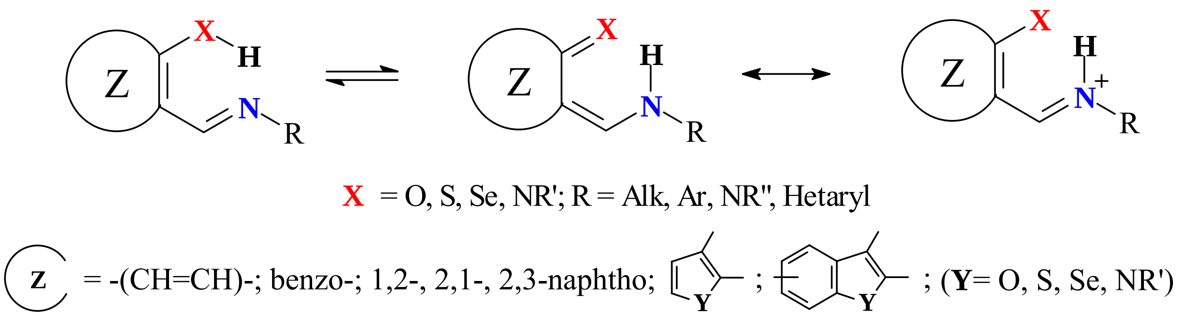
Professor Vladimir I. Minkin
A Tribute

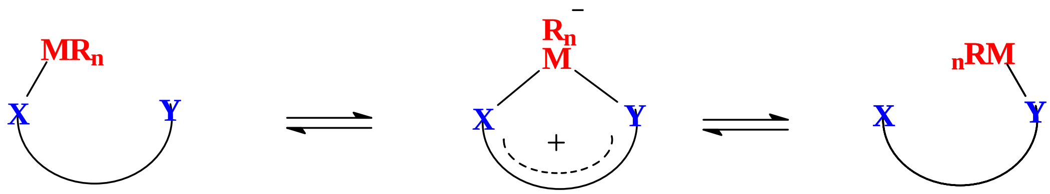
Vladimir I. Minkin was born on March 04, 1935. After graduating from Rostov State University in 1957 he took a position as a technical assistant in Novocherkassk Technical University and in 1958 joined the Department of Organic Chemistry of Rostov State University. In 1959 he received his Candidate (Ph. D.) and in 1966 Doctor of Sciences (Chemistry) degrees. In 1967 he was appointed Full Professor at the same University, and since 1981 he has held the position of Head of the Institute of Physical and Organic Chemistry. He was a visiting professor or visiting scientist at the Havana, Queens (Kingston, Canada), Strathclyde, Regensburg, Marseille, Cornell and Humboldt Universities, received his Dr. *honoris causa* degree from the Mediterranean University of Aix-Marseille and was elected a full member of the Russian Academy of Sciences in 1994. Among his awards are the State Prize of USSR (1989), the Senior A. v. Humboldt Award (1999), the A.M. Butlerov (2000) and L.A. Chugaev (2003) Prizes of the Russian Academy of Sciences and Prizes of the Foundation for Support of Russian Science for “Outstanding Scientists of the Russian Academy of Sciences” (2003, 2004). Prof. Minkin’s research interests include applied quantum chemistry, tautomerism and molecular rearrangements, stereodynamics of metal coordination compounds, photochromism, nonclassical organic and organoelement structures and organotellurium chemistry.

Starting his scientific career as a synthetic chemist (his Ph. D. thesis dealt with the chemistry of quinoline), Vladimir Minkin became interested in physical organic and theoretical chemistry. He was the first to predict by calculations and to confirm by the use of dipole moments and spectral studies, the acoplanar structure of aromatic and heterocyclic azomethines and then continued a study of this class of compounds paying special attention to the problem of benzenoid-quinonoid tautomerism (Scheme 1). His group synthesized and studied wide series of alicyclic, aromatic and heteroaromatic compounds of this type thus enabling the elucidation of the structural and environmental factors affecting relative stabilities of the tautomers. One such factor is the degree of aromaticity of the interconverting species. These studies initiated Prof. Minkin's interest in the problem of aromaticity, which became one of the important topics of his research reflected, among other contributions, by a number of review papers and a monograph.

