a woman, working as a lobbyist for environmental causes in the Utah legislature was demanding and obtaining a faculty position at the university impossible. In the mid-80s, soon after I was elected to the National Academy of Sciences, we became curious about what life was like on the other side of the Rockies and I accepted an offer of a Welch chair at the University of Texas in Austin, where I became a colleague of my erstwhile postdoctoral advisor, Michael Dewar. I enjoyed interactions with him and many of my other new colleagues, like Marye Anne Fox and Allen Bard, and Sara and I both enjoyed the town. However, I soon became disenchanted with excessive red tape and started thinking about moving again. I apparently became hard to live with, since one spring day Sara announced that she was going to move away in August, and if I wanted to, I could move with her. She was willing to move anywhere as long as it was back to Salt Lake City or on to Boulder, Colorado, where we had spent a happy summer some years earlier. I thus only had two phone calls to make. The University of Colorado had an opening and the then chemistry chairman Kevin Peters and other leading figures such as Stanley Cristol, Carl Lineberger, Tom Czech, and Chuck dePuy were encouraging. In August 1990 the family moved, and I turned down further invitations to leave Boulder. Now I had a new set of great and very helpful colleagues, including Barney Ellison and Veronica Vaida, whom I knew from earlier times. For the first time in my life, people whom Sara and I voted for actually often got elected! Sara continued

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to steer me properly through life. When I proudly announced that I was elected to the International Academy of Quantum Molecular Science with a seat in Menton, France, where I later served two terms as president, or a little later to the American Academy of Arts and Sciences, her attitude was that this is very nice and worthy of congratulations, but it would be even better if I had not forgotten to take out the garbage that morning.

In 1989 the communist dictatorship in Czechoslovakia collapsed. We started to visit my relatives and old-time Czech friends in Prague frequently and without fear. I felt again welcome as a visitor at the Heyrovský Institute of Physical Chemistry, where I had earned my PhD degree years earlier, by old-timers like Zdeněk Herman and Petr Čársky, an ex-student of Rudolf Zahradník, and by new friends like the electrochemists Lubomír Pospíšil and Jiří Ludvík, with whom I collaborate to this day. Soon, Zahradník was elected president of the Czech Academy of Sciences, but he and his wife Milena often had time for us at their country house. In 2006 Zdeněk Havlas, another ex-student of Zahradník and the director of the Institute of Organic Chemistry and Biochemistry, offered me a permanent part-time position. I was delighted to accept and acquire a second research group and an additional set of friends, such as the boron chemist Zbyněk Janoušek in my group and Jirka Kaleta and Ivo and Irena Starý in others. Sara added Czech to the four foreign languages that she was fluent in and she could finally fully understand the conversations I was having with our children. She enjoyed the old town, concerts and opera, museums, castles, and hikes in the charming countryside and happily joined the group of my old friends. Still, Boulder and the US West remained our home for the rest of our lives.

Now, back to science and our early days in Utah.

Electronic States of π-Electron Systems (MCD and LD). After I joined the faculty at Utah in 1970, Henry Eyring kindly allowed me to use his MCD spectrometer. This allowed me to fulfill my old dream of accounting for the bewildering variety of MCD sign patterns that we measured in scores of π-electron chromophores formally derived from aromatic perimeters. The interpretation was done at first using numerical (PPP) calculations[56,64],[a] and then, in a more satisfying way, with pencil and paper, using a generalization of the classical perimeter model of Platt and Moffitt.[207] Most of the results were published in a single issue of JACS.[108] The algebraic approach also allowed a formulation of a general theorem for alternant hydrocarbons and ions.[66,89] Much later, it was extended to radicals[389] and chromophores derived from antiaromatic perimeters[444,467,531,686] in collaboration with a German friend, Jörg Fleischhauer. I developed a fondness for developing intuitive understanding using simple algebraically soluble models. In one of my favorite papers of all times Erik Thulstrup and I provided an intuitive explanation of the strikingly different colors of two hydrocarbons with identical ionization potentials and electron affinities, the white anthracene and blue azulene.[74] Thereafter, I used simple algebraic models whenever I could.[208,246,362,410,648]

