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Electronic Structure and Reactivity of Inorganic, Organic, Organoelement and Coordination Compounds: An Experience in the Area of Applied Quantum Chemistry

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Alexei N. Pankratov

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Chapter 2

ELECTRONIC STRUCTURE AND REACTIVITY OF INORGANIC, ORGANIC, ORGANOELEMENT AND COORDINATION COMPOUNDS: AN EXPERIENCE IN THE AREA OF APPLIED QUANTUM CHEMISTRY

Alexei N. Pankratov[*]
Division of Analytical Chemistry and Chemical Ecology, Department of Chemistry,
N. G. Chernyshevskii Saratov State University, 83 Astrakhanskaya Street, Saratov
410012, Russia

Dedicated to my mother Elena M. (Trepak) Pankratova
and to the bright memory of my father Nickolai D. Pankratov
and my grandmother Vasilisa K. (Miron'ko) Trepak

Abstract

A brief overview of the author's line of scientific inquiry has been presented. Discussed are results of the establishment of predictive structure - property relationships, the study of interrelation between the substances reactivity and the molecules electronic structure, the elucidation of mechanisms of chemical reactions and the allowance for medium effects on their proceeding, the solving of other interpretational tasks of chemistry. The methods of different hierarchy and theory level, adequate to the problems to be solved, are used, from semiempirical to modern sophisticated *ab initio* and DFT methods, along with comprehensive approaches and techniques including the NBO, energetic deletion, AIM, orbital interactions, electrostatic potentials analyses, calculation of vibrational, electronic absorption and NMR spectra, scaling of vibrational frequencies, separation and analysis of normal vibrations, ZPVE, thermal and BSSE corrections, localization of transition states, IRC, SCRF, *et al.* The capabilities and potentialities of the current quantum chemistry have been considered. The

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[*] E-mail address: PankratovAN@chem.sgu.ru; PankratovAN@info.sgu.ru,
Web: chem..saratov.ru/pankratov; www.chem.saratov.ru/pankratov; sgu.ru/faculties/chemical/pankratov; www.sgu.ru/faculties/chemical/pankratov

problems of systematization and generalization of the information resources on natural sciences, on ecology are also involved.

The major problem facing the chemistry today and in the future is to predict the time course of chemical process and its ultimate result starting from the information on structure and properties of the molecular systems of reactants, intermediates, products, as well as on the transition states, taking into account the solvation shells, *i.e.* to gain information on the chemical reaction mechanism.

The reaction mechanism is the reaction description in detail, taking into account all the intermediate stages and the substances emerging here (intermediates), the nature of reactive species interaction, the character of bonds cleavage, the change in energy of the chemical system over the whole pathway of its transfer from initial to final state [1].

Reaction mechanism is a sum of information on the nature of reactive species of reactants, intermediates, yield products, including the solvation shells, on the change in concentrations of the above species with time, as well as on the transition states and other specific points on the potential energy surface, in the perfect case - a comprehensive information on the potential energy surface of chemical reaction [1, 2].

The term “reaction mechanism” is at least by the order of magnitude more complicated compared to the term “structure”. The mechanism definition requires obligatorily the description in detail of such items as how the structure and chemical bonds change in reactants during the every separate step of chemical transformation [3].

The reactions proceeding in one step are called simple (elementary) reactions, and the reactions that involve several steps are complex [1].

The term of reaction mechanism is used mainly in two senses. For complex reactions involving several stages, the mechanism is a sum of stages resulting in the transformation of initial substances into products. For the simple reaction (elementary reaction, elementary stage), which could not be subdivided into more simple chemical acts, the elucidation of reaction mechanism means the identification of physical processes underlying the essence of chemical transformation. For single particle (molecule in ground or excited state, ion, radical, ion radical, diffuse pair, singlet or triplet radical pair, complex) or two (rarely three) particles (molecules, ions, radicals, ion radicals, *etc.*) in the definite quantum states, the changes in atomic nuclei positions and electronic states consist the essence of their transformations into another species with the intrinsic quantum states. In the physical processes under consideration, the acts of energy transfer from one species to another in the explicit form are frequently involved. For the elementary reactions in solution, the mechanism comprises the changes in adjacent solvation shell of transformed species [1].

In the case of complex reactions, the unstable intermediate species - ions, free radicals, ion radicals, *etc.* - are formed at some stages. Their relative stability and, consequently, a probability for their formation increases with the more actual possibility of delocalization (dissipation) of charge in ion, or of uncoupled electron in radical [1].

For the comprehensive description of complex reaction mechanism, the following data are usually required:

1) the reaction subdivision into the separate steps and equilibrium stages;
2) the characteristics of intermediate products and evaluation of their lifetime;

3) the description of transition state for every step of reaction on the basis of: i) composition; ii) geometry; iii) solvation viewpoints; iiii) energetics;
4) overall description of the processes, both preceding the every transition state and following that, starting from the information on energy levels (electronic, vibrational, rotational, *etc.*) in the ground and excited states [3].

The aim of studying the reaction mechanism is to gain a possibility of managing the reaction course, its direction and efficiency. A knowledge of reaction mechanisms is by far necessary for managing the yields of any products, optimizing the laboratorial and industrial processes, systematizing the reactions, revealing the resemblance of different reactions, predicting the consequences of altered reaction conditions (the substituent nature and position, solvent, temperature, *etc.*) on the reaction course, predicting new reactions [4]. Finally, the sequential elucidation of chemical reactions at a molecular level provides a considerable intelligence satisfaction. Many chemists look upon this problem as being the essence of chemistry discipline and think that it deserves especially extensive studies regardless to the practical importance of the investigation [4]. Let us refer in this relation to the belief by L.P. Hammett, a leading scientist in physical organic chemistry, one of the founders of correlation analysis: “The successful decoding of a complicated mechanism provides an esthetic satisfaction, and that always attracted chemists, even if they would have none of that sometimes”.

The special role in substantiating the mechanisms of reactions is assigned to quantum chemical modeling of their pathways (routes) with the localization of transition states and the construction of energy profiles.

The prognostic function of chemistry determines a situation, when the necessity for elucidating a relation of physicochemical, analytical and other properties, reactivity, biological activity of substances on the structure of their molecules and ambient factors, first of all the medium (solvent), is brought in the forefront. In the opinion of Professor, Academician of the Russian Academy of Sciences, Nickolai S. Zefirov, the problem of structure - property relationship is the most important in chemistry and, possibly, in the whole natural sciences. The above problem is especially urgent under the conditions when, as Professor, Academician of the Russian Academy of Sciences Vladimir I. Minkin tells, a mutation of chemistry has occurred.

An increasing importance in chemistry for approaching uniformly to two topical chemical problems - constructing the reaction barriers and molecular design, for explaining regioselectivity and ambivalence (nucleophilic-electrophilic dichotomy) ([5, 6] *et al.*), for describing and modeling chemical bond, properties of molecules and crystals [6], intermolecular interactions [7], extraction [8], for treating the chemical subjects phenomena from the viewpoint of general theory of systems [7], gains the concept of electronegativity [9, 10]. The analysis of electronic effects of atomic groups in molecules is extremely important to explore the physicochemical, analytical properties of substances and molecules, reactivity, catalysis, solvation.

In the division “4. Chemical sciences on materials” in the List “The principal lines of fundamental investigations”, ratified by the Presidium of the Russian Academy of Sciences [11], the aforesaid aspects are reflected in the first paragraph: “4.1. Theory of chemical structure and chemical bond, kinetics and mechanisms of chemical reactions, reactivity of chemical compounds, stereochemistry, chemistry of crystalline compounds”. The second paragraph 4.2 includes a point “Synthesis and study of novel substances, development of materials and nanomaterials with the given properties and functions”. Realization of lines of fundamental investigations in chemistry presented in other paragraphs of “The List”, requires the use of methods, approaches, the solvation of definite scientific problems, all of which obeying the kinds of 4.1 and 4.2. The latter is totally concerned with the realization of “Fundamentals of Russian Federation Policy in development of science and technologies for up to 2010 and further prospects” [12].

The aforesaid items occupy one of the central positions within the rating arrangement of the general problems of chemistry, that could be presented [13] as follows: the art of chemical synthesis, chemical structure and function, chemical processes control, chemical materials science, chemical engineering science, chemical energetic science, chemical analytics and diagnostics, chemistry of life.

In the newspaper of Russian educational and scientific community *Search* (in Russian: *Poisk*) [14], the popularity rating of scientific journals included in the database of Scientific Electronic Library of the Russian Foundation for Basic Research, for March, 2000, was published. Of 46 editions concerned the first place by amount of appeals to papers over the above period is occupied by the journal *Chemical Physics Letters*. The third place is for the *Journal of Molecular Structure. Theochem*. For the substantiated conclusions on the structure and dynamics of the scientific interest, the rating analysis over the more prolonged period is required. Nevertheless, it is obvious that the problems of studying the structure, reactivity and mechanisms are the matter of priority for the Russian scientists.

It is likely that the citation index is insufficient and not completely objective criterion of the scientific works evaluation. However, if its value is much greater than the mean quantity in the corresponding branch of knowledge, this fact confirms, to a definite degree, the availability of scientific works. The site [15] contains the information on 1000 famous chemists who possesses the highest ratio of citation number to total number of publications over the period since 1981 to 1997. In the list of these scientists the 1st and 4th places are occupied by A. Bax and R.R. Ernst, respectively, the specialists in radiospectroscopy - an assembly of powerful methods of studying the structure, reactivity and mechanisms of the reactions, the 2nd, 3rd, 6th, 14th, 15th, 22nd, 23rd, 24th, 28th, 35th, 40th - by the theoretically-oriented chemists contributing to the quantum chemistry and its applications: J.A. Pople (Nobel Prize Winner), P.v.R. Schleyer, H.F. Schaefer, D.G. Truhlar, J.J.P. Stewart, P.A. Kollman, M.J.S. Dewar, W.L. Jorgensen, C.W. Bauschlicher, K.N. Houk, R. Hoffmann (Nobel Prize Winner), 5th by G.M. Whitesides (molecular drug design), 41th by A. Zewail, the inviter of femtosecond spectroscopy allowing the reactions (at least, relatively simple ones by now) to be studied in the real-time mode.

In the communication [16], the Russian scientists, whose works were cited until 2000 inclusively not less than 1000 times, are mentioned. Let us list those of them, who has made the outstanding contributions to the development of namely the theoretical chemistry, of the knowledge of structure and reactivity of substances (pointed out in the brackets is number of the position in the list [16]): N.S. Zefirov (3), V.I. Minkin (5), A.A. Ovchinnikov (6), V.I. Nefedov (13), A.E. Shilov (14), I.P. Beletskaya (16), Yu.A. Zhdanov (17), Yu.A. Zolotov (18), A.L. Buchachenko (23), A.F. Pozharskii (24), L.V. Vilkov (26), G.M. Zhidomirov (27), V.V. Boldyrev (28), L.M. Epshtein (33), R.A. Evarestov (39), Yu.N. Molin (45), L.A. Gribov (47), V.L. Tal’roze (48), I.I. Moiseev (52), O.M. Nefedov (54).

The work [17] deals with the citation indices (1991-2004) of chemists-analysts of Russia, some of whom are engaged in solving the problems of theoretical chemistry and apply the methods of quantum chemistry in their scientific research.

All the aforesaid testifies to the doubtless actuality of studying the problems of structure, reactivity, reaction mechanisms in chemistry, including the studies assisted by theoretical and first of all quantum chemical research methods.

One of the avenues of scientific inquiries developed at the Division of Analytical Chemistry and Chemical Ecology, Department of Chemistry of N. G. Chernyshevskii Saratov State University, inexorably associated with the problems of analytical science, could be formulated in the following manner: the establishment of quantitative structure - property relationships in the series of inorganic, organic, organoelement, coordination compounds; the statement of the reactivity interrelation to the molecules electronic structure in the ground and excited states on the basis of refining the understanding of electronic effects, electronegativities of atomic groups, hydrogen bond, generalization of the views on reaction mechanisms (including oxidation and reduction, nitrosation, nitration, azo coupling, alkoxylation, condensations, other electrophilic, nucleophilic and radical processes, complexation, ligand exchange, molecular and ionic association, dissociation, tautomerism and ambivalent reactivity, isomerization, proton, hydrogen atom and “hydride ion” transfer), regioselectivity of homolytic (oxidative and reductive) coupling reactions for the substances of different classes; study of the medium influence on chemical processes occurrence; systematization and generalization of information about Web resources on natural sciences, on ecology.

In 1997 the information on range of scientific interests and line of scientific inquiry was included to *Science Contacts Database* - the edition of Science International (Cambridge). The author refereed manuscripts presented for publication in *Journal of the American Chemical Society*, *The Journal of Organic Chemistry*, *Journal of Coordination Chemistry*, *Journal of Analytical Chemistry (Russia)*. On November 1, 2005 the author has been elected a Regular Member of the American Chemical Society.

There are over 530 publications, among which are articles in *Helvetica Chimica Acta*, *Canadian Journal of Chemistry*, *The Journal of Physical Chemistry A*, *Journal of Molecular Structure. Theochem*, *International Journal of Quantum Chemistry*, *Monatshefte für Chemie*, *Journal of Coordination Chemistry*, *Heteroatom Chemistry*, *Phosphorus, Sulfur, and Silicon and the Related Elements*, *International Journal of Molecular Sciences*, *Journal of Biochemistry and Molecular Biology*, *Food Technology and Biotechnology*, *Online Information Review*, *Internet Journal of Chemistry*, *Journal of the Serbian Chemical Society*, *Croatica Chemica Acta*, *Revue Roumaine de Chimie*, *Afinidad*, *The Journal of the Argentine Chemical Society*, *Indian Journal of Chemistry*, *et al.*, in the academic journals of Russia and Former Soviet Union countries. The author is the scientific editor of two Collections of articles.

The scientific area under discussion is contributed by the Ph. Ds in Chemistry Andrew E. Shchavlev, Inna M. Uchaeva, Alexei V. Shalabay, Assistant Professor of the Saratov State Medical University Olga A. Chaplygina, student Nickolai A. Bychkov and other Colleagues.

Presented below are the selected scientific results.

The quantitative relationships providing a possibility of *a priori* evaluation of heats and free energies of formation, entropies, ionization potentials, electron affinities, potentials of chemical and electrochemical oxidation and reduction, pK_a values, stability constants, dipole moments, vibrational frequencies, electronegativities, inductive and mesomeric parameters of atomic groups of inorganic, organic, organoelement, coordination compounds, products yields and reaction rates of electrophilic, nucleophilic and radical aromatic substitution, rates of enzymatic oxidation of amines and phenolic substrates, transport rate of surfactants ions through nano exclusion membranes (molecular sieves) ([18-43] *et al.*).

A priori evaluation of the above parameters by quantum chemical methods is important for molecular design of compounds with given properties, may serve as a base for expert decision on reasonability of synthesis that is sometimes labour- and time-consuming, requiring complicated device, rigid conditions, expensive and toxic chemicals.

The predictive power of the correlations stated (hundreds of dependences for hundreds of molecular systems) is determined by the fact that those are not of the formal character, but have an explicit physical meaning, are characterized by great values of correlation coefficient, are deduced for a considerable amount of substances in different media, therewith the compounds are various in nature and structure, the substituents in molecules essentially differ by their nature and positions.

For rather simplified obtaining predictive quantitative relations, often the semiempirical quantum chemical methods would be reasonable to use.

Let us present a few examples of predictive interrelationships.

By the semiempirical MNDO, AM1 and PM3 methods, standard values of entropy, heats and free energies of formation, first ionization potentials and dipole moments of the molecules have been computed for the compounds CH_3X (X = H, CH_3, SiH_3, GeH_3, SnH_3, $CH=CH_2$, C_6H_5, CCH, CHO, $COCH_3$, COOH, CN, NH_2, PH_2, AsH_2, OH, SH, $SOCH_3$, SO_2CH_3, OCN, NCO, SCN, NCS, NC, NO_2, F, Cl, Br, I); *n*-$C_5H_{11}X$ (X = H, CH_3, OH, NO_2, F, Cl, Br, I); C_6H_5X (X = H, $CH=CH_2$, C_6H_5, CCH, CHO, $COCH_3$, COOH, CN, NH_2, PH_2, OH, SH, SeH, SO_2H, SO_2CH_3, SO_3H, NCO, SCN, SeCN, NCS, NC, NO, NO_2, F, Cl, Br, I), 90 mono-, bi-, tri-, poly- and spirocyclic non-aromatic hydrocarbons, 148 three-, five-, six-, seven-membered N-, O-, S-, Se-, B-containing unsaturated heterocycles, 91 quinones, 62 tropones and tropolones, 63 anilines, 232 pyridines, inorganic, coordination and organic arsenic, cadmium, antimony, thallium, bismuth compounds [18, 20, 25, 27, 29, 31-35, 41, 43]. Correlation equations allowing one to evaluate *a priori* thermodynamic and molecular properties of various substances have been obtained. Deviations from the above dependences have been noted.

A facilitated theoretical methodology for the prediction of solid-phase (and condensed state in general) heats of formation (ΔH_f) of chemical species has been developed using quinones as the examples [41, 43]. Such a prognosis may be performed on the base of simple semiempirical gaseous-phase calculations. Below given are predictive dependences linking experimental solid-phase ΔH_f values with the computed ones (Table 1; Figures 1-3).

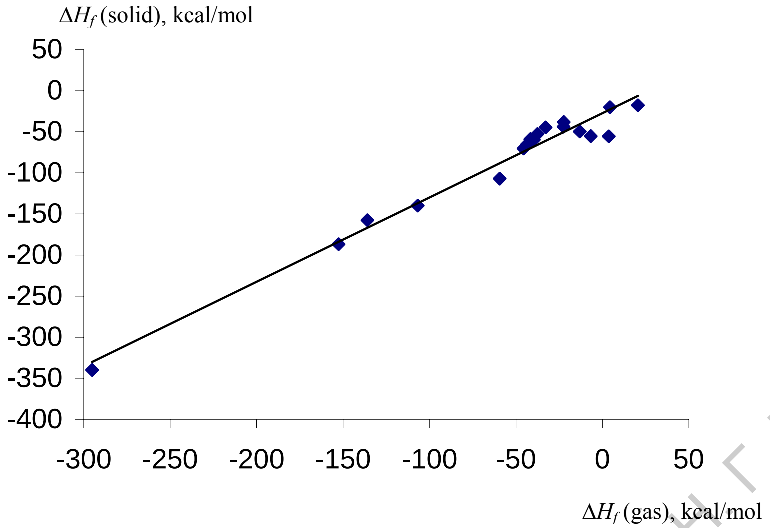


Figure 1. Dependence of standard heats of formation of quinones in solid [44] and gaseous (MNDO) states.

Table 1. Dependences between experimental standard heats of formation of solid quinones [44] and computed standard heats of formation of gaseous quinones[*]

Method	**ΔH_f (solid) = $a + b\Delta H_f$ (gas)**			**ΔH_f (solid) = $c\Delta H_f$ (gas)**		***r***
	***a*, kcal/mol**	***b***	**S_0^2**	***c***	**S_0^2**	
MNDO	–27.23 ± 8.14	1.026 ± 0.091	183.9	1.217 ± 0.134	652.3	0.9842
AM1	–35.90 ± 8.26	1.060 ± 0.102	212.4	1.308 ± 0.194	1133	0.9817
PM3	–26.32 ± 8.20	1.057 ± 0.094	184.3	1.247 ± 0.133	615.6	0.9842

[*] S_0^2 is adequacy dispersion, *r* is correlation coefficient

The values corresponding to abscissae and ordinates start from the same origin. That is why linear regression models both with and without the intercept may be adequate. Confidence limits for the regression coefficients allow any of the two types of relationships mentioned.

In accordance with the criterion of adequacy dispersion, preferable are linear dependences of common type, *i.e.* with non-zero intercept (Table 1). Then the slope is close to unity.

Thus, the crystal field effect over the series of compounds under study makes, with respect to the heat of formation, an essentially constant contribution expressed as a scale shift in the Y direction.

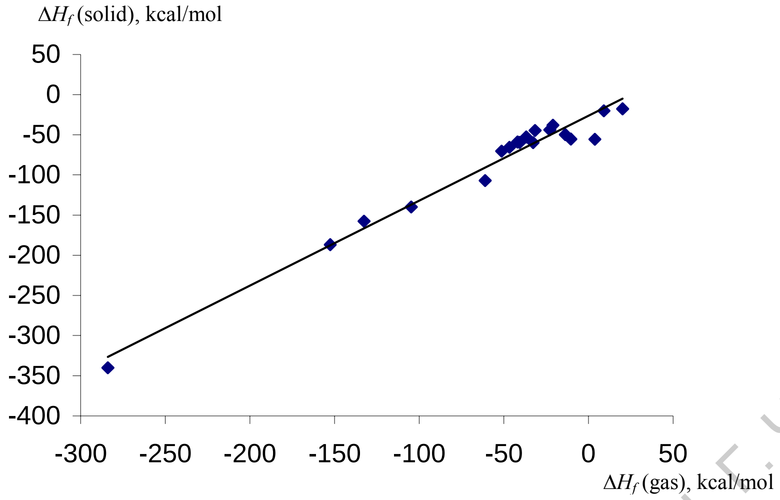


Figure 2. Dependence of standard heats of formation of quinones in solid [44] and gaseous (AM1) states.

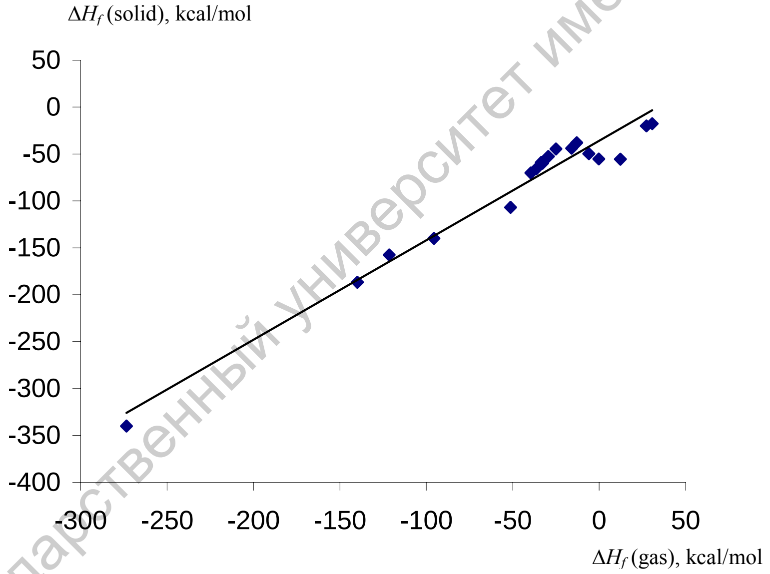


Figure 3. Dependence of standard heats of formation of quinones in solid [44] and gaseous (PM3) states.

Let us emphasize that the sample of compounds we have investigated, for which the linear relationships are valid, includes both *ortho* quinones and *para* quinones. Consequently, the contribution of intermolecular interactions in the solid state has appeared to be constant over the series of substances involving both 1,2-quinones and 1,4-quinones.

The quinone molecules contain the strongly polar C=O bonds. That is why the principal contribution to intermolecular interactions in crystalline structure should be made by electrostatic interactions, especially with the C=O group participation.

Such assumption is favoured by X-ray data [45]: oxygen atoms of the 1,2-benzoquinone molecule participate in shortened intermolecular contacts.