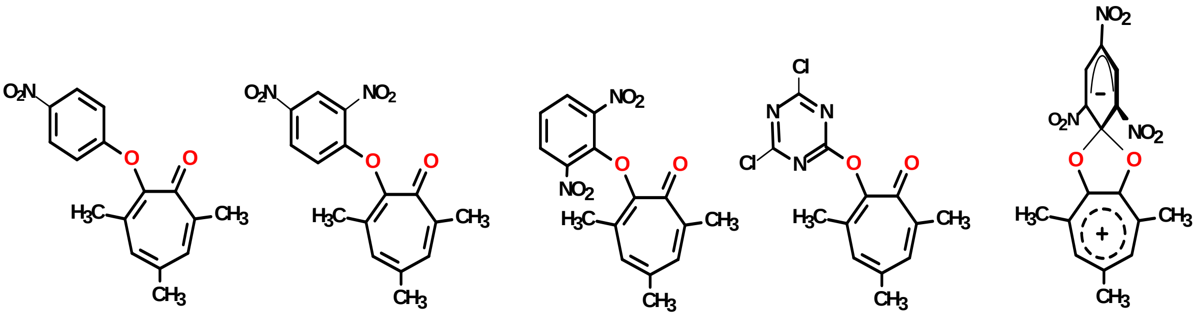


Scheme 1

Along with prototropic tautomerism Prof. Minkin investigated new types of sigmatropic tautomeric rearrangements occurring at rates matching those of proton migrations. On the basis of theoretical modeling aimed at fitting stereoelectronic requirements of the relevant reaction pathways, he developed a systematic approach to the rational design of low-energy barrier intramolecular rearrangements governed by the migration of C, Si, N, P, As, S, and Se-centered groups between nucleophilic centers. It was shown that, where the initial structure of a rearranged compound can be closely fitted to that of the transition state through low-energy barrier conformational or polytopal transformations, the frequencies of the migration of the heavy atomic groups may achieve those for proton migration. The kinetic data below (Scheme 2) exemplify the evolution of the energy profile of the degenerate rearrangements caused by the O,O′-shifts of activated aryl and heteroaryl groups as a function of electrophilicity of the migrant from a double-well shape to the well (energy minimum) corresponding to a stable symmetrical structure of an electrically neutral Meisenheimer complex. Some of the photoinitiated carbonotropic rearrangements of this type have been successfully applied to develop reversible abiotic systems for accumulation of light (including sunlight) energy.



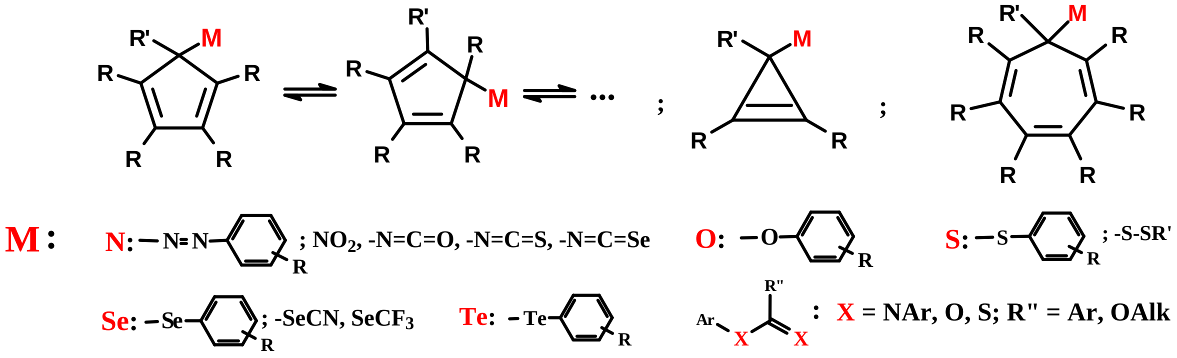
X, **Y** = O, NR', S; **MR$_n$** = Acyl, Aryl, Hetaryl, PR$_1$R$_2$, P(O)R$_1$R$_2$, AsR$_1$R$_2$, SR, S(O)R, SeR



k_{25}, s^{-1}: $<10^{-6}$ ~10^4 $>10^7$ $>10^7$ C_{2v} (min)