The MCD studies combined well with linear dichroism (LD) measurements that took advantage of Thulstrup's stretched polymer technique.[179,257,278,406] We applied MCD, LD, and similar tools to numerous π-electron systems, often using samples supplied by a German collaborator, Emanuel Vogel (e.g., porphycene[350]), or synthesized in our laboratory. Some of the work was done in collaboration with a German friend who had worked with Rudolf Zahradník, Georg Hohlneicher (e.g., hairpin polyenes[188]). Sara and I revisited Denmark repeatedly and it became our third home. Unfortunately, as the Danes themselves say, Danish is not a language, it is a throat disease. Thulstrup visited Salt Lake City many times, and we wrote two books on polarization spectroscopy.[228,310,406] The work included oddities, such as an investigation of the effects of the environment on transition moment directions of weak transitions in symmetric molecules.[183] A gifted long-term group member, George Radziszewski, extended the technique to infrared spectroscopy.[192,241] I believe that it is to this day the simplest way to determine both UV−visible and IR transition polarization directions in molecules soluble in polyethylene, particularly aromatic ones, and we still use it whenever we need this kind of information.

After the mid-70s, when we had rare gas matrix isolation setups and lasers, our optical spectroscopic studies became more sophisticated, particularly thanks to Harry Dewey and Ken Klingensmith, another long-term group member. For instance, we figured out the role of the Kekulé vibration in the L_b transition of a [14]annulene, whose excited state, like the ground state, I remembered from my days with Zahradník to be one of the two combinations of its two Kekulé structures.[279] With help from Frank Harris, who solved an integral that was too hard for me, in an effort spearheaded by George Radziszewski, we performed an algebraic treatment of free-base parent porphyrin photoorientation in solid matrixes with polarized light and used it to assign the symmetries of all of its IR-allowed vibrations.[253,313,401] A planned extension to Raman-allowed vibrations did not take place because an NIH proposal review panel pointed out that parent porphyrin does not occur in nature and therefore is of no interest. To this day, I enjoy analyzing the electronic spectra of new π-electron systems,[610] including organometallic sandwiches[637,663] and, currently, systems of interest for singlet fission.[591,705] In many of these studies, I rely on the pulse radiolysis expertise of another lifelong friend, John Miller (now at Brookhaven National Laboratory). Another branch of this work involved a collaboration with Robert Miller from IBM on the development of a chromophore for a new photoresist that permitted the fabrication of the first 1 Mb chip and remained in use for many years.[206] The project served me as an excellent lesson on how much to trust newspaper articles. I described my minor involvement in an interview with a reporter who made it clear that letting me read the proofs of her article would be beneath her professional dignity. I was subsequently amazed to read in a newspaper that I had in essence saved IBM from bankruptcy by developing for them a new photoresist that worked at much shorter wavelengths, thus vastly increasing (!) the achievable size of a single transistor on a silicon chip.

Organic Photochemistry. I suspect that, however enjoyable, the work on electronic spectroscopy of organic π-electron chromophores is not what earned me a favorable tenure decision at Utah and also offers from the universities in Cologne and Darmstadt in Germany and Princeton in the USA, all of which I turned down because I felt that I would be happier in Utah. I will never know with certainty, but I suspect that my theories and experiments in the field of organic photochemistry were considered more creative. I started those as soon as I had a laboratory and postdoctoral collaborators.[39] Among the first were my classmates from Charles University in Prague, Jaroslav Kolc, Vladimír Dvořák, Václav Kratochvíl, and Jarmila Kratochvílová. My background in organic chemistry,

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photophysics, and quantum theory, acquired during the long postdoctoral years, represented a relatively unusual combination that I was able to put to good use.

