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# Introduction: Designing the Molecular World

Armin de Meijere, born 1939, studied chemistry in Freiburg and Göttingen, receiving a doctoral degree (Dr. rer. nat.) in 1966 in Göttingen, completing postdoctoral training at Yale University in 1967–1969, and achieving Habilitation in 1971 in Göttingen. He was appointed full professor of organic chemistry in Hamburg, 1977–1989, and ever since has been in Göttingen. He was visiting professor at the University of Wisconsin, the IBM Research Laboratories, the Technion in Haifa, Israel, Princeton University, the Universities of Aix-Marseille III, Paris-Sud, Orsay, Rennes, Toulouse, Bordeaux, and Firenze, the Ecole Normale Supérieure, Paris, the Universities of Florida and Colorado at Boulder, the Indian Institute of Science in Bangalore, and the University of Santiago de Compostela, Spain. His awards and honors include German Merit Foundation (Studienstiftung des Deutschen Volkes), “Dozentenstipendium” of the Fonds der Chemischen Industrie, member of the Norwegian Academy of Sciences, Alexander von Humboldt-Gay Lussac prize, member of the Braunschweigische Wissenschaftliche Gesellschaft, Honorary Professor of St. Petersburg State University in Russia, Fellow of the Japan Society for the Promotion of Science, Paul Tarrant Distinguished Lecturer at the University of Florida, Lady Davis Distinguished Visiting Professor at the Technion in Haifa, the Merck-Eurolab Distinguished Lecturer of the French Chemical Society, Novartis Lecturer, Parke-Davies Lecturer, Adolf von Baeyer Medal of the German Chemical Society, and Editor or member of the editorial board of a number of scientific journals, periodicals, and books, including *Chemical Reviews*, *Synlett*, and *Chemistry—A European Journal*. His scientific achievements have been published in over 630 original publications, review articles, and book chapters. His current research interests include the development of new small ring building blocks and their application in the syntheses of natural and non-natural compounds, new highly strained polycyclic compounds and organometallic complexes with interesting properties, and applications of organometallic complexes and catalysts in organic synthesis.

Henning Hopf is Professor of Organic Chemistry at the Technical University of Braunschweig in Germany. He studied Chemistry at the University of Göttingen and the The University of Wisconsin in Madison, WI, where he obtained his Ph.D. degree in 1967. After his return to Germany he worked at the Universities of Marburg, Karlsruhe, and Wurzburg before accepting the position at Braunschweig. His main research areas are the preparation of unsaturated hydrocarbons (allenes, cumulenes, polyenes, acetylenes, cyclophanes, cross-conjugated hydrocarbons etc.) and the study of thermal rearrangments of hydrocarbons. He is the author of the monograph *Classics in Hydrocarbon Chemistry* and has recently co-edited a book on *Modern Cyclophane Chemistry*. For his scientific work he has received numerous awards.

The construction of highly complex organic molecules by the assembly of simple molecular “building blocks” is not at all a new concept in organic synthesis, as, for example, numerous Diels—Alder and other cycloadditions or condensation reactions show. What is new, however, is an immensely increased number of preparative methods for linking the building blocks on the one hand and an enormous variety of types and complexities of employable oligofunctional small molecules on the other. In particular, the numerous metal-mediated processes that have become routine in the synthetic laboratories around the world during the last two decades allow the connection of carbon atoms and heteroatoms of practically any type of hybridization. As far as the building blocks are concerned, not only do they span the wide spectrum from very simple units, such as acetylene, to DNA, a “molecular brick” once regarded as being intractable for molecular construction, but it has also become possible to combine fragments from completely different subdisciplines of organic chemistry—acetylenes and sugars, for example, or fullerenes and porphyrins—giving rise to completely novel hybrid structures.

It still remains a dream that anything can be accomplished, that any mental image of a molecule can be transformed into material reality, as a small list of so far unknown hydrocarbons—themselves only a grain of sand in a mountain of (conceivable) structural complexity—shows: for example,

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all attempts to prepare hexaprismane, tetraethynylallene, (unsubstituted) tetrahedrane, tetra-*tert*-butylethylene, and cyclobutyne have failed so far. However, a designed and subsequently chemically "made" molecular world is within reach. And while this bottom-up approach to ever more complex compounds is being pursued, a top-down progress from biological structures to "real" chemical compounds is occurring, and simultaneously a world of true synthetic biology—a term in which synthetic is to be understood in a chemical sense—is slowly emerging. A parallel development is seen in the area of materials.