An unchanged electrostatic contribution is possible provided that the electron density distributions in the *ortho* and *para* quinone molecules (above all in the carbonyl group) are analogous.

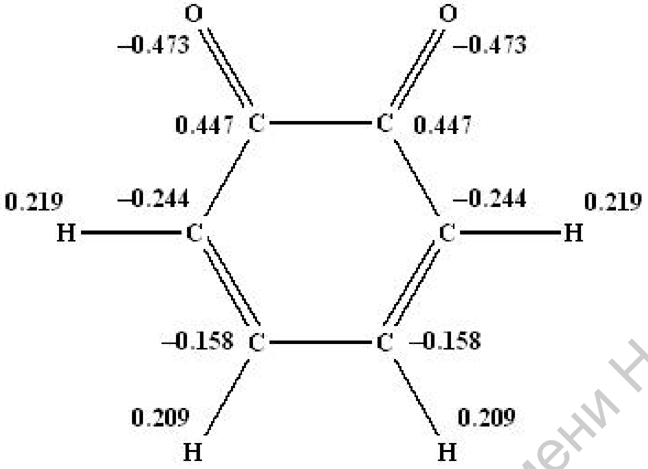


Figure 4. Natural atomic charges in the 1,2-benzoquinone molecule.

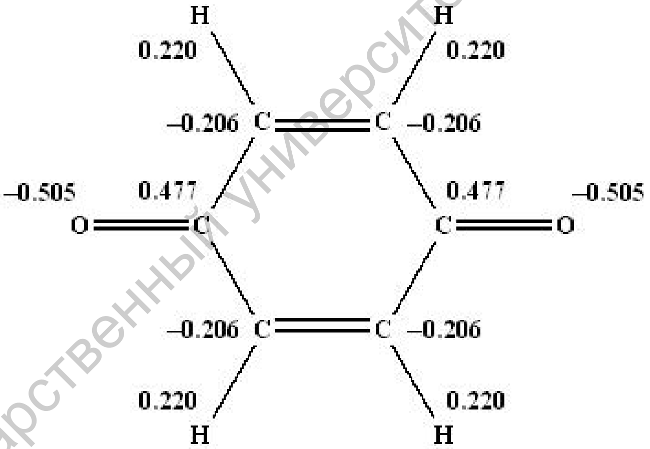


Figure 5. Natural atomic charges in the 1,4-benzoquinone molecule.

For justifying the assumption, we have studied by the hybrid B3LYP/6-311++G(3df,3pd) method within the DFT approach, the electronic structure of the 1,2-benzoquinone and 1,4-benzoquinone molecules. Indeed, the electron distribution in polar carbonyl groups and in adjacent CH groups show similar characteristics for isomeric quinones. Figures 4 and 5 depict natural charges on atoms (according to the NBO-analysis data), which characterize the molecules' electronic structures more objectively as compared to Mulliken charges, and Table 2 - Wiberg bond orders.

Table 2. Wiberg bond indexes in the natural atomic orbital basis

Bond	Wiberg index in the molecule of	
	1,2-benzoquinone	1,4-benzoquinone
C=O	1.800	1.741
C=C	1.771	1.821
C(O)-C(H)	1.071	1.040
C(CO)-H	0.917	0.918

Furthermore, the data of X-ray structure analysis [45, 46] show that elementary cells in the crystal structure of 1,2-benzoquinone and 1,4-benzoquinone contain the same number of molecules, equal to two, and the compounds have close values of density in the solid state (Table 3).

Table 3. Values of solid state density (ρ_{calc}) deduced from X-ray structure analysis data

Compound	ρ_{calc}, g·cm^{-3}	Reference
1,2-Benzoquinone	1.424	45
1,4-Benzoquinone	1.4	46

The character of electron density distribution in molecules and the similarity of structure parameters are a prerequisite for a constant contribution of the crystal field effect to the heat of formation of both *ortho* and *para* quinones.

Therefore, the fact is clarified that the unified linear dependences are valid for series of substances involving such structurally dissimilar compounds as 1,2-quinones and 1,4-quinones are.

The above methodology may be extended to compounds of other classes provided that the intermolecular interactions are near-constant over the series under study. The latter would be fulfilled *e.g.*, at the dominating contribution of the molecule frame (determining the compound's assignment to one or other class or series) or separate atomic groups (in particular, polar ones) in the composition of the frame fragment to the intermolecular interactions. Although the condition of constant energies of intermolecular interactions is not of universal character in general, nevertheless such condition should be naturally followed for the numerous series of the compounds similar in their structures.

The dependence of electronegativity (determined by various experimental and theoretical methods and expressed against different scales), inductive parameter *iota* of substituents X, mesomeric dipole moments upon the molecules CH_3X, XCH_2COOH, n-$C_5H_{11}X$, C_6H_5X, 4-$XC_6H_4NH_2$, 4-$XC_6H_4NO_2$, 2,6-disubstituted pyridines and N-methylpyridinium cations electronic structure indices (according to different quantum chemical methods data) has been stated. The possibility of a facilitated estimation of electronegativity, inductive and mesomeric parameters of atomic groups using 90 correlations has been shown [19, 22].

Commonly used constants following from the linear free energies relationships principle possess a number of limitations (multiplicity of sets, ambiguous interpretation, *etc.*). The quantities evaluated in the works [19, 22] overcome the aforesaid drawbacks to the significant extent, because they are expressed *via* the values having clear physical meaning: effective charge of valence shell, effective principal quantum number, group dipole moments.

It has been shown [38] that aryldiazonium cations present a series of molecular systems, on the basis of which the predictive interrelationships (alternative with respect to those proposed in the works [19, 22]) could be stated for evaluating the mesomeric dipole moments (μ_m) of atomic groups. If this problem is solved using the quantitative relations μ_m *vs* electron affinity, thus the substituted diazonium cations can be involved whether these exist or not really. An important point is solely that phenyldiazonium is appropriate "matrix", on the basis of which the mesomeric effect of substituents is simulated.

Table 4. Logarithms of stepwise stability constants for palladium (II) chloride complexes, *d* and *e* coefficients in equations lgK_{stab} = $d + e\Delta H^0$, and values of correlation coefficient *r*

By the ZINDO/1 data

lgK_1	lgK_2	lgK_3	lgK_4	Ref.	*d*	*e*, mol/kcal	*r*
4.34	3.54	2.68	1.68	47[*]	2.519 ± 0.144	–0.008597 ± 0.001097[+]	–0.9991[+]
					2.531 ± 0.249	–0.008403 ± 0.001867[^]	–0.9973[^]
3.98	3.24	2.30	2.00	48[*]	2.460 ± 0.534	–0.006672 ± 0.004075[+]	–0.9804[+]
					2.467 ± 0.445	–0.006572 ± 0.003337[^]	–0.9864[^]
3.88	3.06	2.14	1.34	49-51[**]	2.083 ± 0.123	–0.008299 ± 0.000938[+]	–0.9993[+]
					2.094 ± 0.093	–0.008128 ± 0.000699[^]	–0.9996[^]

By the PM3 data

lgK_1	lgK_2	lgK_3	lgK_4	Ref.	*d*	*e*, mol/kcal	*r*
4.34	3.54	2.68	1.68	47[*]	2.295 ± 0.370	–0.009484 ± 0.002814[+]	–0.9953[+]
					2.299 ± 0.371	–0.009431 ± 0.002809[^]	–0.9952[^]
3.98	3.24	2.30	2.00	48[*]	2.280 ± 0.494	–0.007435 ± 0.003758[+]	–0.9865[+]
					2.282 ± 0.453	–0.007409 ± 0.003434[^]	–0.9886[^]
3.88	3.06	2.14	1.34	49-51[**]	1.864 ± 0.211	–0.009182 ± 0.001603[+]	–0.9984[+]
					1.868 ± 0.172	–0.009136 ± 0.001304[^]	–0.9989[^]

[*] lgK_{stab} values are determined by means of spectrophotometric method

[**] lgK_{stab} values are determined by means of solubility, potentiometric and spectrophotometric methods

[+] Correlations are found assuming *cis*-[Pd(H_2O)$_2$Cl$_2$] participation in reactions by second and third steps

[^] Correlations are found assuming *trans*-[Pd(H_2O)$_2$Cl$_2$] participation in reactions by second and third steps

On the base of quantum chemical investigations the character of ligands H_2O, H_3O^+, Cl^- mutual influence in palladium (II) complexes has been revealed. By the first three steps, the substitution of hydronium ion in the palladium atom internal sphere is thermodynamically more favourable as compared to the displacing of water molecule from the coordination sphere. Stepwise stability constants (K_{stab}) of the palladium (II) chloride complexes correlate with the computed standard enthalpy values (ΔH^0) of the substitution of water molecules by chloride ion (Table 4) [40].

The existence of the above quantitative lgK_{stab} *vs* ΔH^0 relationships confirms the fact of being constant for aqueous medium contribution to ΔH^0 at all steps of substitution.

Let us mention that the correlation coefficients are sufficiently high, in spite of the fact that non-uniform quantities are compared: the experimental values of stability constants for aqueous solutions and standard enthalpies of the reactions estimated on the basis of gaseous-phase quantum chemical computations. That underlines reliability and predicting significance of the correlations.

Use of the like correlation equations for another central atoms and ligands enables one to evaluate *a priori* the stepwise constants of complexation and to put into practice the directional synthesis of complexes with the given interrelationship of stability constants by different steps.

The results obtained are of importance when studying Pd(II) complexation with organic ligands, including that in analytical chemistry. As shown in the present work, the rate of exchange of hydronium ion by chloride ion in palladium (II) complexes much exceeds the rate of substitution of water molecule. Provided that a certain organic reagent is involved instead of chloride ion, the analytical reaction would be expected to proceed more readily in acidic medium. The reaction should be conducted at such optimal acidity, at which water molecule in the internal coordination sphere of metal atom is protonated, but even though the reagent molecule is protonated, so not to the reaction centre of complexation.

An approach has been developed to the selectivity prediction and molecular design of analytical redox reagents [23, 28]. Selectivity of such reagents is determined by their standard (E^0) or close to them formal (E^f) redox potentials. We have obtained quantitative expressions linking the E^f values with quantum chemically computed Koopmans ionization potentials. Professor Svetlana P. Mushtakova *et al.* (Division of General and Inorganic Chemistry, Department of Chemistry, N. G. Chernyshevskii Saratov State University) have synthesized 5 new reagents and measured their E^f quantities [52]. Using our relationships, we have evaluated the above E^fs theoretically (Table 5).

Table 5. Formal redox potentials (E^f) of sulphodiphenylamines and sulphotriphenylamines: experimental ones determined in H_2SO_4 aqueous solutions [52] and those evaluated from first Koopmans ionization potentials of amines and their conjugate acids

Compound	**E^f_{theor} (V) from ionization potential of**		**E^f_{exper}, V**
	Molecular form	**Protonated form**	
2-Nitro-4’-sulphodiphenylamine	1.07	0.96	0.91
3-Nitro-4’-sulphodiphenylamine	1.15	0.98	0.93
4-Nitro-4’-sulphodiphenylamine	1.16	0.98	1.1
4-Sulphotriphenylamine	0.94	0.91	0.89
4,4’-Disulphotriphenylamine	1.00	0.92	0.94

As it can bee seen, theoretical E^f values coincide well with the experimental ones. The most perfect agreement with the experiment is observed as a rule under the theoretical evaluations based on the ionization potentials of conjugate acids of amines. That confirms indirectly our experimental results on studying the mechanisms of diarylamines oxidation in acidic media, in accordance with which the protonated molecules of substrates undergo oxidation. Commonly the oxidation reactions are treated as electrophilic processes [53]. However, in the given case the cation of amine conjugate acid is attacked by the oxidizing agent anion, and the initial act of reaction is nucleophilic.

Based on the study [54] concerned with the rates (v) of amines and phenolic compounds oxidation catalyzed by laccase of basidiomycete *Lentinus edodes* (Berk.) Sing, as well as on the results of PM3 computations, the linear correlations of v and ln$v$ values with first ionization potentials of the substrates molecules and radicals derived from them, spin densities on N and O atoms of the above radicals, and with the radicals reorganization energies have been obtained [24]. The interrelations found could be used for express facilitated (at semiempirical level) predicting v values, *i.e.* for the directive *a priori* selection of substrates (within the series of compounds similar in structure), for molecular design of substrates with the given behaviour on enzymatic oxidation (maximal or optimal oxidation rate, exclusive ability to be oxidized mediated by certain enzyme, *etc.*), along with the expert decisions working out in respect to promising substances synthesis. Thus sensitivity and selectivity of oxidation reactions would be ruled by the choice of substrates with the necessary properties.

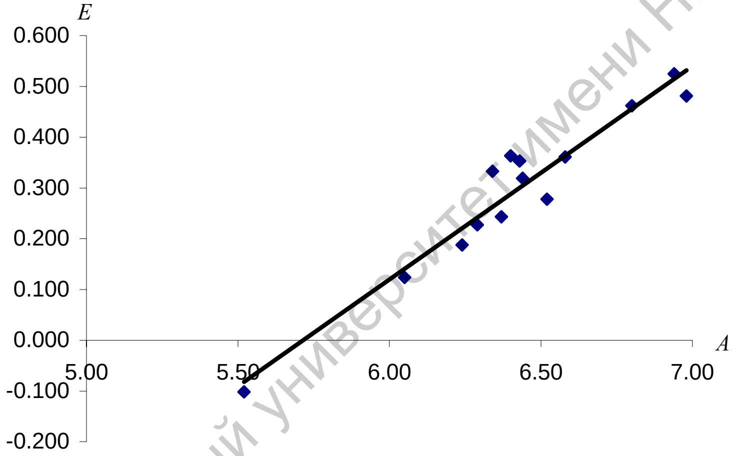


Figure 6. Dependence of half-wave potentials (E, V) of polarographic reduction of aryldiazonium $XC_6H_4N^+{\equiv}N$ cations (measured in nitromethane *vs* saturated Hg_2Cl_2 electrode) upon computed proton affinities (A, eV). X = H, 3-CH_3, 4-CH_3, 4-$N(CH_3)_2$, 3-NO_2, 4-NO_2, 4-OCH_3, 3-F, 4-F, 4-SO_2CF_3, 3-Cl, 4-Cl, 3-Br, 4-Br. Correlation coefficient $r = 0.9662$.

By the fact of finding 43 relationships, we have shown that the reduction potentials, dimerization potentials and potentials in half-equivalent point on titration of aryldiazonium cations $XC_6H_4N^+{\equiv}N$ (chemical reduction with $K_4[Fe(CN)_6]$ and $TiCl_3$ in water, $(C_2H_5)_3N$, (i-$C_4H_9)_4N^{+-}OH$, CH_3OK and $C_{10}H_8^{\bullet-}Na^+$ in acetone; polarographic reduction in nitromethane, sulfolane, and N,N-dimethylformamide) are related linearly to the quantum chemically evaluated electron affinities (A) and to the stabilization energies of radicals formed on diazonium cations reduction. Sixty six linear correlations of frequencies (ν) characterizing a collection of bonds stretching vibrations of the $C\text{-}N^+{\equiv}N$ fragment in the $XC_6H_4N^+{\equiv}NY^-$ salts with different anions in vaseline oil, N,N-dimethylformamide, acetone, ethylacetate, methanol, water, with the bonds orders of N≡N and C-N, with the charges on carbon atoms in *para* positions of the C_6H_5X molecules aromatic rings, with the mesomeric dipole moments (μ_m) of X substituents have been found. Twelve quantitative relationships combining the μ_m

and ν quantities with the *A* values have been established. The interrelations obtained have an explicitly expressed physical meaning, are featured by rather high correlation coefficients and have a predictive power in respect to redox properties, electron affinities, vibrational frequencies of aryldiazonia, as well as to mesomeric dipole moments of atomic groups in organic molecules [38]. Examples of the above correlations are shown on Figures 6 and 7.

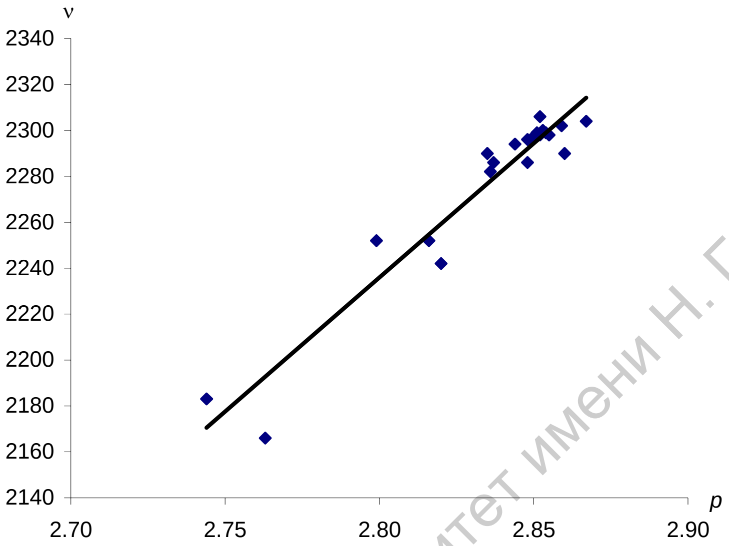


Figure 7. Dependence of stretching vibrational frequencies (ν, cm^{-1}) (in vaseline oil) for fragment C-N^{+}≡N bonds in aryldiazonium $XC_6H_4N^{+}{\equiv}N$ cations upon computed N≡N bond orders (*p*). X = H, 3-CH_3, 4-CH_3, 4-$COCH_3$, 3-$COOCH_3$, 4-$COOCH_3$, 4-$COOC_2H_5$, 4-NH_2, 4-$N(CH_3)_2$, 4-$NHCOCH_3$, 3-NO_2, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 4-F, 4-SO_2NH_2, 3-Cl, 4-Cl, 4-Br, 4-I. Correlation coefficient r = 0.9633.

The cationic localization energies (Λ^{+}) for the reactions of monosubstituted benzenes with nitroyl (nitronium) ion have been computed by the PM3 method. Yields of nitration isomeric products correlate linearly with the Λ^{+} values. The latter lets one predict nitration yields of monosubstituted benzenes isomers (*ortho*, *meta* and *para*) [26].

The substituent rate factors for the interaction of 1-chloro-2-nitro-4-substituted benzenes with methoxide ion in methanol depend linearily upon the anionic localization energies, which lets one forecast kinetic characteristics of the above reactions [30].

The approach developed could be extended over the analogous reactions of polysubstituted benzenes, different classes of compounds, as well as the reactions of homolytic aromatic substitution involving the step of radical σ-complexes formation.

The quantitative interrelations of rates of surfactant ions transport through nanofiltration membranes (molecular sieves) (measured by the “applied potential” method) with ions linear sizes and hydration enthalpies [21] have been established. Using the correlations found, one can predict the actual values of ionic transport rate, which are not always available from an experimental determination owing to a rather complicated synthesis of surfactants with a large hydrocarbon radical or to poor solubility of short-chain surfactants in water.

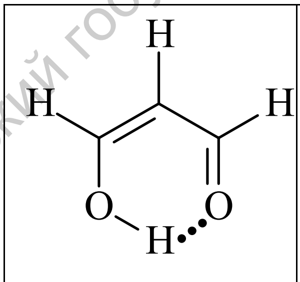
Such an important type of intramolecular and intermolecular interaction as hydrogen bonding is actually under our consideration.

Boiling and melting points, vapour pressure, solubility, molar volume, density, mixing heat, heat conductivity and heat expansion, viscosity, surface tension, dielectric constant and dielectric losses, dipole moment, electroconductivity, segnetoelectric properties, diamagnetic susceptibility, ionization, molar refraction, refraction coefficient, another optical properties, spectra, acid-base, tautomeric, analytical properties, reactivity, biological activity of chemical compounds depend on the presence of intramolecular hydrogen bond (IHB) and its thermodynamic parameters ([55, 56] *et al.*). For the directive synthesis of compounds, the quantum chemical evaluation of the IHB effect on the electronic structure of molecules is of great interest.

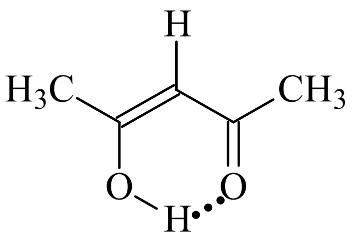
The appropriate model objects for studying IHB are organic molecules with a planar quasicycle. They are widely distributed and play a very important role in chemistry, being promising building blocks for constructing the supramolecular structures with the specific receptor properties. For the planar quasicyclic systems, the effect of IHB on the electronic structure of molecules can be isolated in the explicit form. Usually, the reference objects on studying the IHB are the isomers without IHB. But such the compounds differ substantially by their properties from the isomers with IHB. In the cases of many molecules with a planar quasicycle, more adequate reference compound could be used - a conformer without IHB, with all other specific interactions being the same as those in the molecule with IHB [57, 58].

We have shown that, in relation to the compounds with planar quasicycle, the specifically parameterized semiempirical methods of quantum chemistry (MNDO/H, I-MNDO, MNDO/HB, MNDO/M) are applicable for the preliminary *a priori* semiquantitative estimation of the heat of IHB formation before proceeding to more sophisticated (*ab initio* or DFT) quantum chemical methods and forthcoming aimed synthesis [59].

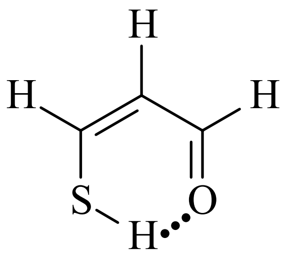
We have studied the effect of IHB on the electronic structure of the planar quasiring molecules (Figure 8) (*ab initio* and DFT). IHB has been established to result in the local electron redistribution embedded at the quasicycle, as compared to the conformer without IHB and to the corresponding *para* isomer (in the case of substituted benzenes). Apparently, IHB does not influence the mechanism of chelation of the organic compounds (including the analytical reagents) with the metal ions. But its cleavage is involved in the reaction energetics, that is of importance for the directive design of analytical reagents [60, 61]. Below, some examples of IHB-involving systems will be considered in more detail in view of the medium effects role description.



Malonaldehyde



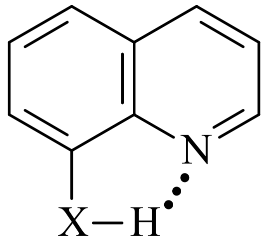
Acetylacetone

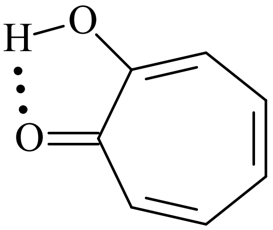


Thiomalonaldehyde

	X	**Compound**
Derivatives of aniline $2\text{-}XC_6H_4NH_2$	CHO	2-Aminobenzaldehyde
	COOH	2-Aminobenzoic (anthranilic) acid
	COO^-	2-Aminobenzoate anion
	NO	2-Nitrosoaniline
	NO_2	2-Nitroaniline
	OH	2-Aminophenol
	OCH_3	2-Methoxyaniline (*ortho*-anisidine)
	SH	2-Aminobenzenethiol
	SCH_3	2-Methylmercaptoaniline
	F	2-Fluoroaniline
	Cl	2-Chloroaniline
	Br	2-Bromoaniline
Derivatives of phenol $2\text{-}XC_6H_4OH$	CHO	2-Hydroxybenzoic (salicylic) aldehyde
	COOH	2-Hydroxybenzoic (salicylic) acid
	COO^-	2-Hydroxybenzoate (salicylate) anion
	NO	2-Nitrosophenol
	NO_2	2-Nitrophenol
	OH	1,2-Dihydroxybenzene (pyrocatechol)
	OCH_3	2-Methoxyphenol (guaiacol)
	SH	2-Hydroxybenzenethiol
	SCH_3	2-Methylmercaptophenol
	F	2-Fluorophenol
	Cl	2-Chlorophenol
	Br	2-Bromophenol
Derivatives of benzenethiol $2\text{-}XC_6H_4SH$	CHO	2-Mercaprobenzoic (thiosalicylic) aldehyde
	COOH	2-Mercaprobenzoic (thiosalicylic) acid
	COO^-	2-Mercaprobenzoate (thiosalicylate) anion
	NO	2-Nitrosobenzenethiol
	NO_2	2-Nitrobenzenethiol
	OCH_3	2-Methoxybenzenethiol
	SH	1,2-Dimercaptobenzene (dithiocatechol)
	SCH_3	2-Methylmercaptobenzenethiol
	F	2-Fluorobenzenethiol
	Cl	2-Chlorobenzenethiol
	Br	2-Bromobenzenethiol

Figure 8. Molecular systems for which the effect of intramolecular hydrogen bond on electronic structure has been studied (continued on next page).