Half a century ago, organic photochemists lacked conceptual understanding of their discipline, although unbenownst to them and to me, the principles had been outlined by a theoretical physicist (E. Teller) decades earlier. The notion of potential energy surfaces, let alone a wave packet moving on such surfaces, was unfamiliar and the connection to photophysics was often mysterious. It was immediately after the Sendai conference, as Sara and I were hiking through the volcanic mountain ranges of Hokkaido, that I realized that the landscape that surrounded me, with access to its craters sometimes impeded by barriers we had to climb, suggested a simple model for organic photochemistry.[51] I recognized the critical importance of biradicaloid geometries for the location of the craters,[93,289] which I referred to as funnels, described the so-called 3 × 3 model as the absolute minimum for the description of their electronic states, used correlation diagrams to deduce qualitative shapes, and published the model in a journal entitled *Molecular Photochemistry*.[44−46] The journal promptly went bankrupt, and I wonder to this day whether there was a causal relationship. I then performed model *ab initio* calculations on H_4 with Ron Poshusta, whom I knew from my postdoctoral days when he was earning his PhD degree with Al Matsen at UT Austin, and who had access to an *ab initio* valence-bond program. We were able to gain an understanding of the relation between excimers and the funnels that return singlet excited molecules to the ground state in pericyclic photoreactions, and to clarify the relation between the valence bond and molecular orbital descriptions of their electronic structure.[80,96] The work started to provide indications of return to the ground state through conical intersections but was discontinued for several years when I lost my struggle with proposal reviewers who felt that there had been enough calculations for H_4. A class I taught on the subject at the University of Münster in Germany resulted in a book coauthored with my kind host, Martin Klessinger, which appeared first in German[299] and then in English.[378] The main friendly competitors with whom I occasionally debated the principles were Förster in Germany, Oosterhof in The Netherlands, Zimmerman in the USA, and Salem in France, with whom I spent a part of my first sabbatical. I spent the rest of it in Melbourne, Australia, where my host was the ghost of Wilse Robinson, who had left for Texas just before I arrived. Fortunately, Graham Fleming, who was left behind, took very good care of me and tried to teach me about picosecond spectroscopy. By the time I left I knew that this was a very exciting discipline that at the time required full-time attention and was not for me, because I was not willing to focus on it to the exclusion of all my other active chemical interests.

I was able to return to calculations. Semiempirical ones were performed in my own group, primarily by John Downing, who initially started as Pete Gardner's graduate student but then realized that all he wanted to do was write computer code. He earned his PhD with me and then volunteered to stay in charge of all of my group's computing. *Ab initio* calculations were done in a very fruitful collaboration with Vlasta Bonačić-Koutecký, the wife of one of my erstwhile teachers. The collaboration resulted in an improved understanding of TICT (twisted intramolecular charge transfer) states and a simultaneous prediction of a molecule whose first excited singlet lies below the lowest triplet,[220] in a recognition of the role of critical biradicaloids at whose geometry the lowest two singlet states touch,[208,270,311] and a first detailed calculation of the potential energy surfaces of such funnels (conical intersections).[231] These efforts were later generalized by Robb, Bernardi, and Olivucci.[424,497,535] The collaboration with Bonačić-Koutecký resulted in a book on the electronic aspects of organic photochemistry,[318] written mostly during sabbatical time in Berlin with the Kouteckýs, which also yielded a definitive formulation of the 3 × 3 model,[246] in Göttingen with Albert Weller, and in Stuttgart with Horst Kramer. I later used the 3 × 3 model to elaborate prior work by Lionel Salem to a general theory of spin−orbit coupling in organic biradicals and biradicaloids.[410] Zdeněk Havlas and I calculated the effects of spin−orbit coupling in a series of biradicals, especially carbene analogues,[418,514,529] and achieved an understanding of the inverse heavy atom effect.[484]

