

CONFERENCE

16th International Conference on Physical Organic Chemistry (ICPOC16)

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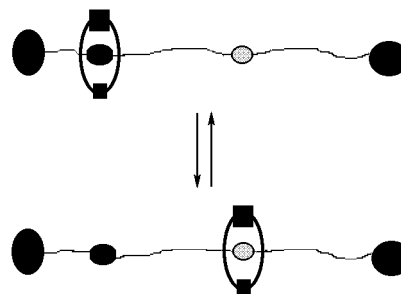
The 16th International Conference on Physical Organic Chemistry (ICPOC16, sponsored by IUPAC) was held on August 4 to 9, 2002 at the University of California, San Diego (USA). More than 300 scientists from 30 countries took part in the Conference which covered a very wide range of research fields, from aromaticity of bimetallic clusters to synthesis of potential biologically active compounds. The present brief survey cannot reflect all interesting problems discussed in 12 plenary and 20 invited lectures, 90 oral communications, and 130 posters. It seems to be reasonable to consider those extensively developing fields of studies which were unanimously recognized as the key “growth points” capable of determining the development of synthetic and physical organic chemistry, as well of related issues in the nearest future. First of all, this concerns nanotechnologies, molecular-level modelling of a number of devices (such as molecular motors, antennas, switches, “plug–socket” devices, etc.), translational motion devices, muscle contraction imitators, etc.

Just the above problems were the subject of the plenary lecture by Prof. V. Balzani (Italy), which was based mainly on his recent excellent review (*Angew. Chem., Int. Ed.*, 2000, vol. 39, p. 3348). The top-down miniaturization of technical devices, from macromaterials to microstructures (>100 nm) and then to a nano level (1–100 nm) has natural limitations due to the necessity of subdividing substances under the condition that properties of particular components be conserved. An alternative down-top approach implies assembly of molecules with fragments capable of participating in reversible interactions to obtain molecular ensembles whose components can change their mutual orientation (i.e., are capable of machine-like moving) by the action of an external factor. The best external factor, i.e., a kind of energy which brings such molecular machines into action, is provided by electrons or photons. By analogy with passing from mechanics to electronics, putting of such molecular devices into operation may be regarded as passing from electronics to “photonics.”

Naturally, the amplitude of motion of particular components of molecular ensembles with respect to

each other should be sufficiently large, i.e., it should exceed the amplitude of common harmonic vibrations by orders of magnitude. This means that the most promising are systems in which the components are linked through donor–acceptor, coordination, and/or *topological* bonds.

Some molecular motors were already created by the nature: their principle of operation is the same as that of such enzymes as ATP-synthase, myosin, etc. Synthetic frameworks of artificial molecular machines are also well familiar to chemists: The synthesis of rotaxanes and catenanes was a prominent advantage in supramolecular chemistry. The simplest example of a molecular shuttle is a rotaxane having two non-equivalent acceptor fragments on its axis (which contain, e.g., quaternized nitrogen atoms). Depending on the pH value (or by the action of electric field or irradiation)) the ring containing donor groups can move along the axis to bind with its one or another part. The lecturer gave numerous examples which are based on the above principle of reversible motion of molecular ensemble components with respect to each other.

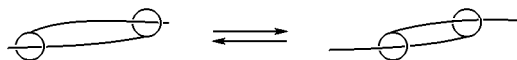


Devices like “plug–socket,” which are turned on by the action of an acid and are turned off by the action of a base, consist, e.g., of a crown ether and an amine. Protonated form of the latter comes into the crown ether cavity, whereas the free base leaves it. When each component contains aromatic substituents, the energy absorbed on photochemical excitation of one fragment can be transferred (in the “on” state) to the other fragment which gives rise to emission at

a different wavelength. Such principle of operation is typical of molecular antennas which are dendrimers having a chromophoric group in the middle of the molecule. For example, these systems are capable of transforming UV irradiation into visible light (λ 500–600 nm) and even into near IR radiation.