Although there will and must be a shift of characterizing these molecules and their properties by classical spectroscopic to advanced and newly developed physical methods—a formidable task in itself—synthesis will stand in the very center of these efforts. As the following contributions show, there is indeed an "intelligent design" in this area of chemistry. The intuition, intelligence, fantasy, and creativity of preparative chemists is the *conditio sine qua non* for building a molecular world of unprecedented complexity, in which—eventually—molecules can be produced for very specific purposes, with the very specific functions that the designer-chemists wants them to have.

One strong motif in modern "designer chemistry" is the deliberate attempt to violate classical bonding situations and classical molecular geometries, that is, to prepare non-van't Hoff structures. In the present issue, this is demonstrated by the contributions of R. Keese on planar tetracoordinate carbon, by R. A. Pascal Jr.'s paper on twisted acenes or R. Herges' review on Möbius molecules, and by several reviews of molecular-bowl hydrocarbons (Y.-T. Wu and J. S. Siegel; V. M. Tsefrikas and L. T. Scott). These efforts contrast very nicely with the studies of D. Kuck on centropolyindanes in which the tetrahedral geometry of the $sp^3$-carbon atom is perfectly maintained.

The already mentioned building block approach remains a powerful route to complex structures, as shown by the contributions of A. de Meijere, S. I. Kozhushkov, and H. Schill (constructs with cyclopropane rings), M. Gholami and R. R. Tykwinski (cross-conjugated enynes), and J. E. Anthony (benzene rings). Fullerene chemistry remains an intensely investigated area; this is not surprising when one considers that fullerenes can serve as host molecules, have inside and outside surfaces for reactions, show an extraordinary diversity of chiral structures (as discussed by C. Thilgen and F. Diederich), or can be used to prepare polymers, as shown by F. Giacalone and N. Martín. Replacement of carbon atoms in fullerenes formally leads to heterofullerenes, an intriguing class of three-dimensional heteroaromatic molecules discussed by O. Vostrowsky and A. Hirsch. Of course, the building of spherical structures is not restricted to the typical "organic elements". In principle, any atom of the periodic table can be employed, with the carboranes described by S. Körbe, P. J. Schreiber, and J. Michl serving as just one example of the fusion of organic and inorganic structural elements. If loops are cut out from an all-carbon sphere, carbon nanorings result that show novel concave−convex $\pi-\pi$ interactions, as discussed by T. Kawase and H. Kurata. The large variety of belt-like structures that can be constructed from benzene rings is further illustrated by K. Tahara and Y. Tobe as well as N. Morohashi, F. Narumi, N. Iki, T. Hattori, and S. Miyano with thiacalixarenes, who present a modern variation of one of the oldest themes of spherand chemistry. One of the strong impulses that changed and extended aromatic chemistry nearly half a century ago was F. Sondheimer's annulene concept. How his ideas survived and inspired modern annulene chemists is shown by the contributions of V. Maraval and R. Chauvin, who present their "*Carbo*-mer" concept from a general standpoint, and by E. L. Spitler, C. A. Johnson II, and M. M. Haley, who demonstrate that a veritable renaissance of annulene chemistry is presently underway. Although obvious, it cannot be stressed often enough that the actual chemical building process consists of bond making and bond breaking and relies on the countless transformations of preparative chemistry. We therefore were happy to receive two contributions dealing mainly with synthetic methodology (by A. Orita and J. Otera and by J. Svoboda and B. König, respectively) to remind us that all progress in molecular construction depends on the development of new efficient synthetic protocols and must start at the bench.

Predictions concerning the next step "upward" to even more complex structures should be taken with a modicum of scepticism. However, it appears obvious to us that many of the future designed molecular objects (DMOs) must be able to perform certain functions—recognizing, transporting, switching, light-emitting, and rotating—more efficiently than their prototypes already known today. And certainly, the "connection" of this molecular world to one of larger dimensions—ultimately our, the human, world—will be a major, if not the greatest challenge.

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