The theoretical work on photochemical reactivity was complemented by experimental studies. These dealt with the adiabatic photochemistry of Dewar naphthalene,[82] with the s-trans/s-cis photoisomerization of 1,3-butadiene, whose s-cis isomer is gauche in the gas phase but planar in a solid matrix,[260,261,327,343,449] and with two-photon photoreactions[130,131] of a type later investigated in more detail by Scaiano. Jointly with an earlier group member Jacek Waluk, we provided an NMR proof that the TICT state of an analogue of *p*-(dimethylamino)benzonitrile indeed is twisted,[487,502] which was disputed at the time, and along with a German friend, Horst Prinzbach, we examined an intriguing photoisomerization of his precursor to pagodane and dodecahedrane.[485]

Reactive Intermediates. Simultaneously, most of my research group engaged in experiments directed to the photochemical preparation and spectroscopic characterization of reactive intermediates. In those days, spectroscopy in rigid organic glasses was common in the physical chemistry community but very rarely used by organic chemists. I decided to take advantage of my prior experience with this technique, combined it with an ability to synthesize suitable precursors, and used UV−visible irradiation for photochemical preparation of indefinitely stable reactive intermediates and for photodetachment from anions[76,111] (later, we also introduced the use of X-rays for the latter purpose,[285] and this was subsequently extensively exploited by another life-long friend, Thomas Bally). We started with pleiadene,[39,55] a highly reactive nonalternant hydrocarbon, in my very first days at Utah. This turned out to be a fortunate choice, as pleiadene exhibited a transition into a doubly excited state,[49,78] one of the very first to be observed. It performed a Woodward−Hoffmann forbidden reaction very easily[132] and provided fertile ground for investigations of the applicability of Woodward−Hoffmann rules. Rational preparation of other reactive intermediates followed, including benzoquinodimethanes[54,62,104,106] and naphthoquinodimethanes.[97,245] We focused on biradicaloids, whose electronic structure related to our theoretical investigations of photochemical reactivity. Following Chapman, we retooled to the use of rare gas matrixes, which permit IR in addition to UV−vis and EPR measurements, and investigated a series of reactive intermediates with strongly twisted double bonds, such as adamantene[144] and many related species. Pyramidalized alkenes were prepared jointly with a life-long friend, Wes Borden, who wasted much of his time trying to teach me Japanese.[373] Reactions of dihalides with alkali metal vapors followed by trapping in frozen rare gas eventually led us to work on small-ring propellanes, using precursors synthesized in

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the laboratory of Ken Wiberg at Yale, whose students came to Utah for extended stays. Ultimately, Wiberg and his student Fritz Walker discovered that the smallest of these remarkable structures, [1.1.1]propellane, does not need to be isolated in a matrix but is sufficiently stable to work with at room temperature.

I became interested in securing a more complete characterization of reactive intermediates by adapting the rare gas matrix isolation method to other kinds of spectroscopy, such as ENDOR (electron−nuclear double resonance),[346] and by using unusual matrixes (alkali halides[224,297]). For matrix isolation NMR, I joined forces with David Grant. These measurements yielded shielding tensors and for their calculation I sent John Downing for a few months to Bochum, Germany, where Werner Kutzelnigg had just developed the first reliable computer program for *ab initio* chemical shift calculations. After his return, we were able to rely on these calculations to help us interpret the observed shielding tensors.[266] After a series of ^{13}C NMR studies of stable species, starting with ethylene,[136] we examined the reactive intermediates benzyne[408] and cyclobutadiene,[280] for which double labeling with ^{13}C allowed a determination of bond lengths. In cyclobutadiene the results confirmed heavy atom tunneling, and matrix isolation Raman[339] and IR[384] spectroscopy were added to examine this species in more detail.[341,369] Our matrix isolation low-energy electron energy loss spectroscopy (EELS) instrument[527] was designed and constructed by Don David, another long-term group member. The original intent was to permit observations of spin-forbidden transitions in matrix-isolated biradicaloids, but it turned out that the much more intense vibrational transitions interfered excessively and we ended up using the instrument primarily to study vibrations.[545] Theoretical support was provided by Petr Čársky.[417,528,569]