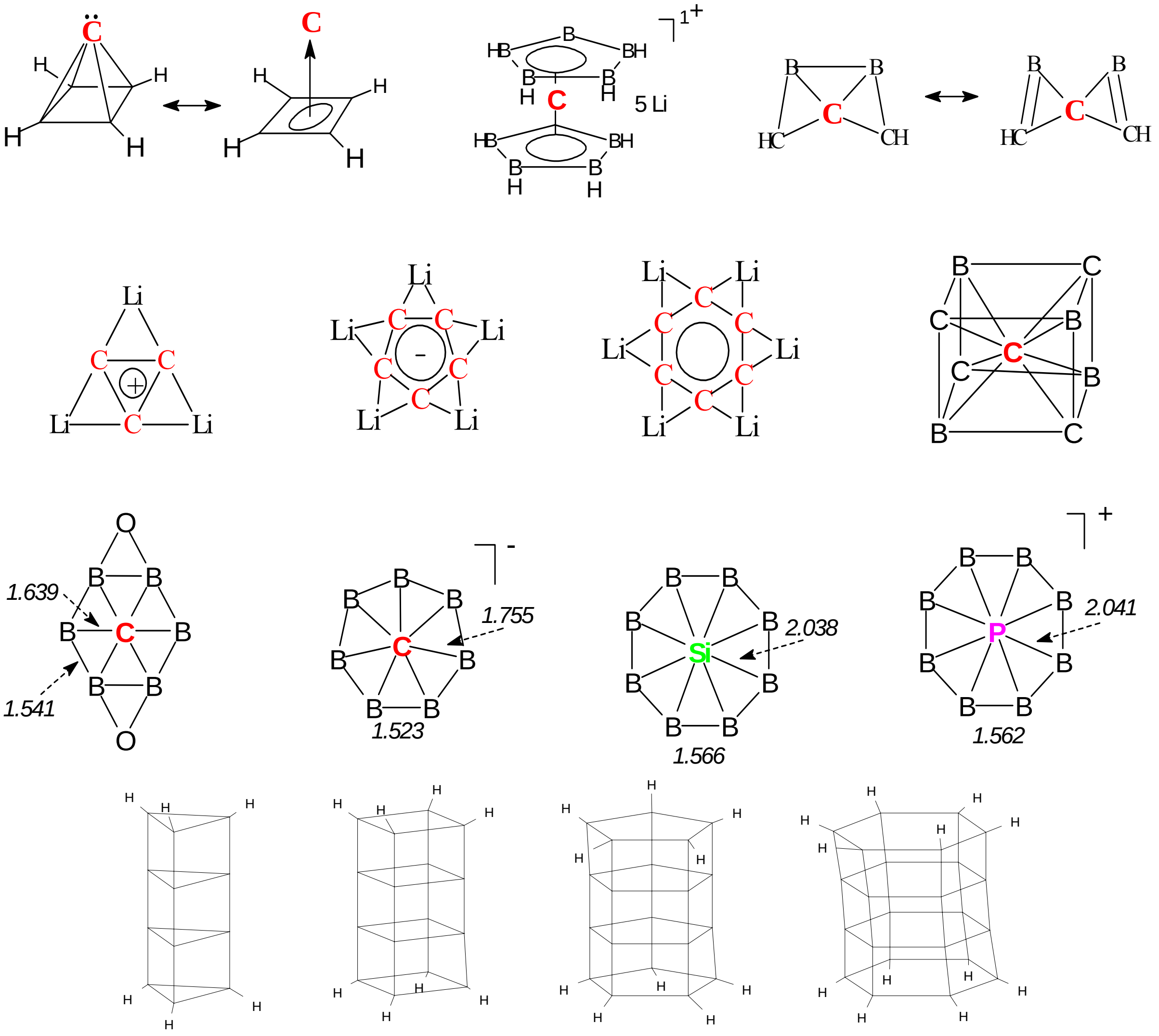
Scheme 2

Low-energy barrier circumambulatory rearrangements are another type of dynamic molecular transformation, of interest to Prof. Minkin. Highly fluxional structures of this type have been known for compounds with almost all metal-centered groups as well as for main (13, 14) element-centered groups. Studies of the degenerate (R=R') and non-degenerate rearrangements of 3-, 5- and 7-membered cyclopolyenes performed by the Minkin research group extended knowledge of these rearrangements to main-group (15-17) element-centered migrants (Scheme 3). Cyclopentadienyl compounds with electron-withdrawing substituents (e.g. R=COOMe) have been found to be highly efficient group-transfer agents acting under very mild reaction conditions.



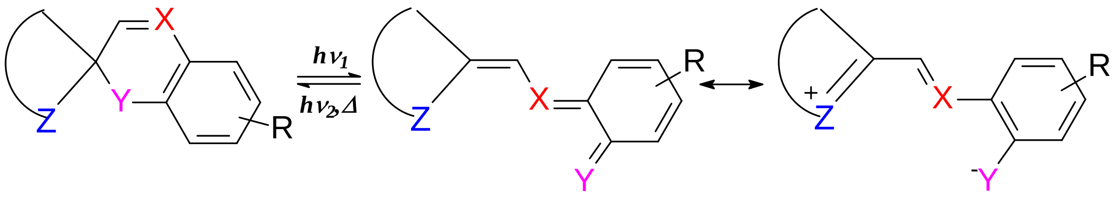
Scheme 3

Theoretical studies occupy an important place in the research activity of Prof. Minkin and his group. Using perturbation theory and the analysis of orbital interactions of molecular fragments they developed a rational strategy for constructing new structural types of nonclassical organic and organoelement compounds with tetracoordinate planar, half-planar and pyramidal carbon atoms and a general approach