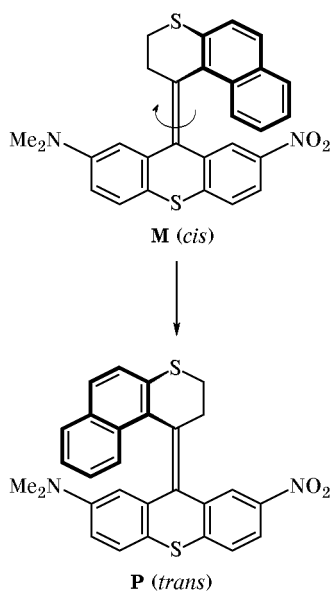
The lecture of Prof. V. Balzani was perfectly supplemented by the plenary lecture of J.-P. Sauvage (France) on catenanes and rotaxanes containing transition metal cations. Molecular parts are bound topologically and are put into motion electrochemically or photochemically, e.g., via changing the degree of oxidation of copper ion. In the initial state, four-coordinate copper(I) cation is linked to two 1,10-phenanthroline fragments, one of which is located in the rotaxane ring, and the other, on the axis. Oxidation gives copper(II) ion which prefers a five-coordinate state, so that it moves to the part of the axis containing a tridentate terpyridine fragment. The reduction of Cu^{2+} to Cu^+ promotes the reverse translation.

Application of the above principle to dimeric rotaxanes, where the tail of one fragment threads the ring of the other and vice versa (so that these fragments can slide along each other), gives a system modeling muscle contractions.



Experimental implementation of such contractions resulted in shortening of the distance between the rings from 8.5 to 6.5 Å.

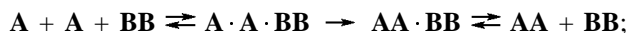
The above topic was also supplemented by very emotional lecture of B.L. Feringa (The Netherlands)



who considered chiroptical molecular switches which change their spirality on irradiation. Light-induced rotation about the formally double $\text{C}=\text{C}$ bond in such systems occurs only in one direction, i.e., this is just the rotation rather than vibration relative to the double bond axis. The speed of rotation can be controlled by chemical modification of the molecule, in particular, via replacement of the sulfur atom by oxygen or nitrogen. As a result, steric hindrance to the rotation is reduced, and the speed increases (for reviews, see *Chem. Rev.*, 2000, vol. 100, p. 1789; *Acc. Chem. Res.*, 2001, vol. 34, p. 504).

S.A. Vignon (USA) performed an NMR study of hexafluorophosphates derived from [2]catenanes having four pyridinium fragments in one of the rings. Using chiral reagents like *N*-[1-(1-naphthyl)ethyl]-acetamide, the authors discovered a new type of chirality which arises from the difference in the dihedral angles between the mean-square planes of two macrorings.

G. Kiedrowski (Germany) reported on chemical modelling of self-replicating nanostructures based on oligonucleotides. Molecular self-replication which underlies life on the Earth has become the subject of extensive studies in the recent years (*Nature*, 1994, vol. 369, pp. 218, 221; 1998, vol. 396, pp. 245, 447; *Angew. Chem., Int. Ed.*, 1999, vol. 38, pp. 3312, 3713). About 10 years ago, such studies have been started with autocatalytic template synthesis. This technique gives products which completely reproduce the template structure. However, in the animate nature molecules never catalyze their own formation. In other words, not the autocatalytic scheme (where the formation of an **AB** template is catalyzed by itself) but the cross-catalytic scheme is operative. The latter implies that the formation of an **AA** template is catalyzed by **BB**:



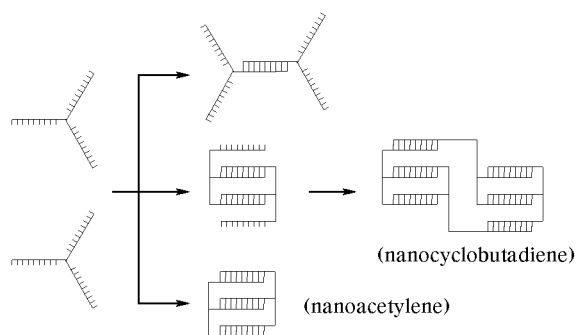
rather than



Also, there is another difference between model reactions in solution and those occurring in living systems; the kinetics of the former follow a power relation rather than exponential which is the necessary condition of the Darwin evolution theory. The author proposed SPREAD procedure (surface-promoted

replication and exponential amplification of DNA analogs) which includes immobilization of a template on a solid support; it reproduces the evolution process as accumulation of mutations, for mutation products are bound to the support more weakly than its exact copies, so that they are extracted into solution more readily. A little later, one more template synthesis scheme with exponential kinetics has been proposed. It is based on redox-controlled covalent binding of substrate to template.