Cluster Ions and Sputtering of Frozen Gases. For matrix isolation mass spectrometry, we used ion bombardment (SIMS). The fragmentation of our reactive intermediates was excessive and we found that the method was not useful for identification purposes, but the experiments took us in an unanticipated direction when we discovered that bombardment of frozen gases with energetic rare gas ions represents an intense source of charged cluster ions. Initial work was done by a Dutch postdoc, Harry Jonkman.[128,133] The triple quadrupole instrument we used later was built by Don David and another long-term group member, Tom Magnera. Tom confessed to me that he joined the group because he liked the photograph of the Wasatch mountains above Salt Lake City that I showed in one of my lectures, at a conference in Hawaii. We studied the ejected clusters for quite a few years, since they contained puzzling products of chemical transformation of the frozen gas.[403,479] For instance, solid O_2 yielded clusters containing mostly ozone.[377] We unraveled much of the chemistry involved,[235] worked out a physical model for the ejection process,[332] looked at the spectroscopy of the intermediates formed, such as the radical N_3, showed by isotopic labeling the intermediacy of a cyclic form of the azide anion,[298] examined the metastability of some of the clusters and assigned it to a gradual release of energy by vibrationally excited N_2 present,[239] measured the binding energies of water molecules on the hydronium[329] and metal[302,308] cations, and ended up by measuring the bond lengths in Ar_3^+ by rotational depletion coherence spectroscopy, developed for the purpose.[385] We stopped when funding agencies lost interest in this type of charged clusters.

Hypovalent and Multiply Bonded Silicon. An attempt to prepare and matrix isolate a transient species with a Si═Si double bond brought us to an extensive collaboration with a silicon chemist, Robert West. He sent his graduate students for extended visits to Utah, where they learned about photochemistry in matrix isolation and rigid glasses and produced results for scores of papers on new silicon structures, mostly previously postulated but not directly observed. Most of them contained a divalent or multiply bonded silicon atom, and some of them were sufficiently sterically protected to be isolable at room temperature. The first report of an isolable disilene[169] in 1980 together with Brook's simultaneous first report of an isolable silene started a new chapter in the history of silicon chemistry.[233]

Polysilanes, Oligosilanes, Linear Chain Conformations, and Sigma Electron Delocalization. A little later, West discovered how to prepare soluble persubstituted polysilanes and I collaborated with him and Bob Miller on their fascinating spectroscopy and photochemistry.[315] They are quite different from the much better known carbon analogues such as polyethylene, because of different sigma electron delocalization. Their electronic states are complicated and are strongly affected by chain conformation,[457,496,509,587,649] as are their ionization potentials.[426,486] This intrigued me and my group started an experimental and theoretical investigation of the electronic states of the conformers of short oligosilanes, starting with disilanes,[503,579] up to hexadecasilane.[357,363,388,413,510] In order to force the chains to adopt unusual conformations we constrained them with polymethylene chains[427] or attached them to staffane-based molecular racks.[429,664] Some of the mysteries that are now understood are the localization of excitation in all-trans chains of seven or fewer silicons[386,440,547] and delocalization in longer ones,[445] the use of five stereoactive valence orbitals by Si atoms that carry localized excitation,[627,635] and variation of absorption intensity rather than energy upon conformational change in tetrasilane.[370,396,405,437,472,477,495,505,646] Some of these computations were performed with Spanish collaborators, Raul Crespo and Mari-Carmen Piqueras. We have only recently gained simple intuitive and general understanding of the conformational dependence of sigma electron delocalization in saturated chains of carbon and its heavier congeners and of the origin of the profound difference between C and Si based chains.[672,689,696]