to systems with planar hexa-, seven and octacoordinate planar main-group element centers including various polyhedral structures with hypercoordinate carbon atoms. In the framework of a general concept of three-dimensional aromaticity they suggested a set of electron count rules governing the stability of certain types molecular polyhedra. A brief selection of the newly devised structures, the unusual molecular architecture and stability of which were confirmed by the results of sophisticated *ab initio* calculations, is given below (Scheme 4).

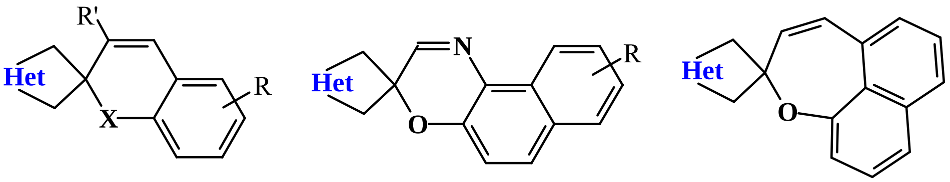


Scheme 4

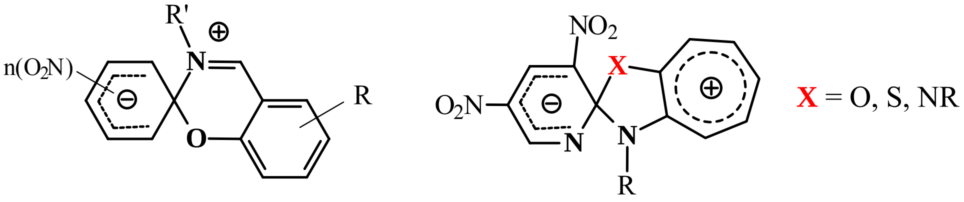
Prof. Minkin has made significant contributions to the synthesis, spectrokinetics and photochemistry of photochromic compounds – bistable molecular systems, whose reversible rearrangements are driven by light (Scheme 5). Starting this work in the 1970s, his group prepared and studied a wide series of spirocyclic compounds including spiropyrans, spirooxazines and spirooxepines (Scheme 6), previously unknown photo- and thermochromic spiro-1,3-oxazines, bipolar spiro-σ-complexes (Scheme 7) and a new family of photo-, thermo- and electrochromic perimidinespirocyclohexadienones (Scheme 8).