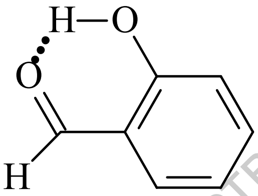
	X = O X = S	8-Hydroxyquinoline 8-Mercaptoquinoline



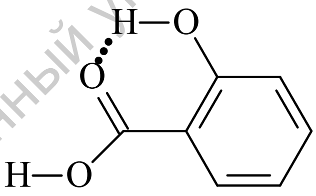
2-Hydroxy-2,4,6-cycloheptatriene-1-one
(tropolone, purpurocatechol)

Figure 8. Molecular systems for which the effect of intramolecular hydrogen bond on electronic structure has been studied (completed).

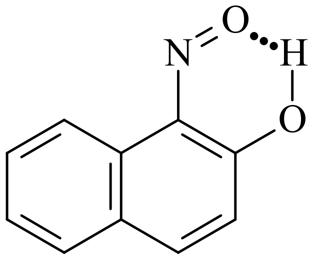
A local character of the IHB effect is reflected also by the IR and Raman spectra formation in the following planar-quasicycled systems studied at the B3LYP/6-311++G(d,p) level of theory (Figures 9 and 10).



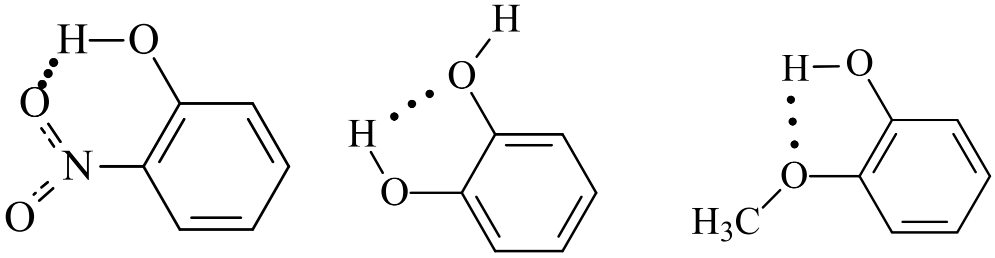
2-Hydroxybenzoic
(salicylic) aldehyde



2-Hydroxybenzoic (salicylic)
acid



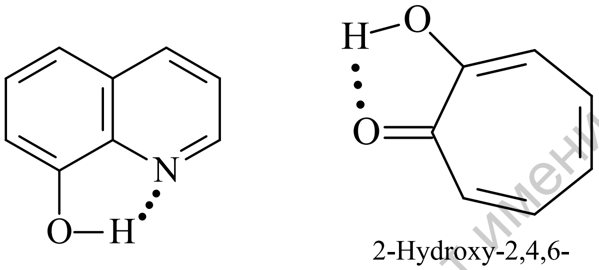
1-Nitroso-2-naphthol



2-Nitrophenol

1,2-Dihydrohybenzene (pyrocatechol)

2-Methoxyphenol (guaiacol)

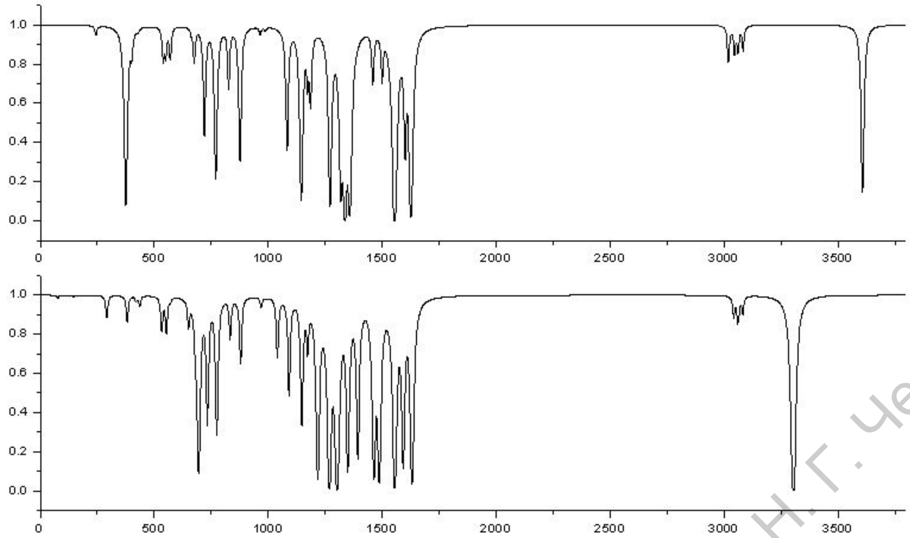


8-Hydroxyquinoline

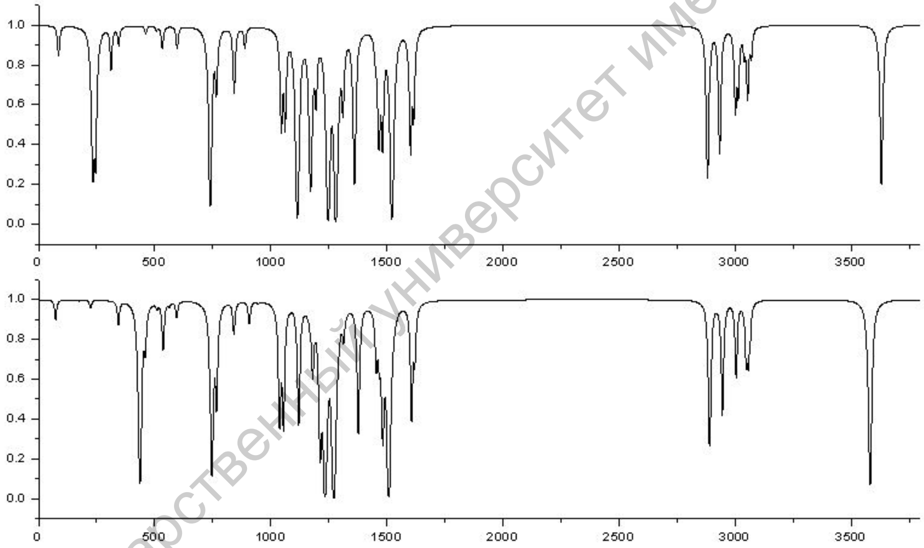
2-Hydroxy-2,4,6-cycloheptatriene-1-one (tropolone, purpurocatechol)

Figure 9. Planar-quasicycled molecules for which the vibrational spectra has been analyzed.

The most profound shifts in frequencies on the IHB formation is exhibited by three vibrations related to the mobility of hydroxyl proton: stretching q(OH) (frequency decreases), planar angular β(OH) (frequency increases slightly), non-planar motion of the OH bond as a kind of torsion (ρ(OH)) (frequency increases) [62]. The effect of IHB on the reactivity of the compounds under study should be expected just in the reactions mediated by the OH group, that is particularly confirmed by the dependence of acid-base properties on the IHB [63]. Minor (~40 cm^{-1}) and, as a rule, low-frequency shifts are observed with the vibrations localized on proton-acceptor group. For the majority of aromatic cycle vibrations, the frequencies enhance ($\Delta\nu \leq$ 10-15 cm^{-1}). The above peculiarities occur for the whole series studied. The decrease in stretching vibration frequency q(OH) and the increase in non-planar vibration frequency ρ(OH) correlate closely to the value of hydrogen bond enthalpy (ΔH). *E.g.*, for 2-nitrophenol $\Delta H = -10.26$ kcal/mol, $\Delta\nu(q(\mathrm{OH})) = -341$ cm^{-1}, $\Delta\nu(\rho(\mathrm{OH})) = +361$ cm^{-1}; and for guaiacol $\Delta H = -4.43$ kcal/mol, $\Delta\nu(q(\mathrm{OH})) = -55$ cm^{-1}, $\Delta\nu(\rho(\mathrm{OH})) = +203$ cm^{-1} [62].



2-Nitrophenol



2-Methoxyphenol (guaiacol)

Figure 10. IR spectra calculated at the B3LYP/6-311++G(d,p) level of theory. The vertical axis is for the transmittance values and the horizontal axis is for frequencies (cm^{-1}). For each compound, the upper spectrum refers to the conformer without IHB, and the lower one - to the rotamer with IHB. Spectral curves were approximated by Lorenz contours with the half-width of 5 cm^{-1}.

The comparison between the experimental and theoretical IR spectra for pyrocatechol and guaiacol has showed that within the range of the OH stretching vibrations display, there are two bands ~50 cm^{-1} distant from each other. This shift agrees well with the values obtained from the quantum chemical computations: $\Delta\nu$ = –41 cm^{-1} (pyrocatechol), –49 cm^{-1} (guaiacol), and testifies to the simultaneous existence of two rotamers of the aforesaid substances in the gaseous phase. In the spectrum of pyrocatechol (conformer with IHB), there is a band of stretching vibration *q*(OH) of the second (free) OH group, therewith $\Delta\nu = +56$ cm^{-1} compared to the band of associated hydroxyl group. For 2-nitrophenol and all other compounds with $\Delta H < -5$ kcal/mol studied, the only intensive band corresponding to the conformer with IHB [62] is observed in the gaseous-phase IR spectra.

Let us consider now the works connected with the amino species oxidation mechanisms and homolytic coupling regioselectivity.

Kinetic, electrophoretic, spectroscopic (electronic absorption spectra, EPR), potentiometric, voltammetric, and quantum chemical investigations have been carried out for aromatic and heterocyclic amino compounds (diphenylamine and its derivatives, triphenylamine, carbazole, acridane, acridone, phenoxazine, phenothiazine and its derivatives), including analytical redox reagents, oxidation mechanisms ([64-66] *et al.*). It has been established that the amino compounds oxidation reactions proceed in acidic, neutral, alkaline aqueous solutions, as well as in acidic organo-aqueous media to form radical intermediates or final products and are of first order in both substrates and oxidants. A limiting stage is bimolecular. A second-order rate constant depends on the medium acidity, that is related to the participation of oxidants and/or substrates in protolytic equilibria.

In particular, on the diarylamines oxidation with the different sufficiently strong oxidants ($Ce(SO_4)_2$, $KMnO_4$, $K_2Cr_2O_7$, NH_4VO_3, $(NH_4)_2S_2O_8$, H_2O_2, KIO_3, KIO_4, *et. al.*), as well as on electrooxidation, the intermediate - cation radical of amine is initially formed (in acidic media, the protonated amine is oxidized, which is commonly attacked by the anion: MnO_4^-, $Cr_2O_7^{2-}$, $HCr_2O_7^-$, VO_3^-, $S_2O_8^{2-}$, $SO_4^{\bullet-}$, IO_3^-, IO_4^-, *et al.* or by the electroneutral species of oxidative agent) ($Ph = C_6H_5$):

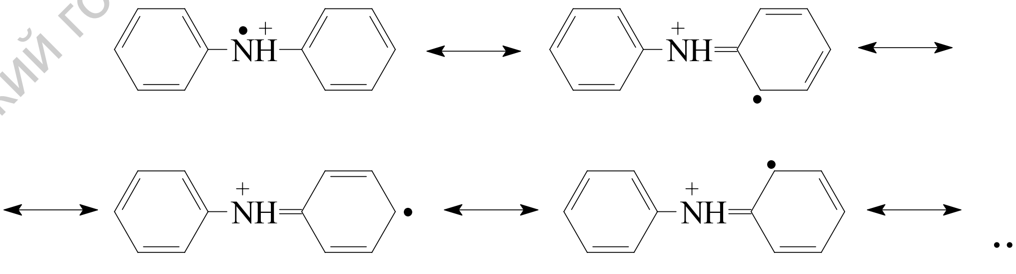
$$Ph_2NH \rightleftarrows Ph_2NH^{\bullet+} + \bar{e},$$

$$Ph_2NH_2^+ \rightleftarrows Ph_2NH^{\bullet+} + H^+ + \bar{e}.$$

The cation radicals of amino compounds are sufficiently strong NH-acids, and in the essentially basic media are capable of deprotonating to yield the diarylaminyl radicals:

$$Ph_2NH^{\bullet+} \rightleftarrows Ph_2N^{\bullet} + H^+.$$

In the cation radicals and diarylaminyl radicals, the spin density of uncoupled electron is delocalized over the aromatic rings:



so that their dimerization is possible involving both the nitrogen atom and the rings carbon atoms. For instance, in the cation radical of diphenylamine, according to our data from the quantum chemical computation at the UB3LYP/6-311++G(d,p) level of theory, the values of spin density on the nitrogen atom, carbon atoms in the *ortho* and *para* positions of aromatic ring are equal respectively to 0.360, 0.119 (0.147) and 0.237, the total spin value (S^2) after annihilation being equal to 0.7713 therewith.

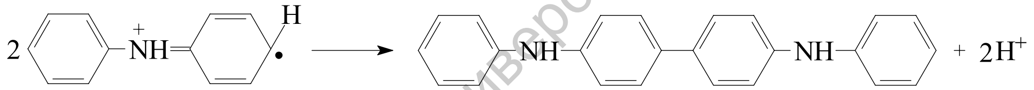
Since the highest spin density in the radical intermediates is focused on the nitrogen atom, thus in the weakly-acidic, neutral and weakly-basic media, the dimerization of the N,N-type occurs in a number of cases:

$$2Ph_2NH^{\bullet+} \rightleftarrows Ph_2N\text{-}NPh_2 + 2H^+.$$

However, in the acidic media the N-N bond is labile, and the C,C-coupling of aromatic rings is realized. Therewith the dimerization *via* the carbon atoms in *ortho* positions of rings does not occur. Thus, we have established that if both *para* positions of the diarylamine molecule are occupied, the amine does not undergo oxidation to form N,N'-diaryl-*p*-diphenoquinonediimine dication.

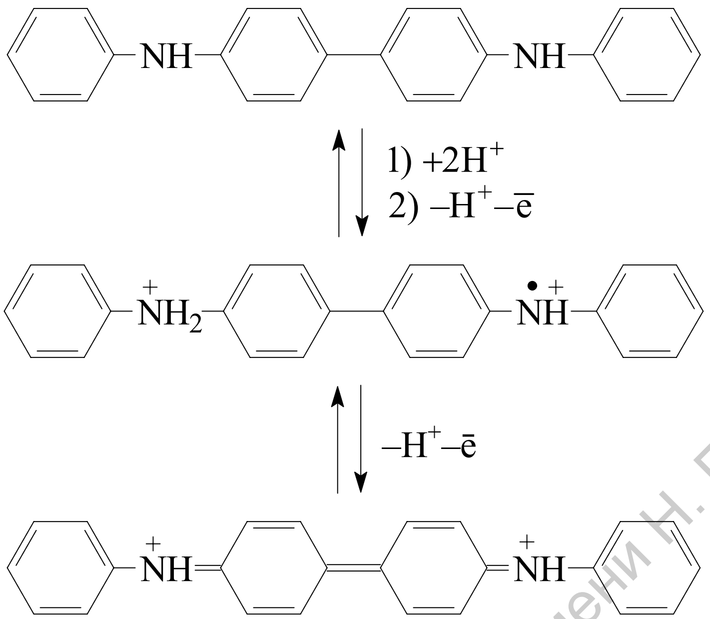
The absence of dimerization has been shown also for diarylaminyl radicals - intermediates of diarylamines oxidation in alkaline media. In particular, 4,4'-dicarboxydiphenylamine can not be oxidized with potassium hexacyanoferrate (III) $K_3[Fe(CN)_6]$ in the medium of 3-10 M KOH.

Consequently, the radical intermediates undergo dimerization by the type of *para*,*para* junction:

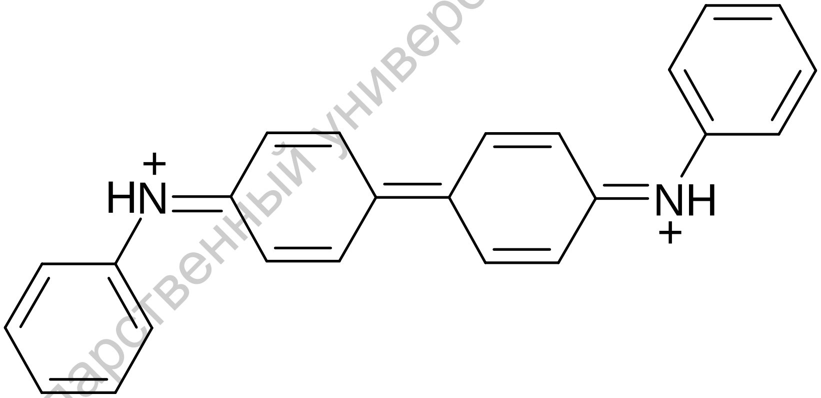


Para,*para* junction of the aromatic rings is more preferable, as compared to the dimerization involving *ortho* carbon atoms, also from the viewpoint of spin density.

The appearing N,N'-diarylbenzidine is capable of being further oxidized (the example for reaction in acidic medium is shown):

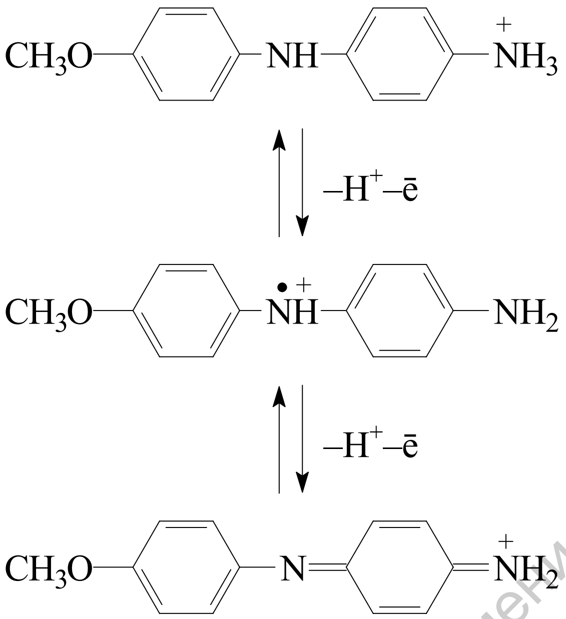


So, the oxidation product of diphenylamine in acidic media is N,N’-diphenyl-*p*-diphenoquinonediimine dication [66]:



The electronic absorption spectrum of this species computed by means of the PPP method with adaptation of parameters (see below) coincides well with the experimental spectrum: λ_{max} = 581 nm (theor.), 580 nm (exper.) [66].

Diarylamines the molecules of which contain NH_2, NHR, NR_2 or OH groups in *ortho* or *para* positions, are oxidized to yield monomeric, not dimeric, products. Below presented is the oxidation scheme of 4-amino-4’-methoxydiphenylamine (Variamine Blue):



The Variamine Blue electrooxidation on glassy carbon rotating disk electrode in aqueous and organo-aqueous media proceeds in two single-electron steps, the second being rate-determining one.

The equation of polarization curve is the following therewith:

$$E = E^0 - [RT/(1 + \alpha)F]\ln(K\delta/Da) - [RT/(1 + \alpha)F]\ln[(i_d - i)/i],$$

where δ is the diffusion layer thickness; D is the diffusion coefficient of depolarizer; a is the hydronium ion activity; i_d is the limiting current; K is the product of rate constants for the first and second steps; α is the transfer coefficient for the second step.

As discussed for aqueous-dimethylformamide solutions, the pH decrease from 2.45 to 4.52 is accompanied by the limiting stage alteration [65].

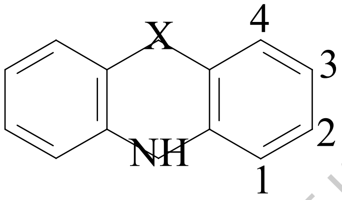
Using 52 substances of different types and their derivatives as examples, the general trends of spin density distribution in radical intermediates, as well as the regularities of reactivity and regioselectivity of homolytic (oxidative and reductive) coupling for organic compounds, have been formulated. For explaining and predicting the said reactions pathways, a quantum chemical consideration has been examined in terms of kinetic (including spin density), thermodynamic, and steric factors [67].

The principal regularities of spin density distribution in radical intermediates of homolytic coupling consist in the following: for aromatic hydrocarbons, pyrrole, furan, evident is similar pattern of delocalization of the above quantity in cation radicals and anion radicals - intermediates of oxidative and reductive homolytic processes, respectively; in the diethylmalonate radical, spin density is localized on the dehydrogenized carbon atom, in the benzoate radical - on the oxygen atoms, in the intermediates of the SH-compounds oxidative dimerization - on the sulphur atom; in the cation radicals and radicals with *n*-electron donor substituents of the NH_2 и OH types, benzyl and methylbenzyl radicals, the excess of spin density takes place on the heteroatom, as well as on the carbon atoms in *ortho* and *para* positions of the aromatic rings; in the anion radicals of benzene derivatives with electron acceptor substituents, pyridine and its 1-oxide - on the carbon atom in the position 4 of the cycle [67].

The regioselectivity of homolytic dimerization of organic substances occurs mainly because of definite spin density distribution in the radical intermediates [67]. Such a reactivity index as spin density appears valid in spite of spin contamination (impurity of the spin state due to the admixing of states with higher multiplicities to the wavefunction).

Table 6 represents an example of reactivity predictions based on the spin density distribution in the cation radicals occurring on heterocyclic amino compounds oxidation.

Table 6. Spin densities on atoms of cation radicals - oxidation intermediates or products computed at the UB3LYP/6-311++G(d,p) level of theory



Compound	X	Position of the molecular system		
		1	3	N
Phenothiazine	S	0.012	0.109	0.256
Phenoxazine	O	0.007	0.137	0.300
Carbazole	–	0.197	0.227	0.322

The S^2 values for the above cation radicals are 0.7576, 0.7591 and 0.7689, respectively, which is rather close to the $S^2 = 0.75$ quantity for pure doublet state, the latter being characteristic for radical species with one unshared electron. Thus, spin contamination practically does not distort the information concerning spin density distribution on atoms in the ground states of the cation radicals under study.

The above results let one predict the order of the species capability to undergo oxidative coupling: phenothiazine < phenoxazine < carbazole, which has been confirmed experimentally.

Thus, the main oxidation product for phenothiazine in acidic media is the cation radical, whether the oxidation is chemical ($Ce(SO_4)_2$, $KMnO_4$, $K_2Cr_2O_7$, NH_4VO_3, $(NH_4)_2S_2O_8$, H_2O_2, KIO_3, KIO_4, *et. al.*) or electrochemical.