The conformational studies of these linear chains led us to the realization that alkanes, with their favored anti configuration and a pair of gauche torsion angles about a single bond, are exceptionally simple, and that a situation with three pairs of conformations (transoid, ortho, and gauche) is the rule with substituents larger than hydrogen.[431] This was initially a computational result[396,462] but was subsequently confirmed by direct observation of the spectra of the three rotamers.[407,464] With larger lateral substituents, the situation is even more complicated.[463,469,473]

Staffanes and a Molecular Construction Set. An accidental observation of radical-induced oligomerization of [1.1.1]propellane made in the mid-80s by a graduate student, Piotr Kaszynski, made me realize that the rod-like oligomers ("staffanes"),[317,391,461] combined with suitable connectors,[494] could be used to develop a molecular construction set.[330,398,399,409,434] We examined the lateral fluorination[468] and chlorination[692] of the bicyclo[1.1.1]pentane cage, developed rod−rod coupling,[439,556] looked at bridgehead-bridgehead

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interactions,[454,549] and characterized the unusual properties of the oligomers thoroughly, (e.g., long-range propagation of spin density[367]). We used them to construct both Langmuir−Blodgett[372] and self-assembled[365] monolayers and then took this idea in three directions. One was constructing and modeling individual dipolar molecular rotors and propellers and another was the assembly of large and regular triangular arrays of dipolar rotors with the ultimate goal of surface ferroelectric behavior. Both of these were pursued jointly with colleagues from the Physics department at Boulder, John Price and Charles Rogers. The third direction was the preparation of two-dimensional polymers.

Dipolar Molecular Rotors and Propellers. We started work with individual molecular rotors[530,544,586,589,610,617] and propellers by doing dielectric measurements[492] and by performing molecular dynamics simulations, introduced to the group by a postdoc, Jaroslav Vacek, to learn about matters such as friction.[511,541,563,618] We found that it should be possible to drive unidirectional rotation both by a stream of gas[433,475] and by alternating electric field, as we actually proved experimentally using an STM tip.[518,537] In preparative work we sometimes relied on classical synthesis[518] but we also used self-assembly,[521,534,540,573] which has recently yielded peculiar oval-shaped macrocycles instead of the expected rectangular ones.[704,707] Among other interesting byproducts was an answer to the question, "do self-assembled cages contain bubbles in solution?" (those we looked at do not[666]).

Molecular Rotor Arrays[639]. The original motivation for making regular arrays was that it might be possible to build ferroelectric surfaces, but this effort has not succeeded so far. We built dipolar rotors into a MOF[578] but soon realized that we did not have enough control to position and orient the rotors properly for ferroelectricity. We also collaborated with Patrick Batail from Angers to examine some neat crystals of rotor molecules,[632,658,683] but currently we are relying on two other approaches for orienting and positioning the rotors in a proper triangular fashion. The first is to form bulk[620,654,662,691] or surface [622,623,640,655] inclusions of dipolar rotors in the channels of host crystalline solids,[639] to which I was introduced by Italian friends, Piero Sozzani and Angiolina Comotti, and the second is to build them into Langmuir−Blodgett monolayers.[656,678,682]

Two-Dimensional Polymers. For decades now,[398−400,402,423,432,434,438,455,490,493,494,557,596] we have worked intermittently on the synthesis of periodic grids on liquid surfaces using covalent bonds alone, or in combination with bonds to metals. Recently, we have constrained our effort to the preparation of porphene, a fully conjugated heterocyclic analogue of graphene, containing fused porphyrin instead of benzene rings. This effort has succeeded in the hands of Tom Magnera and he is now completing the characterization and imaging. Porphene actually is a whole family of polymers, since the porphyrin macrocycles do not need to remain in the form of free base but have been filled with various metal ions, and these can have one or two ligands of various kinds.