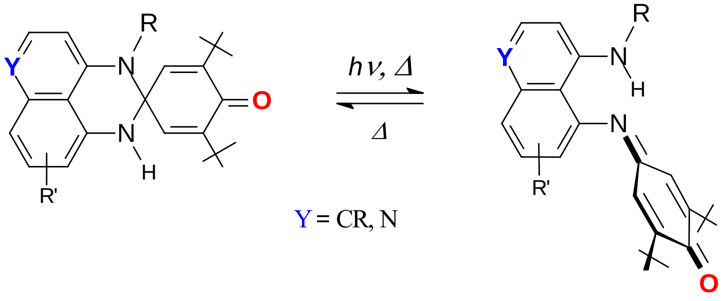
Scheme 5



Scheme 6

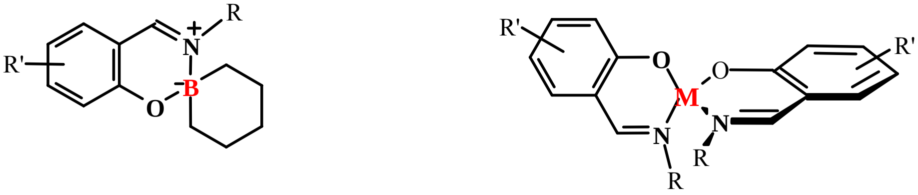


Scheme 7



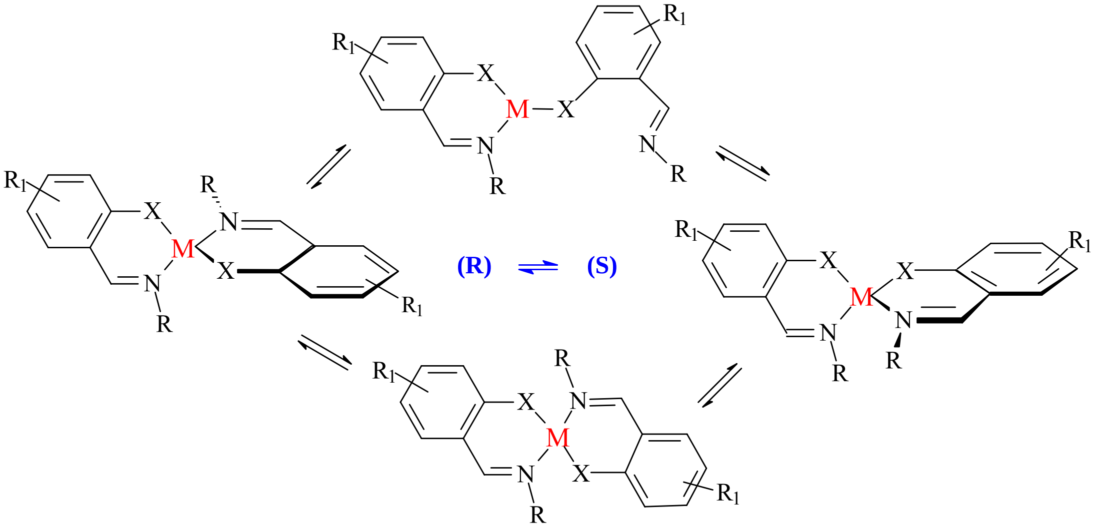
Scheme 8

An important finding in this area was the discovery of photochromism of benzo-1,3,2-oxazaborines and bis-(N-alkyl- or aryl)salicylaldiminates (Scheme 9), which are metal analogues of 2H-chromenes and symmetrical spirooxazines, respectively.