For phenoxazine, the cation radical occurrence within the initial period of the reaction development, is replaced by a two-electron oxidation product formation.

As for carbazole, its interaction with ammonium vanadate in the medium of 4.25-10.3 M H_2SO_4 is featured by the stoichiometry 1 : 2, *i.e.* the cation radical appeared at first turns into the dimer rapidly. Anodic oxidation of carbazole on glassy carbon rotating disk electrode in the sulphuric acid solutions proceeds under the mixed control conditions and involves one electron transfer due to electrode passivation caused by dimers and/or polymers precipitation onto its surface [64].

The similarity in directions (on Figures 11 and 12, marked by asterisk) for electrophilic (nucleophilic) processes and oxidative (reductive) coupling reactions of thiourea, N-phenylthiourea, many C_6H_5X compounds, naphthalene, anthracene, phenanthrene, carbazole, acridane, acridone, 5,10-dihydrophenazine, phenoxazine, phenothiazine, acridine, N-methylpyridinium, pyrilium, thiopyrilium cations originates from a level of qualitative similarity of electron density distribution in the substrates molecules and spin density distribution in the radical intermediates [67].

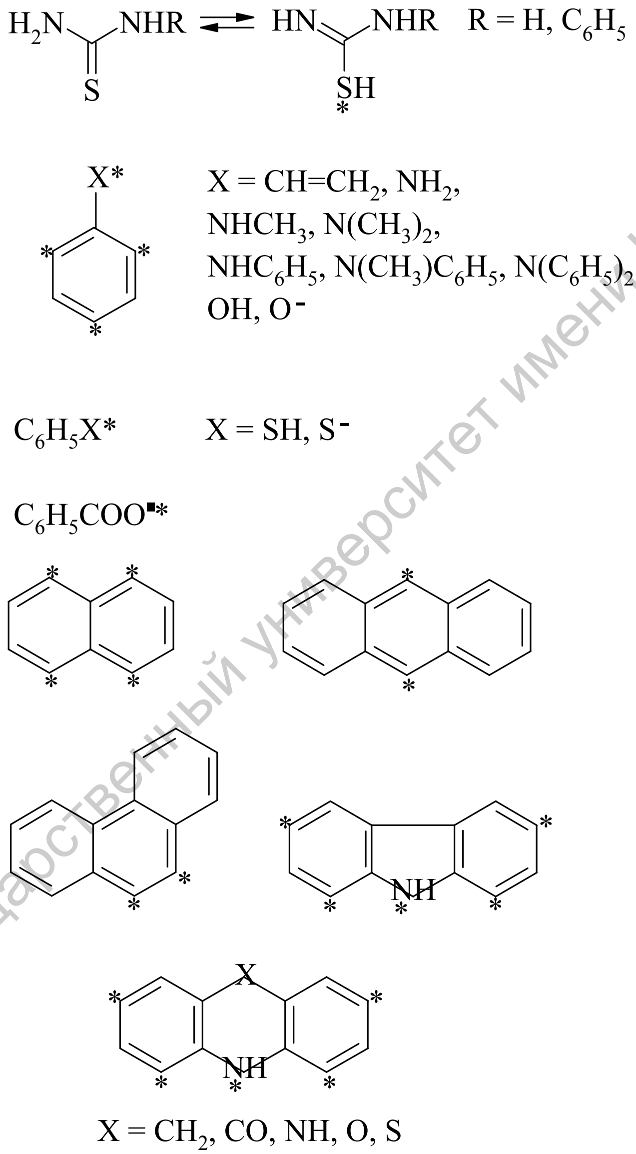


Figure 11. Compounds featured by similar regioselectivity of electrophilic and oxidative coupling reactions.

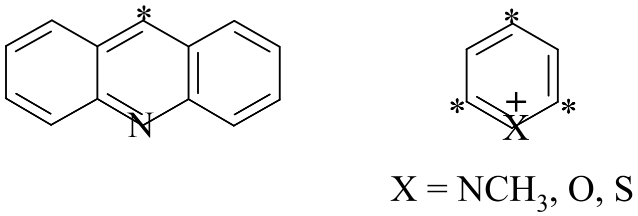
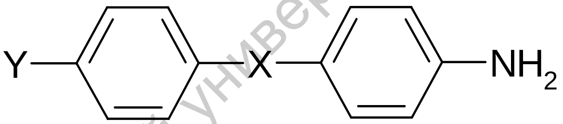


Figure 12. Compounds featured by similar regioselectivity of nucleophilic and reductive coupling reactions.

By means of the ^{14}N NQR method, the electronic structure of nitrogen atom (a reaction centre in redox processes) of diphenylamine and its 4-methoxy, 2,4,4’-trimethoxy and 4-benzoyl derivatives has been explored. Unshared electronic pair donates 0.18-0.27 electrons to π-systems of aromatic rings, that allows this pair to remain reactive with respect to electrophilic attack (oxidation, protonation, *etc.*). A change in both population of the unshared pair orbital and reactivity in electrophilic processes in the aforesaid series of compounds takes place according to signs of mesomeric effect of methoxy and benzoyl groups [68].

Chemical shifts in the NMR ^{13}C spectra of 1-aminohexane, diphenyl, N-methylaniline, diphenylamine and its 4-methyl, 4-methoxy, 2-, 3-, 4-nitro derivatives, phenol, diphenyloxide, are related linearly to charges on carbon atoms of aromatic rings.

It has been shown that substituents in molecules influence both the reactivity of bridge diphenyls:



X = CH_2, CH=CH, NH, O, S; Y = H, NO_2

in electrophilic reactions (protonation, acylation) and the diarylamines oxidation rate predominantly *via* the field effect with no regard to the nature of bridge group (CH_2, CH=CH, NH, O, S).

According to semiempirical data [69], the series of electron-acceptor and electron-donor ability of substituents in organic molecules have been obtained.

An oxidation mechanism ([64-66] *et al.*) commonness for various amino compounds is due to the vicinity of the corresponding amino nitrogen-containing groups in the series of changes of electronic effects and electronegativities of substituents.

A variation of electronic influence is the inductive effect [70]. According to the Glossary of Terms Used in Theoretical Organic Chemistry [71], inductive effect is a polarization of chemical bonds due to a shift of involved electron pairs toward a more electronegative group. Inside a molecule, the inductive effect is transferred through space and determined by the electrostatic forces between the interacting centres. Another original model of inductive effect (G.N. Lewis) is a model with transfer of this effect over bonds by means of consequent polarization of the bonds between dipolar or charged substituent and reactive centre. A quantitative evaluation of the inductive effect of groups (substituents) is given, in particular, by R.W. Taft σ^*-constants for aliphatic compounds and by the inductive σ_I-constants for aromatic substances.

In works of 1990-s, the inductive effect is considered as a sum of electronegativity effect and field effect. Electronegativity effect is a shift of electron density under the action of substituent over the σ-bonds chain. Some chemists identify the electronegativity effect with the inductive effect.

There is another terminology. It introduces the term “polar effect” presenting a sum of inductive effect (it is essentially the electronegativity effect) and the field effect.

We will discuss just the electron displacement along the σ-bonds chain and use the term “electronegativity effect”.

In the pure state, the above effect could be considered using a saturated hydrocarbon chain as an example. In this case, the influence of substituent in aliphatic molecule is not complicated by mesomeric shift of electron density with a participation of π-bonds.

Elucidated (*ab initio* and DFT) are distance and specificity of action of the effect of atomic groups electronegativity in the saturated systems (Figures 13-25), the sequence of weakening the electron-acceptor and electron-donor properties of substituents in aromatic molecules, electronic structure of the molecules of aniline series compounds.

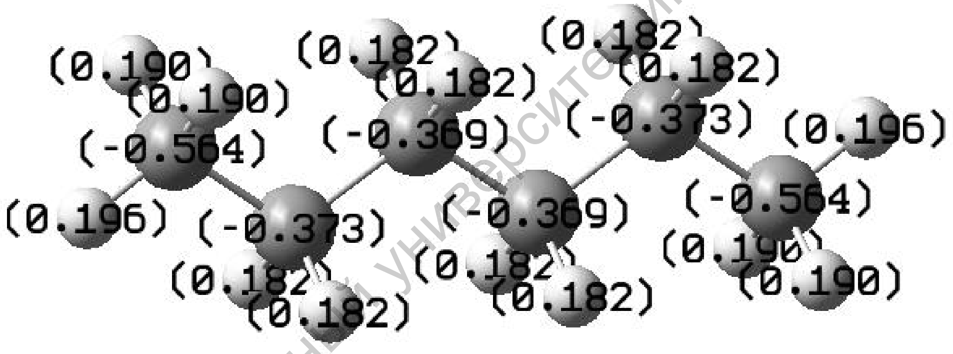


Figure 13. Natural atomic charges in the *n*-hexane molecule at B3LYP/6-311++G(3d,3p).

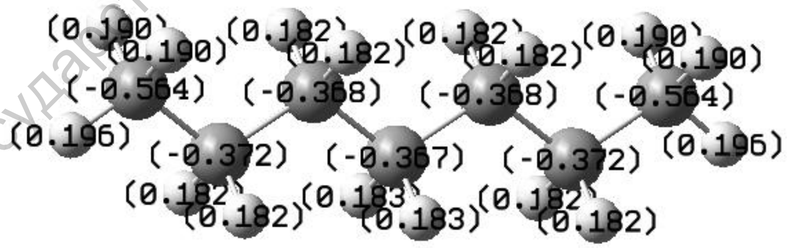


Figure 14. Natural atomic charges in the *n*-heptane molecule at B3LYP/6-311++G(3d,3p).

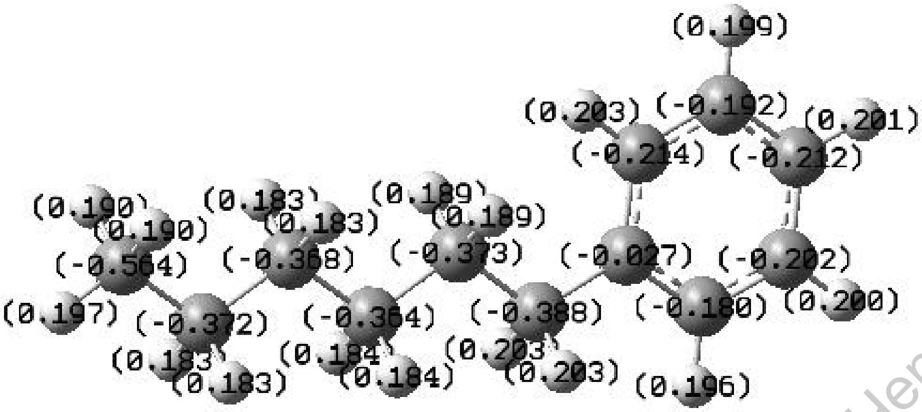


Figure 15. Natural atomic charges in the 1-hexylbenzene molecule at B3LYP/6-311++G(3d,3p).

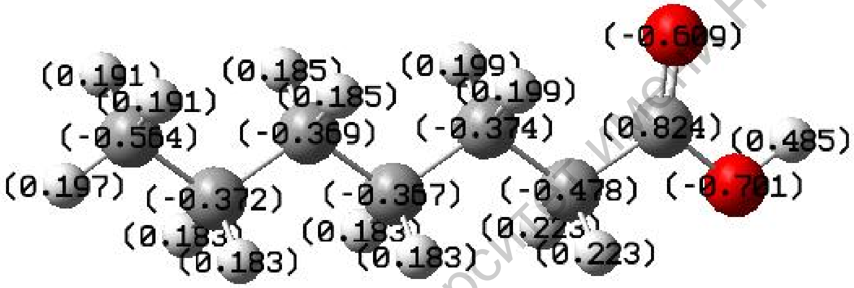


Figure 16. Natural atomic charges in the molecule of 1-heptanoic acid at B3LYP/6-311++G(3d,3p).

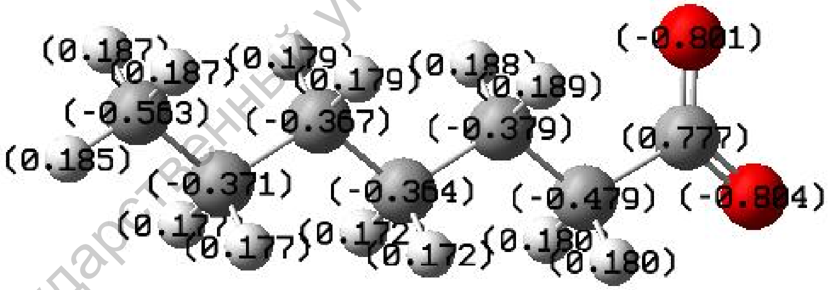


Figure 17. Natural atomic charges in the 1-heptanoate anion at B3LYP/6-311++G(3d,3p).

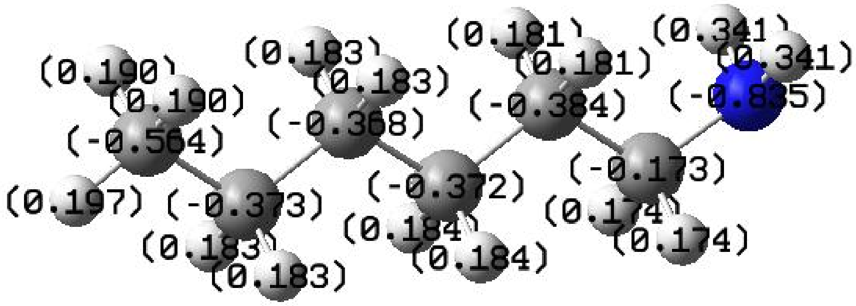


Figure 18. Natural atomic charges in the molecule of 1-aminohexane at B3LYP/6-311++G(3d,3p).

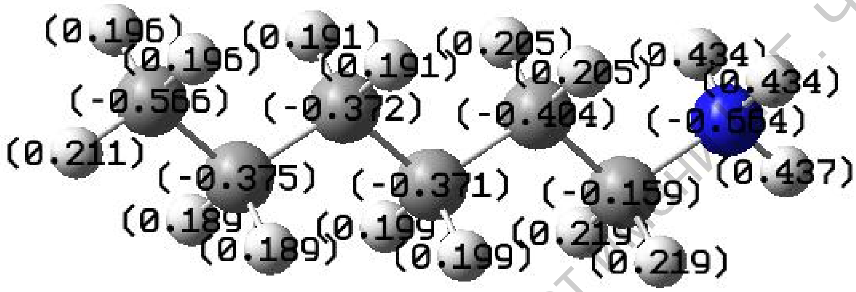


Figure 19. Natural atomic charges in the 1-hexylammonium cation at B3LYP/6-311++G(3d,3p).

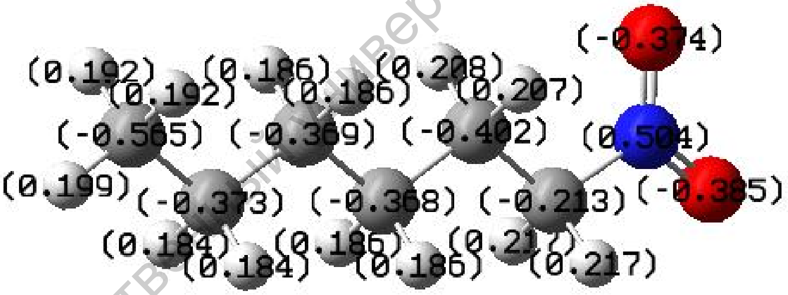


Figure 20. Natural atomic charges in the molecule of 1-nitrohexane at B3LYP/6-311++G(3d,3p).

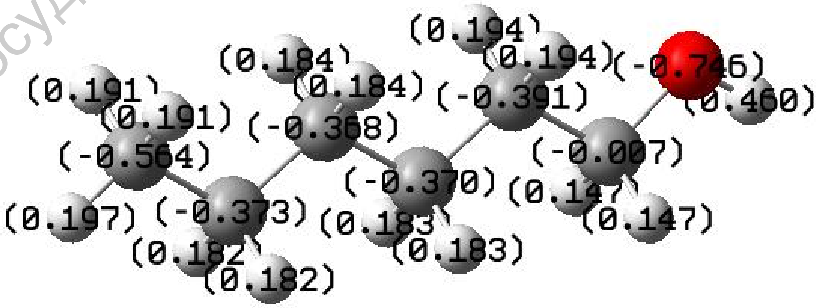


Figure 21. Natural atomic charges in the molecule of 1-hexanol at B3LYP/6-311++G(3d,3p).

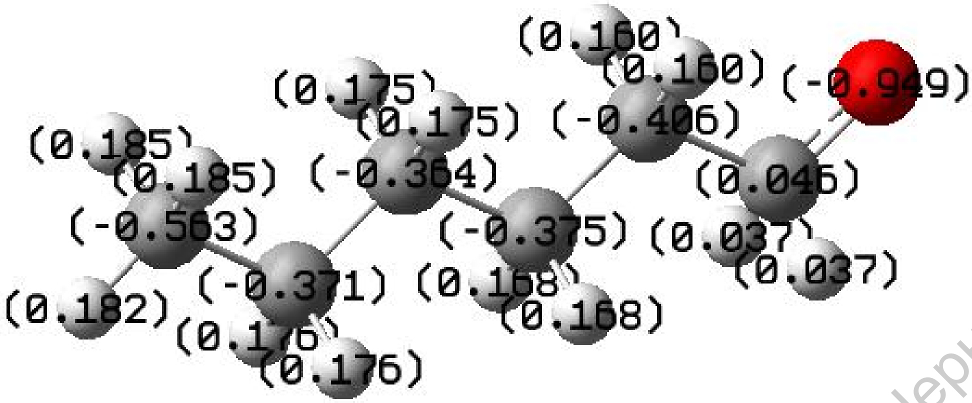


Figure 22. Natural atomic charges in the 1-hexanolate anion at B3LYP/6-311++G(3d,3p).

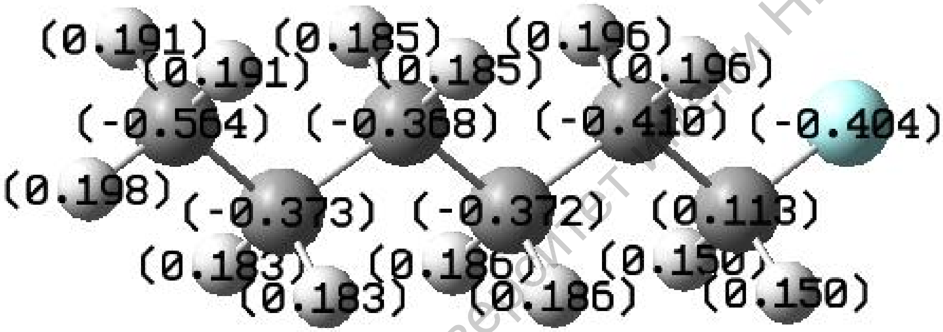


Figure 23. Natural atomic charges in the molecule of 1-fluorohexane at B3LYP/6-311++G(3d,3p).

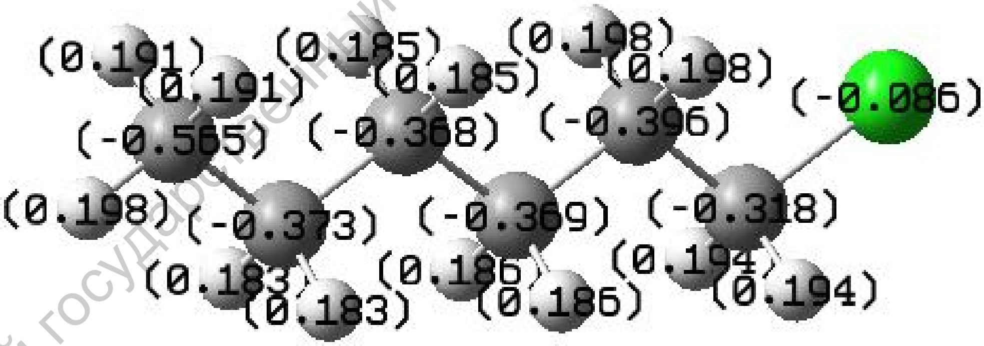


Figure 24. Natural atomic charges in the molecule of 1-chlorohexane at B3LYP/6-311++G(3d,3p).

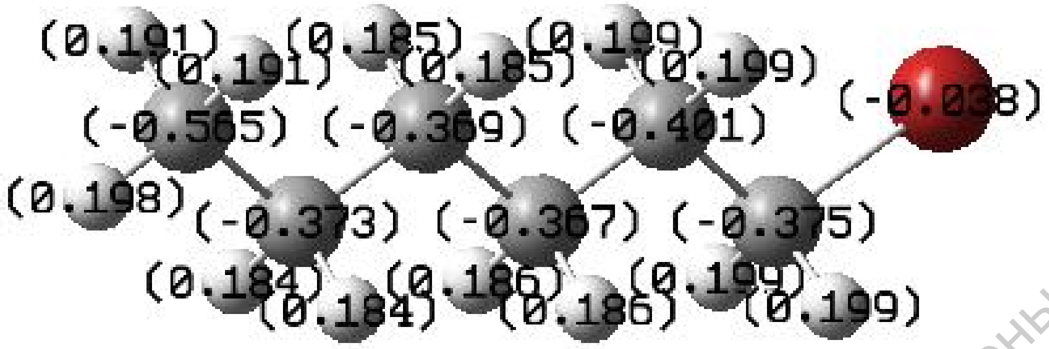


Figure 25. Natural atomic charges in the molecule of 1-bromohexane at B3LYP/6-311++G(3d,3p).

The NBO charge distribution in the molecules of *n*-hexane, *n*-heptane and *n*-octane is in agreement with the ^{13}C NMR data [72-74]. For 1-aminohexane, the ^{13}C chemical shifts [74] correlate linearly with the natural charges on atoms. Thus, the correctness of our evaluations of the electron distribution in molecules is confirmed.