Carboranes. In the mid-80s, while I was spending a mini-sabbatical in Prague, a boron chemist friend, Stanislav Heřmánek, invited me to a boron chemistry conference in southern Bohemia. I thanked him and expressed regret that it would made no sense since I did not know anything about the chemistry of boron clusters. His response was that this was an excellent reason for attending. I decided that he was right and attended. On the first day I had no idea what all those closo, nido, and arachno talks were about. Then, I began to grasp the principles and it seemed to me that the lecturers were playing in a sandbox that was isolated from the rest of the chemical universe. At the end of the week I had a notebook full of ideas about what could be done with the boron clusters, and I started a program in boron chemistry in my laboratory.[560,572,634] Soon we had rods for our molecular construction set built from ten- and 12-vertex *p*-carboranes,[375] we made a small-scale synthesis of the latter practical,[641] and we had monolayers on gold,[598,612] various ylides,[451,645,667,671] and a reversible redox couple consisting of the $CB_{11}Me_{12}(-)$ anion[411,576] and the isolable $CB_{11}Me_{12}(\cdot)$ radical.[420] Both redox forms had remarkable properties.[488] For example, $LiCB_{11}Me_{12}$ is highly soluble in benzene, toluene, and silicon oil, permitting cyclic voltammetry in these solvents.[442,660] Crystal structures of alkali metal cations complexed to aromatics were obtained.[456] The almost naked lithium cations present in the benzene solution are highly reactive[515] and possess catalytic properties[480] that we associate with their high Lewis acidity. Among others, the solution catalyzes radical polymerization of alkenes to highly branched isomers of the usual polyalkenes.[661] Specific methylation of the icosahedral cage was accomplished.[558,600,601] Initially, the preparation of the starting material, $CB_{11}H_{12}(-)$, was problematic, but we came up with a new synthesis,[478] recently much improved,[706] making this anion readily accessible. The determination of spin distribution in the $CB_{11}Me_{12}(\cdot)$ radical represented an unusual challenge.[624] It is a strong oxidant that can be used for the preparation of salts of highly reactive organometallic cations.[470,522] Marvelous mechanistic puzzles awaited us on a nearly weekly basis,[638,708] remarkable reaction intermediates emerged,[525,538,561] and new reactions and mechanisms appeared regularly.[543] Substituted $CB_{11}H_{12}(-)$ anions have strongly positive redox potentials,[669] conjugation between carborane cages poses intriguing questions,[684] and huge structural changes upon reduction make even the neutral carboranes electrochemically unusual.[703]

I decided that if the introduction of 12 CH_3 groups was good for getting an anion that was hard to oxidize, the introduction of 12 CF_3 groups must surely be better. Calculations confirmed the expectations and a very gifted graduate student, Ben King, built a line for work with elemental fluorine in Boulder. Michal Valášek later built an even better line in Prague. $CsCB_{11}(CF_3)_{12}$ turned out to be remarkably resistant to oxidation, strong acids and bases, and all other conditions except scratching with a spatula, which would occasionally bring it to a violent explosion, with graphite and BF_3 as the main products.[471] This can be understood by remembering that the CF bond is very strong, but the BF bond is about 40 kcal/mol stronger. We now only work with the salts of $HCB_{11}F_5(CF_3)_6(-)$, which appear to be safe.[604] Its reversible redox potential is more than 4 V above that of ferrocene, making the isolable blue radical $HCB_{11}F_5(CF_3)_6(\cdot)$ a candidate for the strongest known neutral oxidant.

Gold Surface Alkylation. Accidental observations led me to suspect that solutions of alkylstannanes[595,659,673] and alkylmercurials[596,613,633] might coat the surface of gold with alkyls, and a series of experiments confirmed the suspicion. Some persistent tin oxides are codeposited from the former and easily removable elemental mercury is deposited from the latter, which unfortunately are dangerously poisonous. The alkyl layer deposited from alkylstannanes on gold remains conducting and does not block the electrode. We now have a good proposal for the mechanism for this remarkable transfer

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of alkyls from tin to the gold surface, based on calculations and on identification of byproducts[674] of the surface alkylation reaction.