Scheme 9

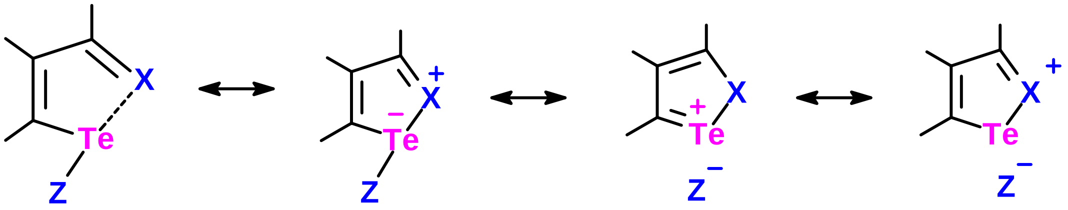
The sets of the bidentate hydroxy(thio-, seleno-)aldimines (Scheme 1) at the disposal of Prof. Minkin's research group allowed preparation of a variety of metal chelate complexes, leading to a systematic study of their structure, and electric / magnetic properties. Special attention was given to gaining insight into the stereodynamics and ligand exchange reactions of the complexes. It was found that, depending on the nature of the metal, ligating atoms and substituents in the rings the rearrangements occurred rapidly ($\Delta G_{25}^{\neq}$ values are in the range of 5-25 kcal mol^{-1}) with inversion of stereochemical configuration at the metal center and, contrary to the Ockham's razor principle, are governed by different mechanistic modes. These involve polytopal digonal twist and bond-breaking/bond-making rearrangements as well as intermolecular ligand exchange reactions (Scheme 10).



M = Be, Zn, Cd, Hg, Pb, Ni, Cu; X = O, S, Se

Scheme 10

Organotellurium chemistry is another area of research activity of Prof. Minkin and his group. They developed new methods for the synthesis of previously known and a variety of novel classes of organotellurium compounds, e.g. tellurium ylides and their aza-analogues, tellurenyl azides, bis-[diaryl(alkoxy)tellurium] sulfates and a number of new Te-containing heterocycles (derivatives of tellurochromone, benzotellurophene, 3H-isotellurazole, telluraxanthene, phenotellurazine, benzo-1,3-tellurole, 1,2,3-tellurodiazine, dibenzotelluro-azepine, 3H-oxatellurole-1,2, oxatellurazocine and others). The convenient precursors of many of the tellurium-containing heterocycles are β-tellurocarbonyl compounds and their imines, the spatial and electronic structure and conformational dynamics of which were thoroughly studied using X-ray, multinuclear NMR and computational methods. These compounds represent an interesting family of cyclic aromatic systems with hypervalent centers, in which the the Te…X distances (Scheme 11) cover the range between van der Waals contact and normal valence bond and the energy of the attractive Te←O(NR) interaction (up to 30 kcal mol^{-1}) exceeds the strength of the strongest H-bonds.



X = O, NR

Scheme 11

Prof. Vladimir Minkin has published over 800 papers and 15 monographs. In 1992 he was elected titular member of IUPAC and was a chairman of the IUPAC working party that created the "Glossary of Terms in Theoretical Organic Chemistry". He is a member of the Russian National Committee of Chemistry, presidium of the Russian D.I. Mendeleev Chemical Society, Fellow of the Royal Society of Chemistry, and a member of Editorial Boards of three international and six Russian chemical journals. He was a plenary or invited speaker at a number of international conferences on physical organic chemistry (Regensburg 1988, Jerusalem 1990, 1996, Ithaca 1992, Florianopolis 1998), photochemistry (Moscow 2000), organic photochromism (Illes des Embiez 1993, Clearwater Beach 1997, Arcachon 2004), coordination chemistry (Rostov, 2001) and others.

Vladimir Minkin is an open, cordial and friendly person. He supervised the work of more than 60 Ph. D. students and 15 Doctors of Science. Many of them continue their research in the Institute headed by Prof. Minkin and form together an active and devoted team of researchers and friends. We are sincerely grateful to Vladimir for his efforts supporting a high level of research in the Institute and the established climate of dedicating to pure science and fair human relationships. We wish him further success in his research and good health in the years ahead together with his wife and family.

Professor Alexander D. Garnovsky, Professor Vladimir A. Bren

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Selected Publications of Professor Vladimir I. Minkin

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