Following the order of changes in the values of charge on the α-C atom, the atomic groups are arranged in the series just below (from left toward right, the charge shifts into negative region):

$$\mathrm{F} \gg \mathrm{O}^{-} > \mathrm{O\text{-}C{\equiv}N} \gtrsim \mathrm{OCH_3} \gtrsim \mathrm{OH} > \mathrm{OPO_3H_2} > \mathrm{OCOCH_3} \gtrsim \mathrm{OSO_3H} > \mathrm{ONO_2} >$$
$$> \mathrm{ONO} \gg {}^{+}\mathrm{N(CH_3)_3} > \mathrm{N(CH_3)_2} \gtrsim {}^{+}\mathrm{NH_3} \gtrsim \mathrm{NHCH_3} \gtrsim \mathrm{N{=}C{=}O} \gtrsim \mathrm{NH_2} \gtrsim \mathrm{N{=}C{=}S} \gtrsim$$
$$\gtrsim \mathrm{N_3} \gtrsim \mathrm{NHCOCH_3} > {}^{+}\mathrm{N{\equiv}C^{-}} > {}^{+}\mathrm{N{\equiv}N} \gtrsim \mathrm{NO_2} > \mathrm{NO} \gg \mathrm{Cl} > \mathrm{C(CH_3)_3} \gtrsim \mathrm{CH(CH_3)_2} \gtrsim$$
$$\gtrsim \mathrm{CH_2CH_3} \gtrsim \mathrm{CH_3} \gtrsim \mathrm{Br} > \mathrm{C_6H_5} > \mathrm{CH{=}CH_2} > \mathrm{CCl_3} > \mathrm{CBr_3} > \mathrm{CF_3} \gtrsim \mathrm{S\text{-}C{\equiv}N} >$$
$$> \mathrm{CONH_2} \gtrsim \mathrm{COCH_3} \gtrsim \mathrm{SH} \approx \mathrm{COOCH_3} > \mathrm{CHO} \approx \mathrm{COOH} \gtrsim \mathrm{COO^{-}} \gtrsim \mathrm{CN} \gtrsim$$
$$\gtrsim {}^{+}\mathrm{S(CH_3)_2} \gtrsim \mathrm{COCl} \gtrsim \mathrm{COBr} \gtrsim \mathrm{SCH_3} \gtrsim \mathrm{S^{-}} \gtrsim \mathrm{COF} > \mathrm{C{\equiv}CH} > \mathrm{SOCH_3} > \mathrm{H} >$$
$$> \mathrm{SO_2CH_3} \approx \mathrm{SO_3H} > \mathrm{SO_3^{-}} > \mathrm{PH_2} > \mathrm{PHCH_3} > {}^{+}\mathrm{PH_3} \gtrsim \mathrm{P(CH_3)_2} > {}^{+}\mathrm{P(CH_3)_3} \gg$$
$$\gg \mathrm{PO_3H_2} \gtrsim \mathrm{BH_2} \gtrsim \mathrm{B(CH_3)_2} \gg \mathrm{SiH_3} > \mathrm{Si(CH_3)_3}.$$

The substituents positioned on the left from H in the above series, result in the shift of natural charge on α-C atom toward positive side as compared with the *n*-hexane molecule. Therewith only the substituents F, O^{-} and O-C≡N change a sign of charge on α-C atom into a positive one. Contrary, the groups positioned on the right from hydrogen enhance a negative charge on α-carbon atom as compared with the *n*-C_6H_{14} molecule.

The range of charge values on α-C atom falls from 0.1126 (X = F) to –0.6975 (X = $^{+}P(CH_3)_3$), –0.7558 (X = PO_3H_2), –0.7623 (X = BH_2), –0.7687 (X = $B(CH_3)_2$) and even –0.8236 (X = SiH_3) and –0.8397 (X = $Si(CH_3)_3$). At X = H the said quantity consists –0.5642.

The charge on carbon atom in β-position, when varying the substituent X, changes within a fairly narrow range: from –0.4103 for X = F to –0.3527 on X = C≡CH, therewith in the case of X = H a charge is equal to –0.3725. The values of natural charge on β-C atom follow the series below (a negative charge being diminished from left toward right):

$$\mathrm{F \gtrsim NO \gtrsim O^{-} \gtrsim {}^{+}N(CH_3)_3 \gtrsim {}^{+}NH_3 \gtrsim NO_2 \gtrsim SOCH_3 \approx Br \gtrsim O\text{-}C{\equiv}N \gtrsim SO_3^{-} \approx}$$
$$\mathrm{\approx {}^{+}S(CH_3)_2 \gtrsim SO_3H \approx SO_2CH_3 \approx Cl \gtrsim N(CH_3)_2 \gtrsim S\text{-}C{\equiv}N \approx OSO_3H \gtrsim ONO_2 \gtrsim}$$
$$\mathrm{\gtrsim ONO \approx OPO_3H_2 \gtrsim OH \gtrsim OCOCH_3 \gtrsim SH \approx S^{-} \approx OCH_3 \approx NHCH_3 \gtrsim SCH_3 \approx}$$
$$\mathrm{\approx {}^{+}PH_3 \approx NH_2 \approx CBr_3 \gtrsim CCl_3 \gtrsim {}^{+}N{\equiv}N \gtrsim PO_3H_2 \approx P(CH_3)_2 \gtrsim N_3 \approx CF_3 \approx COO^{-} \approx}$$
$$\mathrm{\approx CHO \approx {}^{+}P(CH_3)_3 \approx PHCH_3 \gtrsim NHCOCH_3 \approx PH_2 \gtrsim CH(CH_3)_2 \gtrsim COCH_3 \approx}$$
$$\mathrm{\approx CH{=}CH_2 \gtrsim N{=}C{=}O \gtrsim COCl \approx COF \approx COBr \approx COOH \approx SiH_3 \approx CONH_2 \approx}$$
$$\mathrm{\approx C(CH_3)_3 \approx COOCH_3 \gtrsim C_6H_5 \approx H \approx N{=}C{=}S \gtrsim {}^{+}N{\equiv}C^{-} \gtrsim Si(CH_3)_3 \gtrsim CH_3 \gtrsim}$$
$$\mathrm{\gtrsim CH_2CH_3 > BH_2 \gtrsim CN \gtrsim B(CH_3)_2 \approx C{\equiv}CH.}$$

As for the charge on γ-carbon atom, its values fall into even narrower interval compared with β-C: from –0.3754 ($X = O^{-}$) to –0.3624 ($X = BH_2$), including the value of –0.3692 on X = H. The sequence of shifts in natural charges on γ-C atom (from left to right) toward less negative region appears to be as follows:

$$\mathrm{O^{-} \gtrsim {}^{+}N{\equiv}N \gtrsim N{=}C{=}S \gtrsim N{=}C{=}O \approx F \approx {}^{+}N{\equiv}C^{-} \gtrsim NH_2 \approx NHCOCH_3 \gtrsim CN \approx}$$
$$\mathrm{\approx {}^{+}NH_3 \approx OPO_3H_2 \gtrsim OH \approx OSO_3H \approx O\text{-}C{\equiv}N \approx N_3 \approx OCH_3 \approx NHCH_3 \approx OCOCH_3 \approx}$$
$$\mathrm{\approx C{\equiv}CH \gtrsim ONO \approx Cl \approx CF_3 \approx ONO_2 \approx H \gtrsim N(CH_3)_2 \approx PH_2 \approx {}^{+}PH_3 \approx COF \approx}$$
$$\mathrm{\approx {}^{+}P(CH_3)_3 \approx NO_2 \approx Br \approx COBr \approx COCl \approx {}^{+}S(CH_3)_2 \approx S^{-} \approx PHCH_3 \approx COOH \approx CH_3 \gtrsim}$$
$$\mathrm{\gtrsim COOCH_3 \approx PO_3H_2 \approx CH_2CH_3 \approx CONH_2 \approx CHO \approx {}^{+}N(CH_3)_3 \approx SO_3H \approx NO \approx SH \approx}$$
$$\mathrm{\approx SCH_3 \approx S\text{-}C{\equiv}N \approx COCH_3 \approx P(CH_3)_2 \approx SiH_3 \approx Si(CH_3)_3 \approx CCl_3 \approx CBr_3 \approx}$$
$$\mathrm{\approx CH(CH_3)_2 \approx COO^{-} \approx CH{=}CH_2 \approx SO_2CH_3 \gtrsim C(CH_3)_3 \approx C_6H_5 \approx SOCH_3 \gtrsim}$$
$$\mathrm{\gtrsim B(CH_3)_2 \approx SO_3^{-} \gtrsim BH_2.}$$

A character of influence of atomic groups upon the electron density distribution on carbon atoms in α- and β-positions of aliphatic chain is so that the electronegativity effect leads in the cases of X = $CH(CH_3)_2$, $C(CH_3)_3$, CF_3, CCl_3, CBr_3, $CH{=}CH_2$, C_6H_5, CHO, $COCH_3$, COOH, $CONH_2$, $COOCH_3$, COO^{-}, COF, COCl, COBr, NH_2, $NHCH_3$, $N(CH_3)_2$, ${}^{+}N(CH_3)_3$, $NHCOCH_3$, ${}^{+}N{\equiv}N$, N=C=O, N_3, NO, NO_2, OH, O^{-}, OCH_3, O-C≡N, $OCOCH_3$, ONO, ONO_2, OPO_3H_2, OSO_3H, SH, S^{-}, SCH_3, ${}^{+}S(CH_3)_2$, S-C≡N, $SOCH_3$, F, Cl, Br to alternating the signs of charge changes (but usually not charges themselves; solely in going from X = H to X = F, O^{-}, O-C≡N a charge on α-C atom becomes positive). The above fact is in agreement with a knowledge on α- and β-effects in ^{1}H NMR spectroscopy [75]. It is known [75] that for the fragment CH-CHX, the increase in electronegativity of the group X leads to the displacement of signal of the proton at α carbon atom toward weak field, and of the proton at β carbon atom toward strong field.

As seen, α- and β-effects are widespread, but not universal, since the substituent introduction not always leads to the decrease in electron density on α-C atom and to its increase on β-C atom.

It is important to emphasize that under the effect of substituent, the most essential (in the first significant digit) changes occur with the charges on α-C atom. The charges on the second and third carbon atoms vary within the second or third significant digit. Thus, the electronegativity effect in the aliphatic chain readily attenuates.

The electronegativity effect distance over aliphatic chain usually does not exceed three atoms.

Using sum of the charges of fragment C_6H_{13} as a criterion, for the above series of the *n*-$C_6H_{13}X$ molecules, we obtain the following sequence of weakening (from left to right) electron-acceptor ability of substituents X:

$$\begin{gathered}
{}^{+}N{\equiv}N \gg F \gtrsim O\text{-}C{\equiv}N > OSO_3H \gtrsim ONO_2 > OPO_3H_2 \gtrsim {}^{+}NH_3 \gtrsim {}^{+}N(CH_3)_3 \gtrsim OCOCH_3 > \\
> ONO > OCH_3 > OH > {}^{+}N{\equiv}C^{-} > NO_2 \gtrsim N{=}C{=}S > N{=}C{=}O \gtrsim NHCOCH_3 > N_3 > \\
> N(CH_3)_2 > NO > NHCH_3 > NH_2 > Cl \gtrsim {}^{+}S(CH_3)_2 > CCl_3 > CBr_3 > CN \gtrsim Br > COBr > \\
> COCl \gtrsim C_6H_5 > CF_3 \gtrsim C(CH_3)_3 > COF \gtrsim COOH \gtrsim CH{=}CH_2 \gtrsim COOCH_3 \gtrsim S\text{-}C{\equiv}N \gtrsim \\
\gtrsim CH(CH_3)_2 \gtrsim CH_2CH_3 \gtrsim CH_3 \gtrsim CONH_2 \gtrsim CHO \gtrsim COCH_3 > C{\equiv}CH > O^{-} \gtrsim {}^{+}PH_3 > \\
> SH > SO_3H \gtrsim SCH_3 > SO_2CH_3 \gtrsim SOCH_3 > {}^{+}P(CH_3)_3 > COO^{-} > H > PH_2 > SO_3^{-} \gtrsim \\
\gtrsim PHCH_3 \gtrsim PO_3H_2 > P(CH_3)_2 > S^{-} > BH_2 > B(CH_3)_2 \gg SiH_3 > Si(CH_3)_3.
\end{gathered}$$

For X = ${}^{+}N{\equiv}N$ we have $\Sigma = 0.5083$; for X = F, $\Sigma = 0.4027$; for X = H, $\Sigma = -0.1963$; for X = S^{-}, $\Sigma = -0.2873$, for X = BH_2, $\Sigma = -0.3192$, for X = $B(CH_3)_2$, $\Sigma = -0.3448$, for X = SiH_3, $\Sigma = -0.3910$, for X = $Si(CH_3)_3$, $\Sigma = -0.4218$.

As obvious from the discussion presented above, the distance and specificity of electronegativity effect do not depend directly upon the overall electron-acceptor ability of atomic groups.

A position of SO_2CH_3 substituent in the last series seems at first glance to be contradictory to such well-known facts as the electron-acceptor character of SO_2 fragment, that assists the appearance of superacidic properties of substances. Obviously, the electron-acceptor properties of SO_2CH_3 group are displayed by the stabilization of anions formed as a result of acidic dissociation of the corresponding molecules.

The Σ values do not correlate with the constants σ^*, σ_I and other inductive constants following from the linear free energy relationships principle. Since the series we constructed display the effect of substituents on the electronic structure of molecules over a chain of bonds, but not through space, thus the absence of such-kind correlations testifies indirectly to the fact that the inductive σ-constants involve the information on field (*via* space) interaction.

At the same time, with the Σ values for atomic groups X = H, CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$, $CH{=}CH_2$, C_6H_5, CN, CHO, $COCH_3$, COOH, $CONH_2$, $COOCH_3$, COCl, $Si(CH_3)_3$, NH_2, $NHCH_3$, $N(CH_3)_2$, $NHCOCH_3$, N=C=O, NO_2, OH, OCH_3, $OCOCH_3$, SH, SCH_3, F, Cl, the inductive parameter *iota* (ι) does correlate linearly [76]:

$$\iota = (z^* + 1)n^*.$$

This characteristic reflects (by means of two parameters: z^*, the effective charge of valence shell, and n^*, the effective principal quantum number) the effect of substituents over the bonds chain: $\iota = f + g\Sigma$, $f = 2.328 \pm 0.048$, $g = 1.657 \pm 0.258$, correlation coefficient $r = 0.9330$, adequacy dispersion $S_0^2 = 0.01302$.

Besides, the index Σ is related linearly to the atomic groups electronegativity values obtained by various experimental and theoretical methods and expressed on different scales, with the correlation coefficients from 0.95 to 1.

Therefore, the Σ value can serve as a measure of electronegativity of the substituent X in molecule. Earlier, W.F. Reynolds, S. Marriott, R.W. Taft and R.D. Topsom [77, 78] assumed a criterion of electronegativity to be a value $1 - Q_H$, where Q_H is a Mulliken charge on hydrogen atom in the HX molecule, computed at the HF/6-31G(d) level of theory. The advantage of the criterion Σ compared to the analogous index $1 - Q_H$ consists in the adequate allowance, by the Σ value, for the possibility of electron density dissimilation within the limits of sufficiently extended σ-core fragment C_6H_{13} (core σ-relaxation).

In the course of quantum chemical studies, including those of reaction mechanisms, hydrogen bonding interactions and electronic absorption spectra, the aqueous and non-aqueous media effect on the reactivity has been considered, doing so by different methods. The following approaches are used therewith.

1. *The explicit allowance for hydration in the supermolecule approximation*.

The corresponding clusters contain more than 100 water molecules. Therewith a density of water molecules distribution approaches to this value for liquid state [79]. Thus, actual aqueous solutions are simulated (*e.g.*, Figure 26).

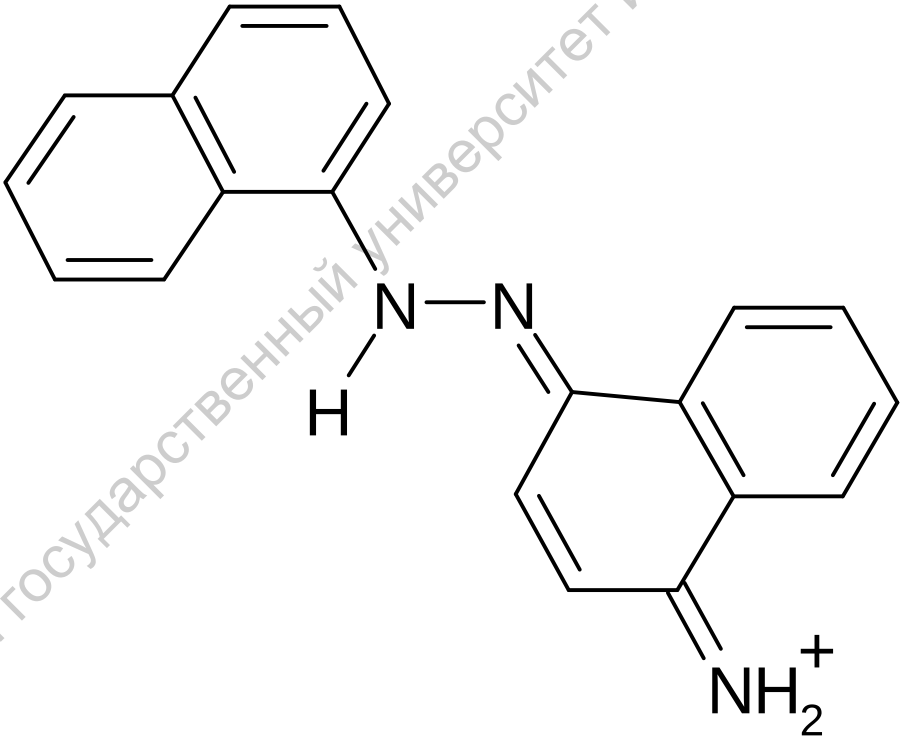


Figure 26. Product (analytical form) of the azo coupling reaction of naphthalene-1-diazonium cation with naphthalene-1-amine in the environment of water molecules (continued on next page).

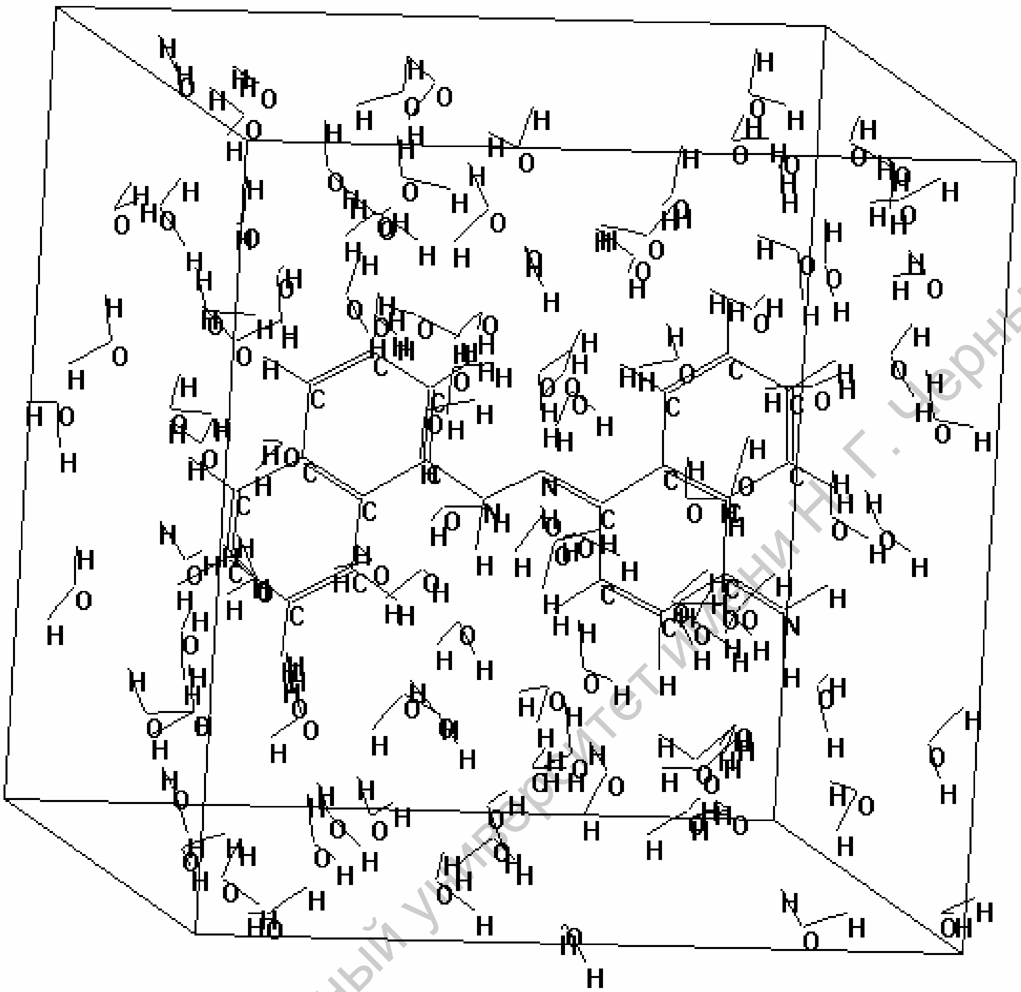


Figure 26. Product (analytical form) of the azo coupling reaction of naphthalene-1-diazonium cation with naphthalene-1-amine in the environment of water molecules (completed).

Scientific bases of the analytical characteristics prediction for azo coupling reactions have been created [80, 81]. The reactions have been found to be frontier-controlled, and their regioselectivity is unequivocally determined by thermodynamics of the intermediates - σ-complexes, as well as by the effect of aqueous medium. The latter defines high positional selectivity, providing the decision between two possible routes of reaction predicted on the basis of quantum chemical computations for separate molecular systems (*e.g.*, on Figure 27, the coupling proceeds *via* position 4 of the naphthalene-1-amine molecule). Furthermore, aqueous medium makes the selection of analytical forms - protonated azo coupling products with quinonehydrazonic structure (as for the example given on Figure 27, within the set of possible protonation centres - nitrogen atom (*p*) of primary amino group, α and β azo nitrogens - namely β nitrogen atom undergoes protonation):

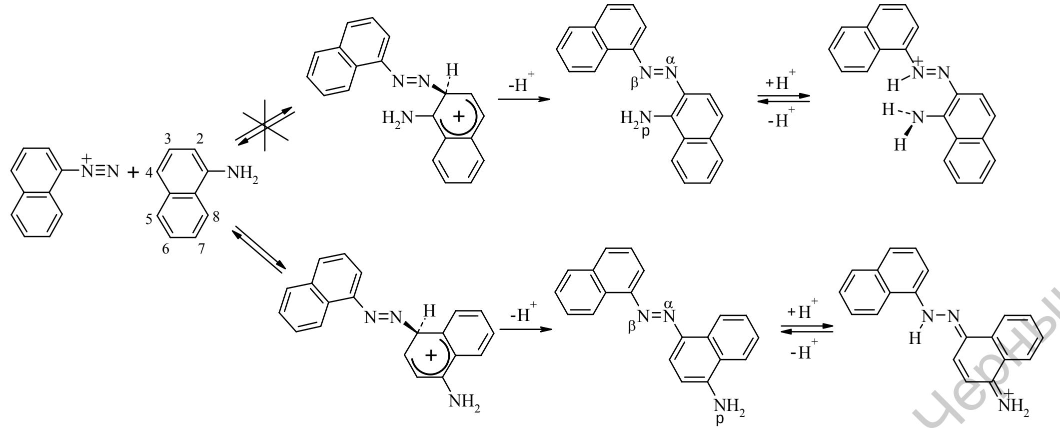
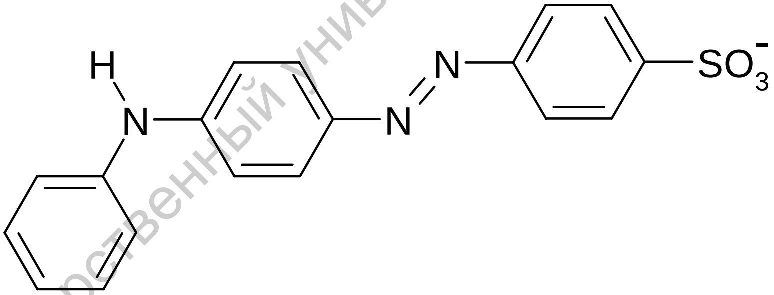


Figure 27. Azo coupling: possible directions of the reaction between naphthalene-1-amine and naphthalene-1-diazonium cation; regioselectivity of aminoazonaphthalenes protonation.