Singlet Fission. This project originated at a workshop I co-organized at Quilmes, an archeological site in the Argentinian Andes. Sitting next to me at dinner, Art Nozik from NREL made the mistake of asking me what I was working on. After half an hour of tales of wonderful exploits in physical organic chemistry of reactive intermediates and photochemical reaction mechanisms, he got in a word edgewise. He looked me firmly in the eye and asked: "Why don't you work on something useful?" I was taken aback and asked feebly: "And what would that be?" His answer was a brief lecture on the importance of solar energy conversion for the survival of civilization. He explained the crucial significance of increasing the efficiency of cheap solar cells by overcoming the Shockley–Queisser limit and pointed out that he had just realized that singlet fission was one of the possible ways of accomplishing it. I asked him how to pronounce Queisser and he was not sure. That intrigued me since it obviously depended on Queisser's nationality. I later met Queisser in Stuttgart and asked him—he turned out to be German and that settled the matter. I also asked Art what singlet fission was. It is a process in which a singlet exciton splits into two triplet excitons, the reverse of triplet–triplet annihilation. If used just right, it would improve the efficiency of a solar cell by nearly one-half. The problem was that very few materials supported singlet fission, none of them were practical, and Art did not know where to look for more. He said it would take an organic chemist like me.

I always respond well to flattery and started to think about the matter. Soon I realized that biradicaloids would meet the requirements.[550] My group used the realization to design and test the first material that had actually been intentionally designed to perform singlet fission well, 1,3-diphenylisobenzofuran.[599] I am still proud of that even though it was clear from the outset that this very material would never be practical. I read up on all the information that had been published on singlet fission and coauthored two review articles on the subject with a postdoc, Millie Smith, in which we also worked out some matrix elements and generally had a lot of fun, or at least I did.[602,629] This endeavor had two undesirable consequences. The first one was that Millie left science, married, and became a lady of leisure. The other was that the first review article has since been cited in nearly every new publication on singlet fission, well over a thousand times, and every journal that receives a new manuscript on the subject now asks me to review it.

In collaboration with Sara's and my cross-country ski partner Art Nozik at first and Justin Johnson, also at NREL, subsequently, and several others in this country and in Europe, my two groups have contributed to further development of the understanding of the immense complexity of singlet fission and related phenomena, which have now become a cottage industry all over the world. We are looking for new chromophores[592,625] and exploring the properties of known ones,[700,709] especially diphenylisobenzofurans.[642,657,676,693] I have been long interested in the effect of molecular packing within a solid on the rate of singlet fission.[602,626,697] In a joint effort with Zdeněk Havlas, currently a vice-president of the Czech Academy of Sciences who still finds the time for annual visits to Boulder, we attempt to identify all optimal chromophore packing motifs in the solid state. We have published a procedure that accomplishes this for a pair of molecules[648,677,681,699] and it has been applied to several chromophores.[698,700,701] It involves an exhaustive search for all local maxima of a function of six geometrical variables. We already know that this is insufficient and are now working on developing exhaustive search methods for 12- and 18-dimensional spaces, for all possible arrangements of three and four molecules at a time, respectively. The next questions will be, how to force molecules to adopt the favorable geometries found and how to identify and avoid geometries that favor competing processes. We are still far from a practical material at this time. Every year, Justin Johnson and I run a singlet fission workshop in the mountains above Boulder, where I try to attract new students to the field of singlet fission, an act of contrition to compensate for driving Millie Smith out of science.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.1c01405.

Publications of Josef Michl (PDF)
CV of Josef Michl (PDF)

■ ADDITIONAL NOTE

[a]Reference citations refer to the list of publications in the Supporting Information.

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