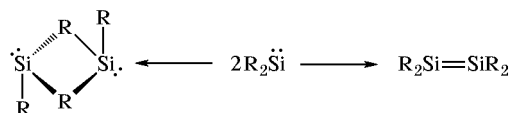
Very interesting studies were performed on the formation of DNA nanostructures from tris-oligonucleotide units which on fast cooling (under conditions of kinetic control) give rise to small complexes with different topologies rather than to polymeric networks. The formation of a single, double, or triple carbon-carbon bond may be imagined as junction of tetrahedra through apices, edges, or faces. Likewise, tris-oligonucleotides could be linked through one, two, or three double nucleotide chains. Each of such double nucleotide chains may be regarded as a topological analog of C-C bond. Then, the simplest complex has a topology of "nanoacetylene", in keeping with the scheme shown below (see also the color inset to *Angew. Chem.*, 1999, vol. 111, p. 3513):



The plenary lecture of J. Klinman (USA) was devoted to theoretical analysis of hydrogen transfer in enzymatic reactions. The classical concept implies the following conditions to be met: $(k_D/k_T)^{3.3} \approx k_H/k_T$ and $A_H/A_D \approx 1.0$ (where A is preexponential factor). In the case of hydrogen tunneling (corner cutting process), these relations change to $(k_D/k_T)^{3.3} \ll k_H/k_T$ and $A_H/A_D \ll 1.0$. In the recent years, increasing number of examples have been reported, where the above relations are violated, i.e., $A_H/A_D \gg 1$. Therefore, a new approach to description of hydrogen tunneling processes has become necessary. Such a description appeared on the basis of the recent analysis (*Can. J. Chem.*, 1999, vol. 77, p. 1085) which takes into account the effect on hydrogen

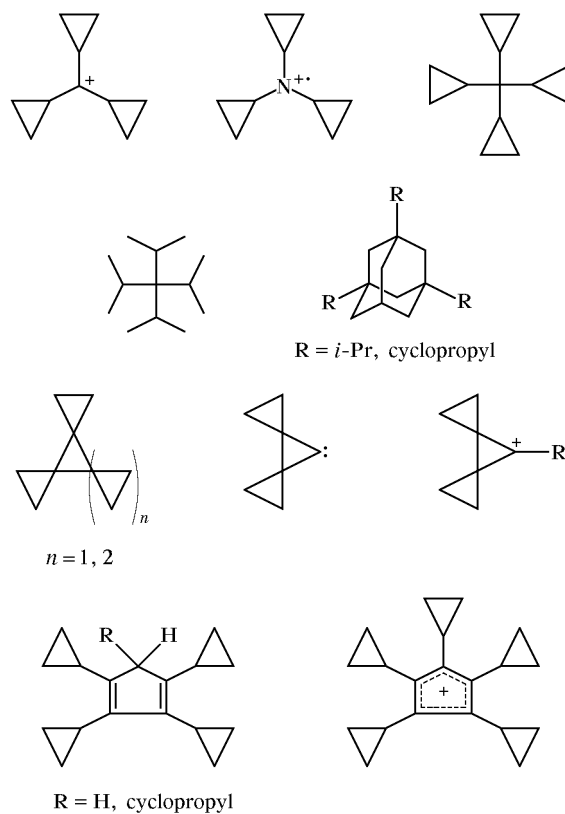
transfer of reorganization of heavy atoms in the environment. It provides explanation for many experimental findings, in particular the absence of temperature dependence for the kinetic isotope effect in some hydrogen transfer reactions.

As concerns more traditional but permanently interesting topics, the plenary lectures read by Y. Apeloig (Israel) and A. de Meijere (Germany) must be noted. The first of these dealt with theoretical analysis of alternative routes of silylene dimerization with formation (by analogy with carbenes) of a double Si=Si bond or bridged structures which have no analogs in organic chemistry.



When R is an alkyl or aryl group, the disilylene structure is preferred, whereas in going to R = F, OH, NH₂ it becomes less favorable, and the calculation gives no stable disilylene structure at all for R = NH₂.

The second lecture summarized the results of enduring studies on triangulanes. Some structures are shown below. A considerable part of these studies was



performed in collaboration with Russian chemists. The specific chemical and spectral properties of triangulanes, as well as of ions and radical ions derived therefrom, is determined by a strong donor effect of cyclopropyl groups.

General approval was caused by encouragement of young scientists: by the end of the conference, three

reports from each of the two poster presentations, which were made by young scientists from different countries, were awarded prize money by the Organizing Committee.

The next, 17th International Conference on Physical Organic Chemistry (ICPOC17) will be held on summer 2004 in Shanghai.