Aqueous medium has been established to exert a considerable influence upon the reaction rate for 4-carboxybenzenediazonium, 4-nitrobenzenediazonium and 4-sulphobenzenediazonium cations with diphenylamine. Furthermore, this medium stabilizes predominantly the σ-complex occurring on electrophilic attack by 4-sulphobenzenediazonium of *para* position in the diphenylamine molecule, and in doing so it chooses between two alternative routes of azo coupling reaction, which are predicted by the quantum chemical computations of isolated σ-adducts. Thus, the reaction product has the following structure:

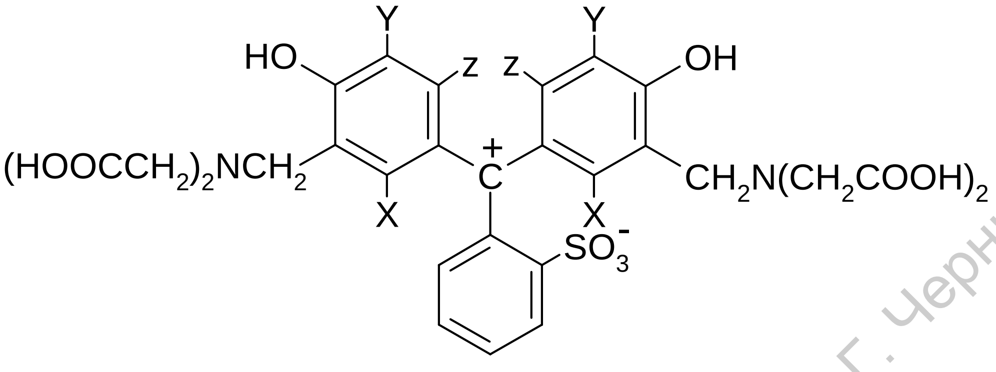


Hydration enthalpies of phenothiazine, N-acetylphenothiazine and their conjugate acids have been evaluated. The difference between the amino compounds basicity in gaseous phase and in aqueous media is connected with differentiating hydrating ability of water in relation to amines and ammonium cations.

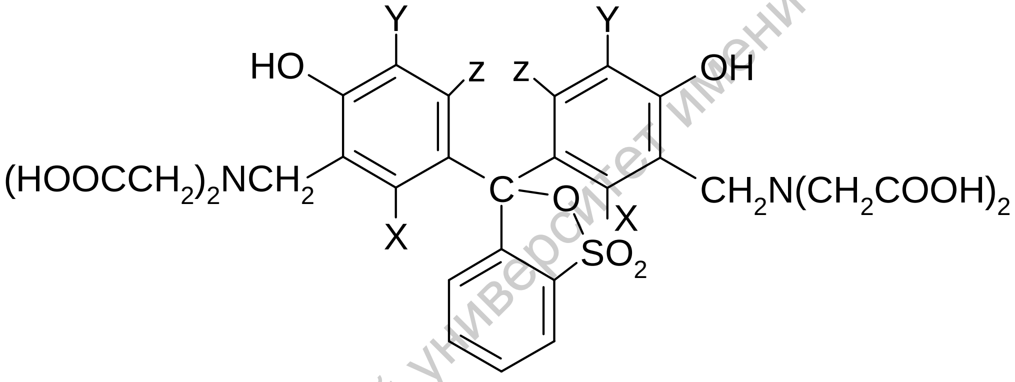
For aromatic amines, carbonyl and azo compounds, 2-pyrrolidone, acridone, phenothiazines, it has been established that the protonation promotes hydration. It is natural, since the hydrophilic hydration is contributed mainly by electrostatic interaction which increases w-hen molecular system gains charge.

It has been cleared up that the protonation of anilines proceeds *via* the amine nitrogen atom, even if other possible centres of electrophilic attack do exist in the molecules [82].

On the basis of quantum chemical study it has been shown that for isolated molecules of sulphophthalexons (Figure 28), the heterocyclic form (H) is more thermodynamically stable than the open zwitterionic one (Z). The latter, on the contrary, is prevalent in aqueous medium [83].



Z



H

a) X =Y = Z = H; b) X = Z = H, Y = Cl; c) X = Z = H, Y = Br; d) X = Z = H, Y = CH_3;
e) X = Y = CH_3, Z = H; f) X = CH_3, Y = $CH(CH_3)_2$, Z = H; g) X = Y = H, Z = CH_3

Figure 28. Zwitterionic (Z) and heterocyclic (H) forms of sulphophthalexons.

2. *Study of the environment influence by the self-consistent reaction field (SCRF) method.*

IHB interactions in 8-hydroxyquinoline in relation to its zwitterionic tautomer and the rotamer without IHB have been studied by the B3LYP and MPW1K density functionals. The rotation of O-H bond and intramolecular proton transfer reactions were studied theoretically. The following theory levels have been applied: B3LYP/6-31G(d,p), B3LYP/6-311++G(d,p), MPW1K/6-311++G(d,p), MPW1K/6-311++G(2d,3p)//MPW1K/6-311++G(d,p). The effect of environment (benzene, chloroform, tetrahydrofuran, 1,2-dichloroethane, acetone, water) was simulated by the self-consistent reaction field (SCRF) method within the polarizable continuum model (PCM) at the MPW1K/6-311++G(d,p) theory level. The evolution of geometry, relative energies, rotation (around the O-H bond) and tautomerization barriers heights, IHB energies and ΔG(solv) have been systematically investigated. The results obtained have shown the failure to neglect some changes of the aforesaid characteristics in polar media with respect to the gaseous phase. The IHB energy diminishes with the solvent polarity growth. The NBO analysis at the B3LYP/6-311++G(d,p) theory level has shown that the O-H$\cdots$N interaction satisfies the indicative criteria for hydrogen bonding. The charge transfer occurs from the lone pairs of nitrogen and oxygen to the aromatic system. Electron density diminishes on the OH hydrogen and increases on the N atom, *i.e.* is redistributed between the atoms - direct participants of hydrogen bonding. Our calculations have demonstrated also that the structure and properties of 8-hydroxyquinoline can be adequately discussed within the framework of hybridization. The zwitterions formation process has a barrier of ~20 kcal/mol (MPW1K/6-311++G(d,p)) both in the gaseous phase and in the presence of solvent. The reverse proton transfer reaction has no barrier almost at all in the gaseous phase and a considerable barrier (~5-10 kcal/mol) in polar solvents. The results obtained indicate that the zwitterization reaction is difficult to be realized experimentally in any medium [84].

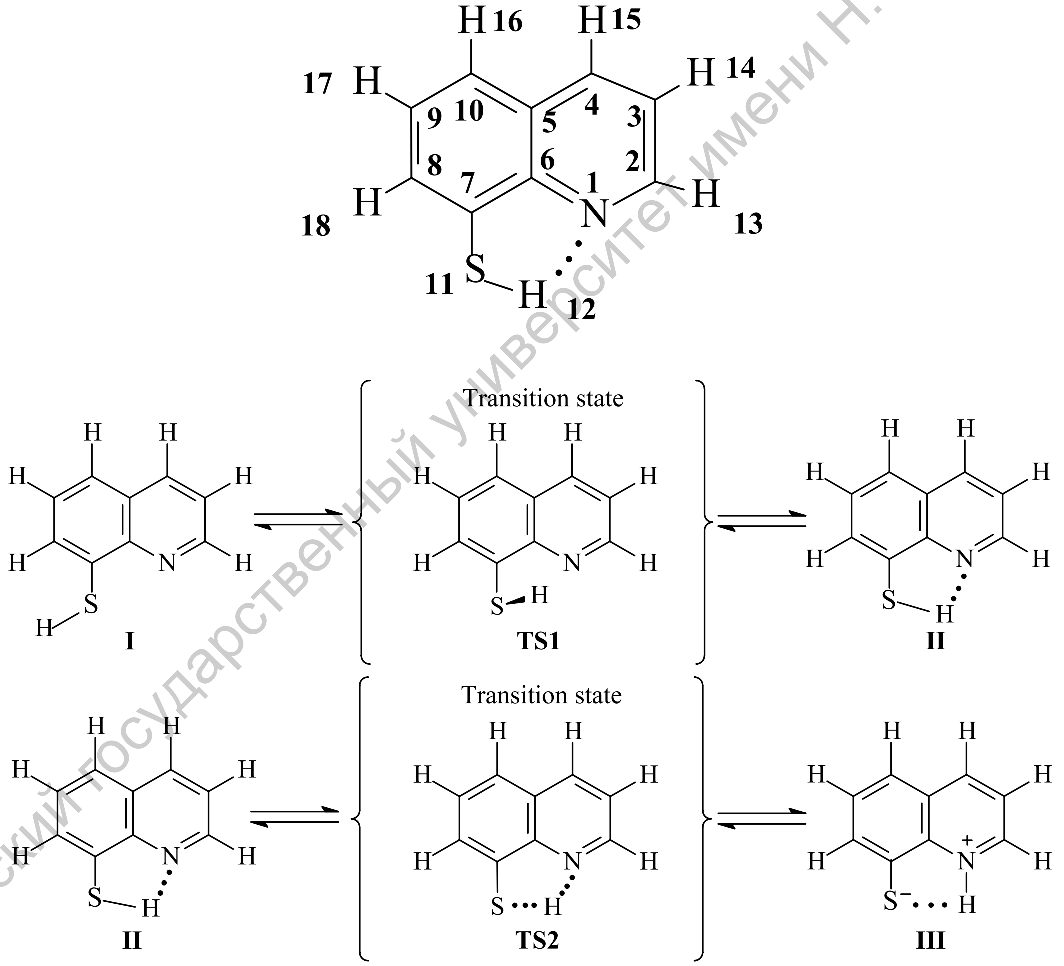


Figure 29. Rotamers and tautomers of 8-mercaptoquinoline.

A theoretical quantum chemical study of the IHB interactions in 8-mercaptoquinoline has been carried out. Special attention has been paid to the rotation (I $\rightleftarrows$ II) of S-H bond and intramolecular proton transfer (II $\rightleftarrows$ III) reactions (Figure 29). Therefore B3LYP/6-311++G(d,p), B3LYP/6-31+G(2d,2p), MPW1K/6-311++G(d,p), MPW1K/6-31+G(2d,2p), BH&HLYP/6-311++G(d,p), G96LYP/6-311++G(d,p) methods have been used. The most successful result of the IHB energy about 2.3 kcal/mol (difference of sums of electronic and thermal enthalpies) was computed using MPW1K/6-311++G(d,p) level. The Onsager and PCM reaction field methods at the MPW1K/6-311++G(d,p) и B3LYP/6-311++G(d,p) theory levels have been applied to study solvent (benzene, 1,2-dichloroethane, ethanol, nitromethane, water) effects on hydrogen bond energies, conformational equilibria, rotational barriers and tautomerism. Natural bond orbital (NBO) analysis has been performed to study the IHB in the gaseous phase and in aqueous medium.

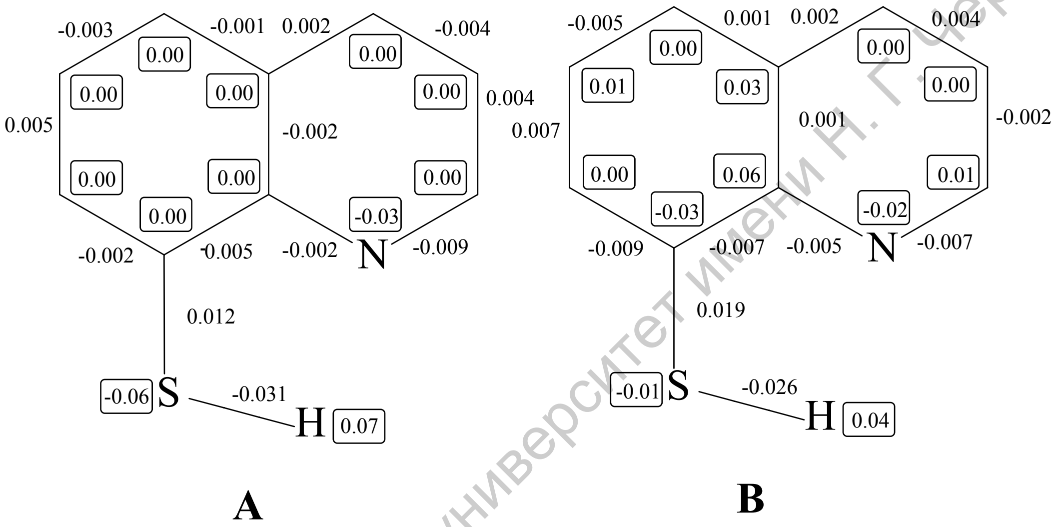


Figure 30. Changes in natural charges (circled, in atomic units) and Wiberg bond orders in II with respect to I from NBO analysis at the B3LYP/6-311++G(d,p) level in the gaseous phase (A) and in aqueous solution (B) using the PCM method.

The effect of the IHB has been studied by comparing two conformers I and II. We assume that the differences in the charges obtained by the NBO analysis, as well as in Wiberg bond orders, reflect the effect of IHB on the electron density distribution in the molecule. The changes in the natural charges and in the bond orders of II with respect to I from B3LYP/6-311++G(d,p) calculations in the gaseous phase and in aqueous solution are depicted in Figure 30. The charge distribution of II shows that the weak (as compared to I) character change of the bonds involved in the hydrogen-bonded five-membered quasicycle takes place. The electron density on sulphur and nitrogen atoms increases, on labile hydrogen - diminishes, the smaller change being in aqueous solution. In the latter, the greatest increase in the electron density is observed on C7, and some diminution on C5 and C6. The involvement of C5, C6 and C7 atoms in the electron density changes in solution, in contrast to the gaseous phase, is in agreement with significant BD*(C5-C6) → BD*(C7-C8) donor-acceptor interaction occurring only in the aqueous medium. The latter interaction may be a result of a strong augmentation of the attractive electrostatic terms and solvent polarization. The charges on the other ring carbons does not alter under the above intramolecular interaction. Among the parameters of II, the S11-H12 bond order shows a significant decrease, and C7-S11 bond order increases appreciably as a result of the IHB formation. These tendencies occur in the both media.

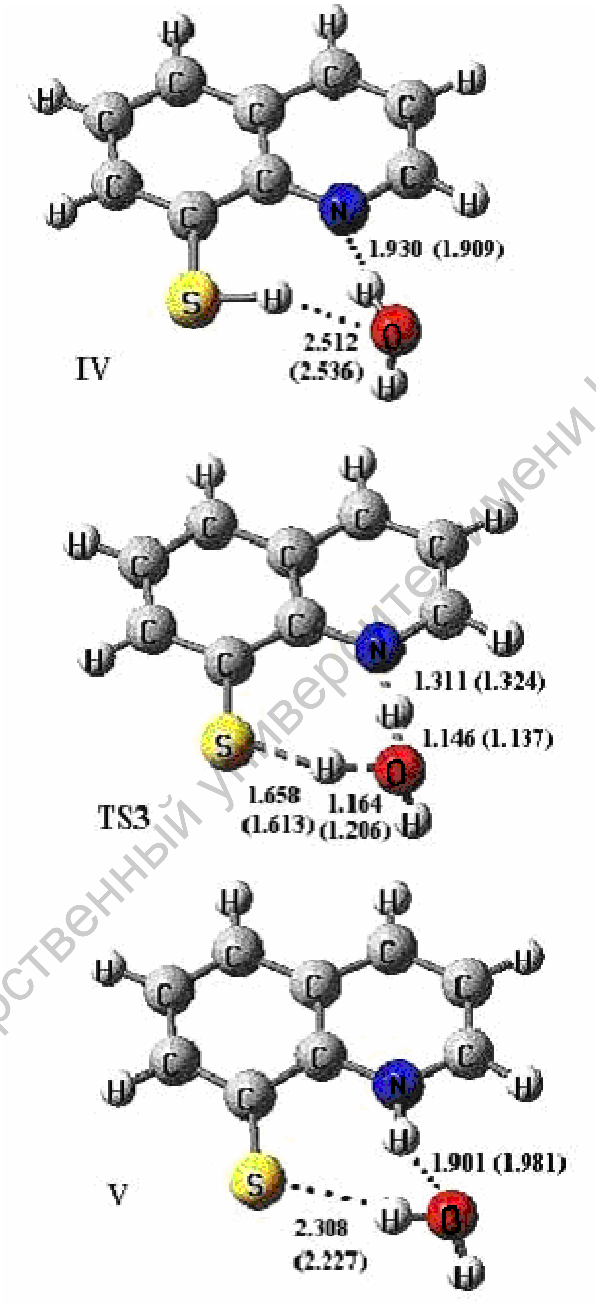


Figure 31. Some interatomic distances (Å) of tautomers IV, V and transition state TS3 at the MPW1K/6-311++G(d,p) level for the gaseous phase and aqueous solution (in parentheses).

The proton transfer on zwitterization is featured by a gaseous-phase barrier about 10.5 kcal/mol, and the reverse proton transfer nearly has no barrier [85].

Double proton transfer in the prototropic tautomerization of 8-mercaptoquinoline complex with one water molecule (IV $\rightleftarrows$ V) (Figure 31) in the gaseous phase and in solution has been studied.

To clear up a question whether any high-energy intermediate exists along the reaction path, we have computed the energetic profile (intrinsic reaction coordinate) for double proton transfer at the B3LYP/6-311++G(d,p) level starting from the transition state TS3. The results are shown in Figure 32. There is no intermediate along the intrinsic reaction coordinate, and the reaction proceeds smoothly from reactant to product. It is safe to say in this connection that two protons in the gaseous phase transfer concertedly and synchronously. In the transition state TS3 (Figure 31), both protons of the water molecule are disposed closely to the oxygen atom.

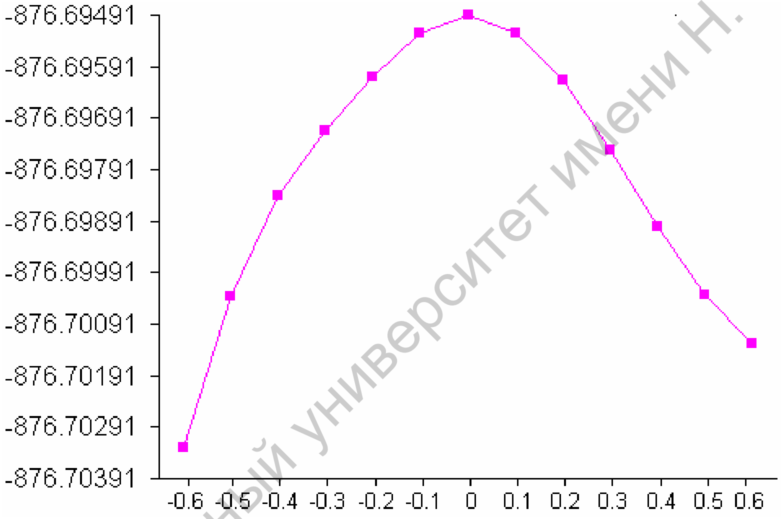


Figure 32. Energetic profile (intrinsic reaction coordinate) for 8-mercaptoquinoline water-assisted tautomerization IV → V calculated for the gaseous phase at the B3LYP/6-311++G(d,p) level. The vertical axis is for the total energies in Hartree/particle and the horizontal axis is for reaction coordinate in the units of Bohr.

The water-assisted tautomerization is kinetically less and thermodynamically more favourable than the single proton transfer. The tautomerization energy and barrier height are decreased as the dielectric constant is increased both for single proton transfer and water-assisted reaction, which imply that the tautomerization of 8-mercaptoquinoline occurs faster and more completely in polar solvent. The stability of studied forms in solution, on the contrary to that for 8-hydroxyquinoline, does not coincide with one in the gaseous phase, implying that the electrostatic influence of solvent is very important [85].

There are the manifest principal differences in the extent of influence of the electrostatic solvent effects on the relative stability of various forms of 8-hydroxyquinoline and 8-mercaptoquinoline. For the former of the above reagents, the contribution to stability, which is intrinsic for the conformers and tautomers as themselves, occurs to be determining.

Contrary, in the case of 8-mercaptoquinoline, the polar medium plays a decisive role for governing the relative stability of different forms.

It is known [86] that the principal consequences of the specific interaction with solvent could be taken into account provided that the complex of the studied molecule with one solvent molecule is explicitly considered. When regarding the water-assisted proton transfer and placing the 8-mercaptoquinoline complex with water molecule in the dielectric continuum of the solvent, we simultaneously take into account the effect of specific and universal solvation on the reactivity within the discrete-continuum approach. On studying the water-assisted reaction we have shown a possibility of a by-step proton transfer as that occurs in real water with its complex structure, the profound distant-order elements in a liquid state. The regularities elucidated therewith in respect to the effect of complexation with water molecule on the mechanism, kinetics and thermodynamics of tautomerization could compose the basis for the directive regulation of the reactions with the aim of obtaining the compounds with desirable properties.

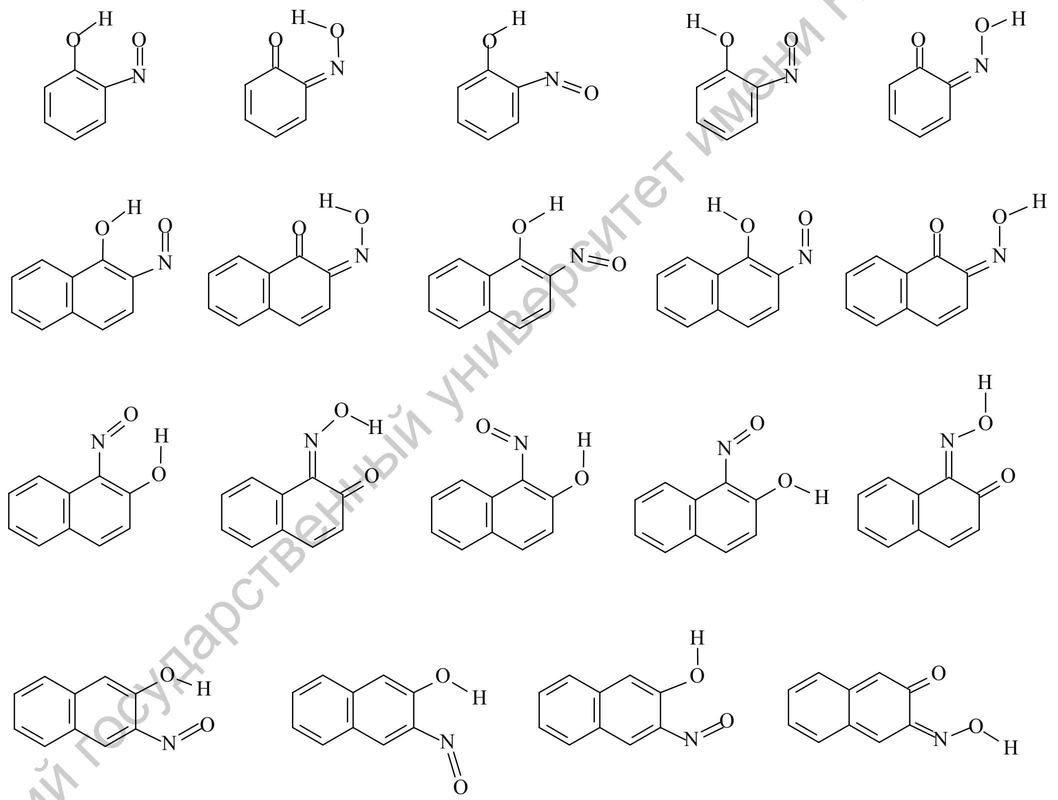


Figure 33. Different forms of 2-nitrosophenol, 2-nitroso-1-naphthol, 1-nitroso-2-naphthol, 3-nitroso-2-naphthol.

Intramolecular hydrogen bonding (IHB) interactions and molecular structures of 2-nitrosophenol, nitrosonaphthols and their quinone-monooxime tautomers (Figure 33) were investigated at *ab initio* (HF/6-31G(d,p), MP4/6-311G(d)//MP2/6-31G(d,p)) и DFT (B3LYP/6-311++G(d,p), MPW1K/6-311++G(d,p)) and density functional theory (B3LYP/6-311++G(d,p), MPW1K/6-311++G(d,p)) levels. Possible conformations with different types of the IHB of the tautomers were considered to understand the nature of the hydrogen bonding among these conformers. The effect of solvent on hydrogen bond energies, conformational equilibria, and tautomerism in aqueous solution were studied by means of SCRF within the PCM model. Natural bond orbital analysis was performed to study the IHB in the gaseous phase and in aqueous medium. The NMR ^{1}H, ^{13}C, ^{15}N, ^{17}O chemical shifts in the gaseous phase and in solution for the studied compounds were calculated using GIAO approach. The optimized geometrical parameters and ^{1}H NMR chemical shifts are in good agreement with previous experimental data [87].

It has been elucidated that the hydrogen bond energy formation for nitroso tautomeric forms is a larger than for oxime ones. The analysis of charge density has shown that all the systems studied here satisfy the indicative criteria of hydrogen bonding interactions.

Careful conformational analyses of given molecules show that both that the size and charge differences between oxygen atoms in these compounds are very important factors not only for comparing their conformational behaviour but also for understanding the nature of hydrogen bonding.

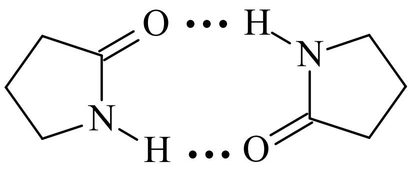
Besides, good correlations between O···H distance and the difference of charge density ($Q_H - Q_A$, where A is the atom - acceptor in the H···A hydrogen bond), electron density, Laplacian density at bond critical point, and ellipticity has been found.

The results of NBO analysis indicate that interactions in nitroso forms are stronger than those in oxime ones (except for 2-nitrosophenol). The hydrogen bond is stronger in the *syn*-oxime structure of 2-nitrosophenol than that of the others, especially in aqueous medium.

The results of this study also show that the topological parameters may be applied to estimate the H-bond strength. The NMR ^{1}H chemical shifts may be useful descriptors for the strength of intramolecular H-bonds.

By means of the B3LYP, MPW1K and B3PW91 methods with the 6-311++G(d,p) and AUG-cc-pVDZ basis sets, the equilibrium geometries and vibrational frequencies of stable conformers of the feasible monomers and dimers of 2-pyrrolidone have been studied [88].

The problem of 2-pyrrolidone hydrogen-bonded dimers formation (Figure 34) is of great interest, since all hypothalamus hormones are low-molecular peptides, many of them carry a fragment of pyroglutamic acid [89], *i.e.*, in essence, the fragment of 2-pyrrolidone. Such hormones are thyroliberin, gonadoliberin, melanostatin, *etc.* The sites of synthesis of hypothalamus hormones are nerve endings - synaptosomes of hypothalamus. The large amounts of hormone associates have been discovered just here. It cannot be excluded that the aforementioned associate species are stabilized by hydrogen bonds of the pyroglutamic acid fragment.



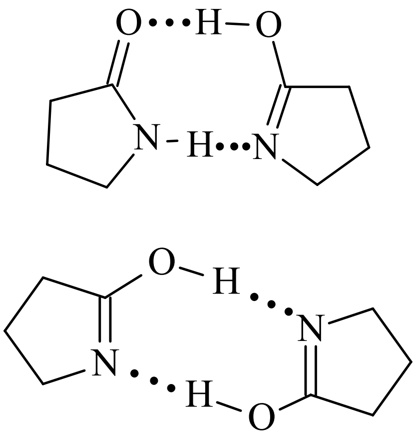
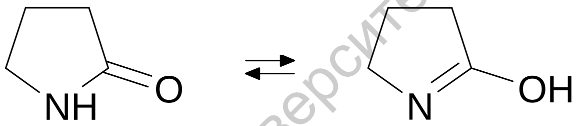


Figure 34. Theoretically possible dimers of 2-pyrrolidone based on its different tautomers.

As we have shown [88], the intramolecular proton transfer in the monomer, 2-pyrrolidone, has a barrier of ~50 kcal/mol and is essentially independent on the solvent. Double proton transfer in the hydrogen-bonded dimers proceeds concertedly and synchronously with a low barrier. Therefore, the prototropic tautomerization of 2-pyrrolidone:



occurs *via* the intermolecular mechanism.

The dimers have been investigated by performing the topological analysis of electron density at bond critical points within the framework of the Bader's atoms in molecules (AIM) quantum theory, the analyses of NBO, orbital interactions, electrostatic potential. As a whole, the undertaken studies have shown that all the systems under consideration can meet the criteria for hydrogen bonding. The dependences between the N-H (O-H) bond's stretching vibration frequency and this bond's length; between the intermolecular hydrogen bond length in dimer, the dimerization energy and the electron density at bond critical point have been found. The NBO analysis has led to a conclusion that all the complexes incorporate the strong intermolecular interactions of the type of charge transfer from the lone electron pairs of heteroatoms to the σ^*(N-H) and σ^*(O-H) antibonds. As a consequence, the occupancy of these antibonding orbitals is fairly high.

3. *Indirect elucidation of the medium contribution by observing deviations from linear dependences between the experimental values of molecular properties in solutions* (*e.g., pK_a values*) *and gaseous-phase characteristics obtained by the quantum chemical methods (in particular, proton affinities*).

Revealing the character (*specific or conditionally universal solvation*) *and value of medium effect from equations linking some properties of substances in solution and in the gaseous phase*.

Predictive linear interrelations linking the benzenethiols (thiophenols) pK_a values with the quantum chemically evaluated enthalpies and free energies of the benzenethiolate anions proton affinity (*PA*) have been established. Differential influence of organo-aqueous media on the benzenethiols acidity has been estimated.

For the anions (A^-) formed on 27 benzenethiols (AH) dissociation, we have computed the proton affinity (Table 7) represented by enthalpy [90-93] and free energy of reactions of proton detachment in gaseous phase $AH \rightarrow A^- + H^+$:

$$\Delta\Delta H_f = \Delta H_f(A^-) + \Delta H_f(H^+) - \Delta H_f(AH),$$
$$\Delta\Delta G_f = \Delta G_f(A^-) + \Delta G_f(H^+) - \Delta G_f(AH).$$

The objects under study were the XC_6H_4SH compounds, where X = H (VI), 2-CH_3 (VII), 3-CH_3 (VIII), 4-CH_3 (IX), 3-$COCH_3$ (X), 4-$COCH_3$ (XI), 2-COOH (XII), 4-COOH (XIII), 3-$COOCH_3$ (XIV), 4-$COOCH_3$ (XV), 4-NH_2 (XVI), 4-CH_3CONH (XVII), 3-NO_2 (XVIII), 4-NO_2 (XIX), 4-OH (XX), 3-OCH_3 (XXI), 4-OCH_3 (XXII), 3-CH_3SO_2 (XXIII), 4-CH_3SO_2 (XXIV), 4-F (XXV), 3-Cl (XXVI), 4-Cl (XXVII), 3-Br (XXVIII), 4-Br (XXIX), 3-I (XXX), 4-I (XXXI), as well as 2,4-dichlorobenzenethiol (XXXII).

Starting from the modified equation of isobar of chemical reaction, $\Delta G^0 = -RT\ln K_p$ (ΔG^0 is the change in standard free energy in the course of reaction, K_p is the equilibrium constant), we have the right to predict the linear interrelation between pK_a and free energy of proton affinity: $pK_a = h + i\cdot\Delta\Delta G_f$. Therewith for perfect system (gaseous phase), the intercept (*h*) and the slope (*i*) have the following values: $h = 0$, $i = (\ln 10\cdot RT)^{-1} = 0.7330$ mol/kcal. The change in entropy remains near-constant in the similar-type reactions with the participation of relative compounds of close molecular geometry. Therefore, the linear dependence between pK_a and enthalpy of proton affinity, $pK_a = h + i\cdot\Delta\Delta H_f$, could also exist.

We have found that the literature pK_a values of benzenethiols in the aqueous-acetone, aqueous-ethanol media and in methanol do correlate linearly with the gaseous-phase proton affinity $PA = \Delta\Delta H_f$, $\Delta\Delta G_f$ (Table 7; see the example in Figure 35; *m* is number of points in correlation equation, *r* is correlation coefficient).

Table 7. Correlations of the benzenethiols pK_a values with the benzenethiolate anions proton affinities (*PA*) (continued on next page)

Conditions of pK_a determination*	***PA***	**Set of compounds**	***m***	***h***	***i*, mol/kcal**	***r***
1	$\Delta\Delta H_f$	VI-IX, XVII, XXV, XXVII, XXX	8	–71.84 ± 33.50	0.2395 ± 0.0998	0.9234
1	$\Delta\Delta G_f$	VI-IX, XVII, XXV, XXVII, XXX	8	–93.70 ± 21.74	0.3134 ± 0.0667	0.9787

Table 7. Correlations of the benzenethiols pK_a values with the benzenethiolate anions proton affinities (PA) (completed)

Conditions of pK_a determination[*]	***PA***	**Set of compounds**	***m***	***h***	***i*, mol/kcal**	***r***
2	$\Delta\Delta H_f$	VI, VIII-XV, XIX-XXII, XXVI, XXVII, XXIX-XXXII	19	–49.22 ± 9.89	0.1690 ± 0.0298	0.9453
2	$\Delta\Delta G_f$	VI, VIII-XV, XIX-XXII, XXVI, XXVII, XXIX-XXXII	19	–49.45 ± 10.73	0.1743 ± 0.0332	0.9368
3	$\Delta\Delta H_f$	VI, VIII-XV, XIX-XXII, XXVI, XXVII, XXIX-XXXII	19	–53.05 ± 11.14	0.1849 ± 0.0335	0.9423
3	$\Delta\Delta G_f$	VI, VIII-XV, XIX-XXII, XXVI, XXVII, XXIX-XXXII	19	–53.28 ± 12.08	0.1907 ± 0.0374	0.9335
4	$\Delta\Delta H_f$	VI, VIII, IX, XVIII-XXIV, XXVI, XXVII, XXIX-XXXII	16	–47.10 ± 8.81	0.1627 ± 0.0265	0.9619
4	$\Delta\Delta G_f$	VI, VIII, IX, XVIII-XXIV, XXVI, XXVII, XXIX-XXXII	16	–46.87 ± 9.48	0.1665 ± 0.0293	0.9558
5[**]	$\Delta\Delta H_f$	VI, IX, XVI, XIX, XXII, XXVII, XXVIII	7	–49.06 ± 30.23	0.1709 ± 0.0907	0.9080
5[**]	$\Delta\Delta G_f$	VI, IX, XVI, XIX, XXII, XXVII, XXVIII	7	–50.30 ± 28.91	0.1797 ± 0.0892	0.9180
5[***]	$\Delta\Delta H_f$	VI, IX, XIX, XXII, XXVII, XXVIII	6	–42.03 ± 21.90	0.1493 ± 0.0659	0.9531
5[***]	$\Delta\Delta G_f$	VI, IX, XIX, XXII, XXVII, XXVIII	6	–43.03 ± 23.81	0.1567 ± 0.0737	0.9472

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[*] 1 - Determined by potentiometric titration in water - acetone mixture (1 : 3 by volume) at 27 ºC [94]
2 - Determined by potentiometric titration in 48.9 vol. % aqueous ethanol at 20-22 ºC [95]
3 - Determined by potentiometric titration in 95 vol. % aqueous ethanol at 20-22 ºC [95]
4 - Determined by spectrophotometric technique in 48 vol. % aqueous ethanol at 25 ºC [96]
5 - Determined by potentiometric titration in methanol [97]

[**] Correlation series involves the PA and pK_a values for all the compounds, for which the pK_a values in methanol have been measured

[***] Data for the species XVI (X = NH_2) are excluded

The interrelations found are indicative of the regularity - the approximately constant contribution of medium to the protolytic properties of benzenethiols.

A measure of the influence of constant component of medium contribution on the benzenethiols acidity can be: 1) the deviation of i value in Table 7 from the theoretical slope of dependence pK_a *vs* $\Delta\Delta G_f$, the latter being equal to $(\ln 10 \cdot RT)^{-1}$ = 0.7330 mol/kcal and assigned to gaseous phase; 2) the absolute h value equal to zero in the case of gaseous phase.

We have estimated differential effect of solvent for aqueous-ethanol media with varied ethanol content. There is the equation $pK = j + k/\varepsilon$ valid for the constants of various equilibria [98]. That is why the universal (electrostatic) or conditionally universal (corresponding to the conservation of energy of specific interactions) solvation, that depends upon the dielectric constant ε, should contribute at least to the coefficient i in the equalities $pK_a = h + i \cdot PA$, therewith $i \sim \varepsilon^{-1}$. The higher the alcohol content in aqueous-ethanol medium, the greater is the pK_a value, *i.e.* the weaker are the acidic properties of benzenethiols. The relationship of pK_a with ε has an antibate character. At the same time, the h value in going from 48.9 vol. % ethnol to 95 vol. % ethanol decreases slightly. Therefore, the conditionally universal solvation, that depends on ε, does not determined by the h value. For the explicit proton-donors ArSH, the obvious is the occurrence of specific interactions with the aqueous-ethanol media, that diminish pK_a compared to the gaseous phase. Provided that the above interactions would be displayed by the coefficient h, thus the increase in h value with the increase in the ethanol content in the aqueous-ethanol mixture should be assumed, since water assists the proton ejection from the molecule of benzenethiol ArSH to a somewhat greater extent (the values of pK_b for water and ethanol are 15.77 and 16, respectively [99]) and stabilizes more effectively the anion ArS^- formed as a result of ArSH dissociation (the acceptor numbers of water and ethanol are 54.8 and 37.3, respectively [98]) as compared to ethanol. The actual coefficient h is somewhat more negative in the case of medium enriched with ethanol.

The increase in the i value, as we observed in going from 48.9 vol. % ethanol to 95 vol. % ethanol, agrees with the corresponding effect on pK_a exerted by both the polarity (the ε value for water and ethanol are 78.39 and 24.55, respectively [98]) and the specific interactions. Consequently, the influence of both conditionally universal and specific solvation is comprised into the coefficient i. Differential effect of medium manifests itself in the component $i \cdot PA$ of the equality $pK_a = h + i \cdot PA$. The coefficient h likely has no physical meaning, but presents a scaling factor [37].

It would be reasonable to stress that the coefficient i values for the solutions of benzenethiols in 48.9 vol. % and 95 vol. % aqueous ethanol differ only slightly, that is natural for two media close in composition. However, it is difference in the coefficient i, being even small, that provides nevertheless the predomination of $i \cdot PA$ component over the h value in correlation equations. As a consequence, the experiments show the increase in pK_a in going from 48.9 vol. % ethanol to 95 vol. % ethanol.

With a series of solvents with different dielectric constants at hand, the conditionally universal and specific contributions of medium to the slope of the proton-affinity dependences of pK_a could be separated, and the system's "solute - solvent" shift to imperfection estimated ("gaseous phase", or an isolated molecule of solute) separately due to each type of solvation.

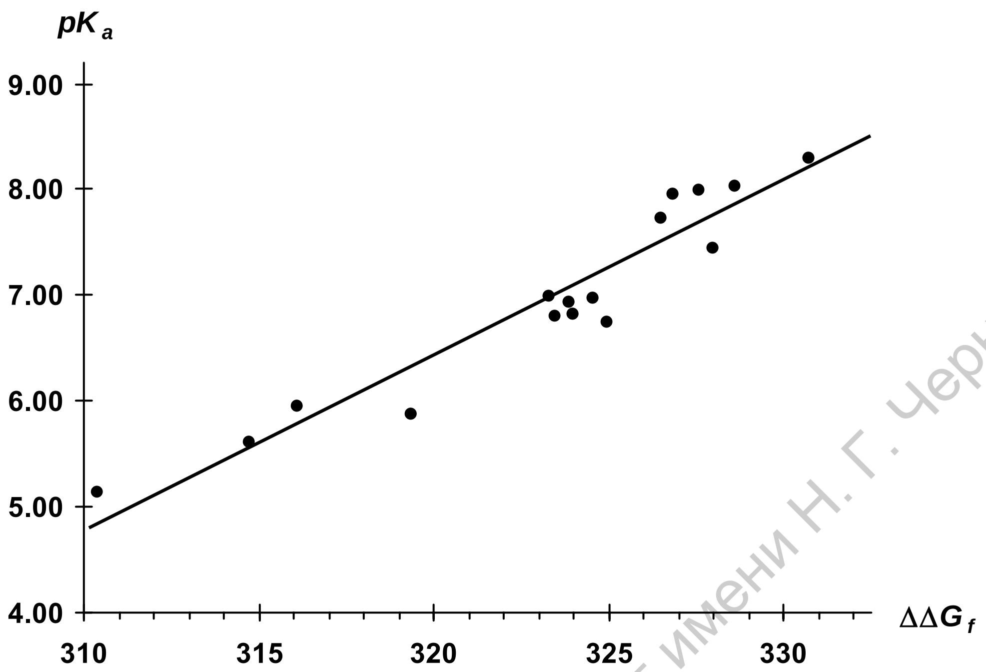


Figure 35. Dependence of benzenethiols XC_6H_4SH pK_a values determined by spectrophotometric technique in 48 vol. % aqueous ethanol at 25 ºC [95] *vs* $\Delta\Delta G_f$ (kcal/mol). X = H, 3-CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 4-OH, 3-OCH_3, 4-OCH_3, 3-CH_3SO_2, 4-CH_3SO_2, 3-Cl, 4-Cl, 3-Br, 4-Br, 3-I, 4-I. Correlation coefficient $r = 0.9558$.

Let us also offer another example. We have computed enthalpies and free energies of gaseous-phase proton affinity (*PA*) for aniline and its 62 derivatives with different kinds of electron-donor and electron-acceptor substitution in aromatic ring and at nitrogen atom. Linear correlations of the type pK_a *vs PA* have been found. Deviations of the data for some *ortho* substituted anilines from the above relationships have been discussed in view of possible hydrophobic hydration [100] of the molecular fragments adjacent to the protonation centre.

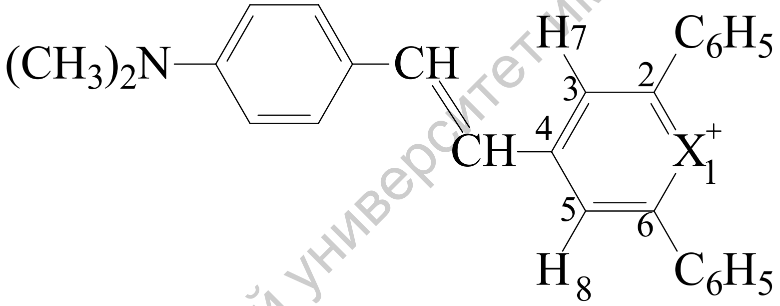
4. *Indirect knowledge on a character of hydrate shell developed from the information on charge localization or delocalization in molecular system.*

The effect of electrostatic, hydrophobic factors, as well as, using (1), (2) and (4) approaches, of hydration on reactivity, physicochemical and analytical properties is studied. In particular, in terms of the analysis of the mentioned effects, the regularities of phenothiazine fluorescence in micelles of cationic, anionic, non-ionic surfactants, the formation and extraction of ionic associates of 2,6-diphenyl-4-(4-dimethylamino)styrylpyrilium (XXXIII) and -thiopyrilium (XXXIV) cations with anionic surfactants [101] have been substantiated.

In Table 8, presented are new (obtained at a higher level of theory) data, as compared to those discussed in [101], on the electronic structure of the XXXIII, XXXIV systems, along with there selenium analog XXXV.

In the cation XXXIV, the overall charge of hetero ring is somewhat shifted to the positive side as compared to XXXIII, and positive charge is localized in significant extent on sulphur atom, whereas in the system XXXIII the charge of hetero ring is delocalized, and oxygen atom possesses even negative charge. Therefore the cation XXXIV characterized by higher charge density is evidently surrounded by more closer hydrate shell in aqueous solutions compared to the molecular system XXXIII. As a consequence, the cation XXXIII with anions of surfactants and inorganic ions in aqueous media forms the ionic associates, which are more stable and capable of being easier extracted by toluene as compared to the cation XXXIV. At the same time, in toluene extract, ionic associates and their components are not hydrated, and in accordance with the aforesaid peculiarities of cycles' charge distribution, ionic associates of the cation XXXIV with counterions are more stable than ionic pairs containing the cation XXXIII. The value and localization extent of charge in the cations of organic reagents XXXIII and XXXIV influence the magnitudes of stability constants and associates' distribution constants, as well as the reagents selectivity with respect to inorganic ions.

Table 8. Natural charges on atoms in chalcogenopyrilium cations at B3LYP/6-311G(d)



XXXIII X = O; XXXIV X = S; XXXV X = Se

Cation	X	Natural charge on the atom								
		1	2	3	4	5	6	7	8	Σ*
XXXIII	O	–0.463	0.426	–0.260	0.052	–0.251	0.427	0.225	0.228	–0.069 (0.384)
XXXIV	S	0.513	–0.088	–0.214	0.040	–0.207	–0.089	0.221	0.225	–0.045 (0.401)
XXXV	Se	0.638	–0.131	–0.225	0.042	–0.218	–0.132	0.219	0.222	–0.026 (0.415)

*Sum of charges on atoms of the heterocycle: the first number - without H7 and H8, in parentheses - including H7 and H8

From the viewpoint of charge distribution in the heterocycle, and due to slightly more positive total charge of the ring, for the selenium-containing cation XXXV one can expect more pronounced incapability of forming close ionic pairs in aqueous solutions, more difficult extraction by inert solvents, but, at the same time, occurrence of more stable ionic associates in the extracts as compared to the sulphur analog XXXIV.

5. *A specific kind of indirect medium consideration within the problem of quantum chemical calculation of electronic absorption spectra*.

The possibility of quantitative predictions of absorption maxima in electronic spectra of unsaturated organic compounds by means of the Pariser - Parr - Pople (PPP) method with adaptation of parameters has been examined. In this viewpoint, a schematic classification of quantum chemical methods has been proposed which is based on the idea of extrapolating: 1) from elementary particles (physical constants) to molecule; 2) from atoms to molecule; 3) from fragments to molecule [102, 103].

To reproduce quantitatively the wavelenghths of long-wave absorption bands, a possible way out is decreasing the “height” of the leap involved in the quantum chemical method which now may be designated as “fragments - molecule” (the case 3 among mentioned ones). Its advantages consist in the following:

[i] Fragments, being separate molecules, may be placed into the same medium as the initial molecule. It is of importance, since an explicit consideration of the solvation effects in electronic spectroscopy represents a complicated problem (*e.g.* [104] and Ref. therein), it is rarely possible to attain a quantitative agreement of calculated transition energies with experimental data.

[ii] The choice of the parameters is made using electronic molecular spectroscopy which is more accessible than atomic.

[iii] Fragments, in contrast to atoms and elementary particles, allow for a gradual complexation which provides for possible correction of errors at each step; the total error is the error of the last step, thus appearing minimal.

For realization of the above-described idea it is advisable that at a minimal complexation of the molecule only one unknown parameter would appear. In the case of the PPP method, the parameter to be corrected is two-electron one-centre Coulomb integral (its evaluation is the main object of criticism in the whole method [105]). The correction implies that deviations exceeding their conventional values by more than 30 % are highly undesirable.

Practical use of the method consists in the following. A series of compounds is built, in the beginning of which there is an appropriate conjugated hydrocarbon (it corresponds to the first parameter in the scheme to be corrected, *i.e.* the Coulomb integral of the carbon atom), and the terminal is the molecule under study. In going from one compound in the series to the neighbouring one, one new type of π-centre corresponding to the latter must appear (note that it may be several identical π-centres). The spectra of the compounds in this series should, as far as possible, be recorded under similar conditions. After that the parameters of each π-centre, by one at each step, are selected with fixation of all the parameters determined at preceding steps.

Thus the calibrated parameter “remembers” all the factors accounting for deviations of the experimental spectrum from the theoretical one and reproduces them at each following step.

For correct reproduction of spectral wavelengths, the construction of complete series of compounds, beginning with a hydrocarbon, with the appearance of a new type of π-centre at each step is not always necessary; spectra may be calculated according to a “cut-down” scheme using one or more model systems for calibration of the parameters.

The PPP method with adaptation of parameters has been used to calculate the electronic spectra of some unsaturated, aromatic and heterocyclic compounds, such as: N,N’-diphenyl-*p*-diphenoquinonediimine dication (oxidation product of diphenylamine in acidic media) [66] and derivatives of ethylene, benzene, naphthalene, quinone, pyridine (substituted and condensed), pyrimidine, some other azaheterocycles, thiopyranone and furan [102, 103].

The third group of methods (extrapolating from fragments to molecule) can hardly be expected to expand on account of all-valence methods, since the latter do not provide for the appearance of the only one parameter to be calibrated, and not several ones simultaneously, after a minimal complexation of the molecule structure. In going from one group to the neighbouring one with a higher number, the amount of computational work exhibits a clear tendency towards its decrease, while that of experimental (spectroscopic) work tends to grow.

Let us discuss the relation between the methods of the first and the second groups from one hand, and the third group, from the other hand. There is an important advantage that the *ab initio* and DFT approaches, as well as the all-valence semiempirical models as CNDO, INDO, PNDO, NDDO *et al.* have over the PPP, the latter even with adaptation of parameters. Through automatic core (sigma) relaxation they need not distinguish between different kinds of the same atom, *e.g.* aniline (pyrrole) and pyridine type nitrogen, phenol (furan) and carbonyl type oxygen, *etc.* The above-mentioned all-valence semiempirical methods, unlike the PPP method with adaptation of parameters, use unique sets of parameters for all molecular systems. Therefore, they are, in general, less accurate in prediction of electronic transition energies, especially for large molecules. The fact that the PPP approach used deals with different sets of parameters for different kinds of molecules reduces the predictive power of the method. However, it gives an opportunity to reproduce in many cases real absorption wavelengths of rather complicated organic compounds within minimal CI both without use of any combination of single and double configurations selected on the basis of some threshold criteria with the possibility of making additional corrections due to excluded configurations by means of the perturbation theory [106], and without explicit consideration of medium effects.

It is necessary to note that on calibration, the parameters become somewhat (in the cases of benzoic acid, aniline, phenol, furan - by 3-5 eV) greater compared to the original ones. That should lead to the undesirable enhancement of energies of the excited states disposed higher than the first one. Being within the framework of the formulated problems, the aforesaid seems appropriate.

The methods of the third group seem to have some advantages at present, in the cases when the quantitative reproducing of any characteristics (in particular, a wavelength in electronic spectrum, which is necessary, for example, at chemical substances identification) is aimed. For indirect confirmation of structure of reaction products, especially for those which can not be isolated and characterized by means of IR, NMR, mass-spectrometric, X-ray and other investigations, computations of electronic spectra and comparison with experiments are expedient. Detailed analysis of energetics and nature of molecular systems stationary states, the establishing of the corresponding regularities in the series of compounds and solvents, require the methods belonging to the first or the second group.

Further, we mention some other interpretational tasks of chemistry which we have dealt with.

Basing on the analysis of comparative thermodynamic stability of various configurations, the consideration of experimental and computed dipole moments, the allowance for polarity of medium, it has been concluded that the molecules $(C_6H_5)_3AsCl_2$, $(C_6H_5)_3SbCl_2$, $(C_6H_5)_3Sb(OH)Cl$, $(C_6H_5)_3BiCl_2$, $(C_6H_5)_3Bi(ONO_2)_2$ exist as solutes in the form of trigonal bipyramid with two axial inorganic ligands [25, 33, 35]. An example has been displayed on Figure 36.

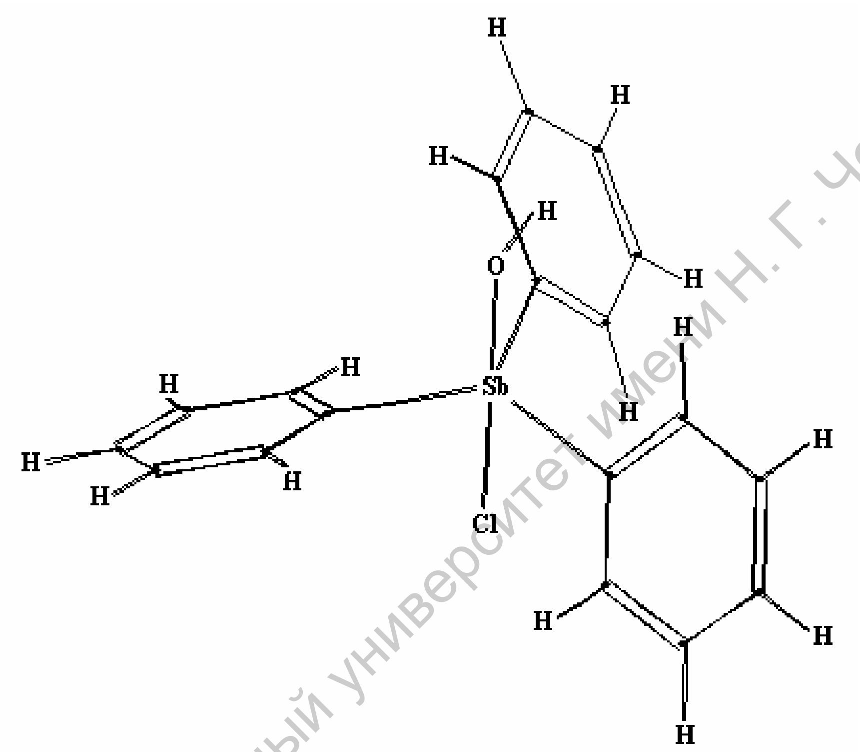
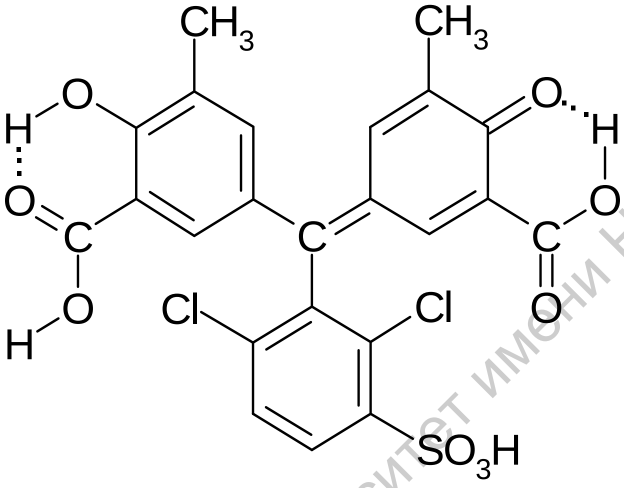


Figure 36. Optimal configuration and conformation of triphenylstibinehydroxychloride $(C_6H_5)_3Sb(OH)Cl$.

It has been established that in gaseous phase and aqueous solution, the most thermodynamically stable tautomer of 2-pyrrolidone is lactam. According to quantum chemical evaluatons with an explicit account for aqueous medium, the state of tautomeric equilibrium serves as a prerequisite to participation of 2-pyrrolidone's lactim tautomer (pyrroline-2-ol) in complexation with palladium (II) in aqueous solution. 2-Pyrrolidone protonation in gaseous phase and aqueous medium has been shown to proceed *via* oxygen atom, that corresponds to knowledge on mesomeric displacement of electron density in amide fragment. Aqueous medium stabilizes 2-pyrrolidone's lactim tautomer to the greater extent compared to lactam, and O-protonated cyclic amide compared to N-protonated one. Stereodirective character of palladium (II) complexation with chloride ion and pyrroline-2-ol has been explained. The initially formed tetragonal-pyramidal adduct with axial organic ligand then regroups into precursor of *cis* product - intermediate with extracoordinated axial chlorine atom. Less thermodynamically stable *cis* isomer of the complex $[PdCl_2(Prol)_2]$ (Prol = pyrroline-2-ol) appears due to the fact that its structural precursor is the most preferable, in respect to energy, intermediate of associative nucleophilic substitution. At a supermolecular level, *cis* product is capable of being stabilized by means of intermolecular dipole-dipole association in a crystal [107]. The said reaction stereoselectivity treatment is of importance, since namely *cis* complexes of palladium (and also platimum) show pronounced antitumour activity.

Spatial and electronic structure of the molecules of aluminon, chromoxane violet B, chromoxane purely-blue B, eryochrome cyanine R, sulphochrome, chromazurol S



Chromazurol S

was considered. In the context of the analysis of electrostatic potential (ESP) of the reagents molecular systems, primary dissociation of carboxylic group in *ortho* carboxyphenolic ring was substantiated. The ESP character allowed us to present in more detail the steps of reagents complexing with metals cations at different pH levels. Favourable topology of nucleophilic interaction of non-ionic surfactants' hydroxyethyl fragments with protons of carboxylic and hydroxy groups of phenolcarboxylic acids of triphenylmethane series, serving as a prerequisite to the reagents solubilization in non-ionic surfactants micelles, was shown. Much the same contribution of medium to acid-base properties of phenolcarboxylic acids of triphenylmethane series, that conceives the similar characteristics of hydrophilic and hydrophobic hydration of the molecular systems of reagents and their conjugate bases, was established. The substrate specificity of the reagents chromoxane purely-blue B and chromazurol S to non-ionic surfactants is evidently caused by local properties of chloro substituents and atomic basins in the vicinity of the latter (volume and hydrophobicity of chlorine atom combined with a comparatively high polarity of the C-Cl bonds) [108].

Ab initio, electronic structure of the molecules HOCN, HSCN, HNCO, HNCS and the anions $[OCN]^-$, $[SCN]^-$ has been investigated. The higher thermodynamic stability of the HNCO and HNCS molecules as compared to HOCN and HSCN, respectively, has been shown. The series of the protolytes strength alteration: HSCN > HOCN, HNCS > HNCO, HOCN > HNCO, HSCN > HNCS have been substantiated. The computations taking into account the electronic correlation reflect the general sequence of change in proton-donor properties: HSCN > HOCN > HNCS > HNCO, coinciding with the raw of descending hydrophobicity of the compounds. A higher degree of the stabilization-by-hydration for the oxygen-containing anion compared to the sulphur-containing analog has been confirmed, however, that does not govern the sequence of changes in acidic properties of the different forms of hydrogen oxonitridocarbonate (IV) and hydrogen sulphidonitridocarbonate (IV). Comparative proton-donor ability of the above acids in aqueous solutions is determined basically by the electronic structure and size of their molecules and anions $[OCN]^-$, $[SCN]^-$, but not by the medium effects [109].

Of great inportance in chemistry are reactions involving a step that may be conceived formally as hydride ion transfer [110]. Transformations of 1,5-dicarbonyl compounds and chalcogenopyrans into the mixtures of chalcogenopyrilium salts and chalcogenacyclohexanes or chalcogenopyrilium salts and other reduced products serve as examples [111].

For a wide range of chemical compounds, the following mechanisms of "hydride" transfer are discussed [110].

1. Direct splitting-out of a hydride ion $(-\ H^-)$.
2. Consequent withdrawing of an electron, a proton and yet another electron $(-\ e^- - H^+ - e^-)$.
3. Extraction of an electron and a hydrogen atom $(-\ \bar{e} - H^{\bullet})$.
4. Transfer of a hydrogen atom and an electron $(-\ H^{\bullet} - \bar{e})$.
5. Deprotonation followed by a transfer of two electrons $(-\ H^+ - \bar{e} - e^-)$.

The mechanism of "minus electron minus electron minus proton" $(-\ \bar{e} - \bar{e} - H^+)$ type is not realizable, since there is little likelihood of a dication radical formation.

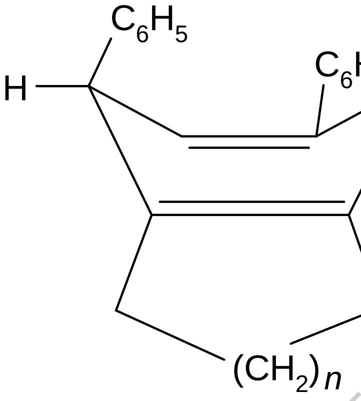
Outside the domain of this discussion, one more mechanism probably exists which involves primary protonation of heteroring and final step of H_2 [112] or another electroneutral molecule [113] liberation. Feasibility of heterocycle protonation at a chalcogen atom has been unambiguously proved in the works by J.B. Lambert and S.I. Featherman [114].

Table 9. Correspondence between steps of "hydride" transfer and reactivity indices describing the above steps

Mechanism	Steps of transfer	To be analyzed	
		Index	For molecular system
1	$BH \rightarrow B^+ + H^-$	*HIA*	B^+
2	$BH \rightarrow BH^{\bullet+} + e^-$	*IP*	BH
	$BH^{\bullet+} \rightarrow B^{\bullet} + H^+$	*PA*	$B^{\bullet}$
	$B^{\bullet} \rightarrow B^+ + e^-$	*IP*	$B^{\bullet}$
3	$BH \rightarrow BH^{\bullet+} + e^-$	*IP*	BH
	$BH^{\bullet+} \rightarrow B^+ + H^{\bullet}$	*HAA*	B^+
4	$BH \rightarrow B^{\bullet} + H^{\bullet}$	*HAA*	$B^{\bullet}$
	$B^{\bullet} \rightarrow B^+ + e^-$	*IP*	$B^{\bullet}$
5	$BH \rightarrow B^- + H^+$	*PA*	B^-
	$B^- \rightarrow B^{\bullet} + e^-$	*IP*	B^-
	$B^{\bullet} \rightarrow B^+ + e^-$	*IP*	$B^{\bullet}$

We have proposed [115] a strategy of the quantum chemical study of “hydride ion” transfer based on the analysis of correspondence of the sequences of changes in ionization potentials (*IP*), enthalpies and free energies of the affinities to hydride ion (*HIA*), to hydrogen atom (*HAA*) and to proton (*PA*) of substrates molecules, as well as their derivatives as cations, cation radicals, radicals, anions, to the experimentally substantiated series of “hydride” mobility (Table 9).

We have shown that for six chalcogenopyrans based on “semicyclic” 1,5-diketones:



X = O, S, Se
n = 1, 2

the experimental series of “hydride” mobility S > O ≈ Se [116-118] is not inconsistent with: i) ionization potentials (*IP*) of the molecules studied; ii) hydrogen atom affinities (*HAA*) of radicals formed by abstraction of hydrogen atom in heterocycle position 4 from the initial molecular systems.

Let us compare that to the data from the Table 9. The *IP* index describes an electron extraction from the substrate’s molecule BH - the first step of the mechanisms 2 and 3. The ejection of a hydrogen atom from the initial molecule BH (the *HAA* value corresponds just to this process) presents the first step of the mechanism 4. Provided that the first step is rate-determining one, the experimental results’ correlation with the ionization potentials implies the mechanisms 2 or 3 realization, and the experiments’ agreement with the radicals $B^\bullet$ affinity to hydrogen atom means the mechanism 4.

Therefore the mechanisms 1 and 5 are to be rejected. The mechanisms 2 to 4 are feasible provided that the first step is limiting one in every case.

Thus, the direct splitting-out of hydride ion and primary deprotonation of substrates followed by two electrons withdrawing have been elucidated to be unlikely. Feasible are the mechanisms of “hydride” mobility, the first step of which consists in electron or hydrogen atom transfer from chalcogenopyrans molecules [115].

The results obtained allow the experimenting researchers to focus their attention on the problem of substantiating the actually possible mechanisms of “hydride” transfer in the chemistry of chalcogenopyrans.

Molecular spatial parameters and polarity of acrylic acid proposed as an additive to methylsilicone OV-1 appear to work well in fitting the corresponding characteristics of stationary phase (SP), that has been proved by quantum chemical computations. The modified SP formed demonstrates a complementary gas chromatographic behaviour in the cases of test hydroxylic compounds used. Using packed columns with OV-1 as a SP certainly modified with appropriate amounts of acrylic acid, a simplified gas chromatographic technique for the rapid determination of benzoic and heptanoic acids directly in aqueous solutions has been elaborated [119].

On the basis of quantum chemical modeling, the interpretation of silica sorption properties has been presented: the most active ion-exchange centres are silanolic groups, but not a mineral structure defect, related to the isomorphous substitution of silicon by aluminum; the closer the defect to the sorbent surface, the more acidic are protons of silanolic groups [120].

A considerable amount of investigations in the area of physical chemistry of morphogenic proteins of higher fungi has been carried out in collaboration with Colleagues from Laboratory of Microbiology and Mycology, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, Saratov, Russia (above all, Senior Researcher Olga M. Tsivileva and the Head of the said Laboratory Professor Valentina E. Nikitina).

The dependence of the extracellular lectin activity of *Lentinus edodes* (Berk.) Sing [*Lentinula edodes* (Berk.) Pegler] and the formation of a pigmented mycelial film in the submerged culture upon the presence of essential amino acids in a synthetic medium has been studied. The pronounced effect of asparagine in the presence of Ca^{2+} or Mn^{2+} cations on the formation of the above vegetative structure has been found. Quantum chemical *ab initio* calculations of the electronic structure of zwitterions of asparagine and its nearest structural analog have been performed. The van der Waals surface and volume of molecular systems, as well as refraction, polarisability and lg$P$ (P is a distribution coefficient in the system of 1-octanol - water) have been computed. On the basis of the research carried out, the supposition was made that the different character of the interaction of amino acids with the aforementioned ions is due to differences in the hydrophobicity (lipophilicity) of the amino acids rather than to differences in the electronic structure of the amino acids zwitterions [121, 122].

The activity of extracellular lectins of the basidiomycete *Lentinus edodes* (Berk.) Sing [*Lentinula edodes* (Berk.) Pegler] has been shown to be related to the presence of definite double-charged metal cations in the synthetic liquid medium of cultivation. The effect of Fe^{2+}, Co^{2+}, Ni^{2+} on the lectin activity has been demonstrated to change with a symbate character in respect to the energies of chelating reactions of metals hexaaqua complexes with the model ligand ethylene glycol, computed *ab initio*. At the initial steps of the lectins biosynthesis, the above metals cations exert a much greater influence upon the lectin activity of *Lentinus edodes*, as compared to the results of subsequent interactions between the cations and proteins under study in the culture medium [123].

An invited review [124] in the area of mycology, including our scientific results on quantum chemical interpretations in mycology, has been published.

Within the area of our attention are the classification aspects and the analysis of Web resources, too.

Classing generalizations on reactions in homogeneous and heterogeneous systems (theories of acids and bases, intramolecular factors effecting protolytes strength, types of complex compounds, kinds of co-precipitation, precipitate aging mechanisms) have been drawn [63, 125, 126].

The alternative classification of the methods of quantum chemistry has been proposed [102, 103].

The data on information resources on natural sciences, on ecology, have been systematized and generalized. Information on a large amount of Publishers of scientific literature (publishing houses, scientific institutions and organizations, educational schools, societies, associations, federations, unions and companies) contributing greatly to publishing printed and electronic production, as well as of electronic libraries, search systems, databases and catalogs of natural-scientific and ecological literature, referred to Web-addresses, has been collected. Valuability of the work carried out is high the more so as the sites of a number of publishing houses, search systems, databases, catalogs offer the information search by authors, paper title, name of journal, of book, by research subject, science area, key words, *etc.* Many electronic libraries provide an access to the Publishers Web sites, that facilitates substantially a process of obtaining the detailed information on the corresponding journals (addresses, Editorial Board, aims and scope, audience, subscription information, guide for authors, Copyright information, Tables of contents, abstracts, full text papers, news, *etc.*) on Web sites. The information on status changes for many scientific journals is presented. The creation of journals (newly or on the basis of the old ones), discontinuation of issues, journals incorporation in other ones, combined and divided journals are mentioned [127-130].

In general, the investigations carried out are concerned with a voluminous scope of scientific interests, among which are physical organic, inorganic, organoelement and coordination chemistry, structure and reactivity, quantitative structure - property relationships, reaction mechanisms, medium role in chemical processes, applied quantum chemistry and molecular dynamics, theory of analytical reagents action, hydrogen bond, physical chemistry of morphogenic proteins of higher fungi, Internet in natural sciences and in ecology.

A considerable component of the studies conducted is presented by the methods of quantum chemistry.

The quantum chemical consideration of the chemical problems is not solely the application of powerful up-today research methods. That is also new ideology of chemistry science, its modern language, the achievement of qualitatively distinct, true scientific, *i.e.* predictive, level.

The use of quantum chemical methods combined with the physical, physicochemical, chemical research methods is key for gaining the principally important information on the reactivity, chemical reaction mechanisms, analytical properties of reagents, biological activity of substances, for establishing the prognostic quantitative structure - property relationships.

Theoretical, including quantum chemical, modeling of chemical compounds with virtual testing of their various properties, the study of substances' reactivity, reaction mechanisms in relation to the electronic structure of molecules, render chemistry a predictive science, *i.e.* permit its contemporary level and the trends of development.

Therewith the general (with numerous fine details at closer consideration) methodology of investigations regardless of the essence of subjects (inorganic, organic, organoelement, coordination, high-molecular compounds, including biopolymers, as well as molecular complexes, exciplexes, excimers, overexcited Rydberg molecules of up to 1000 Å sizes, ionic and molecular crystals, clusters (supermolecules, nanostructures), permolecular, supramolecular, surface structures, adsorption, catalytic systems, by-electrode layers, *etc.*), of the structure peculiarities (charge and spin multiplicity of the molecular system, ground and excited electronic, vibrational, rotational and other levels), of the types of interaction in molecules or between them (electrostatic, van der Waals, "guest - host", hydrophobic, chemical), of the character of chemical bond (ionic, covalent, donor-acceptor, hydrogen, dative, agostic, metallic; banana, multicentral, interstitional; two- and three-dimensional electronic delocalization [131]; aromaticity and related phenomena, including antiaromaticity, quasiaromaticity, or non-classic aromaticity, heteroaromaticity, homoaromaticity, Y-aromaticity, spiroaromaticity, bicycloaromaticity and bicycloantiaromaticity, intra-plane, or radial, aromaticity, cross-aromaticity, metalloaromaticity, three-dimensional, in plane, spherical aromaticity, σ-aromaticity and σ-antiaromaticity [132], superaromaticity, induced aromaticity [133]), of aggregation state, of a type of solvation (universal, specific), demonstrates the universality of chemistry (and quantum chemistry) as a science.

Quantum chemistry is as unbounded and inexhaustible as the whole chemistry, equally as the surrounding reality, just reflected in chemistry science. It is not accident that the specialists have troubles understanding their colleagues working in different branches of quantum chemistry and its applications. So, the researcher solving a wide set of interpretation tasks with the use of quantum chemical methods, does not rank below the scientist who use a combination of different experimental methods, in multilateralism and variety of aspects of his scientific activity.

Nevertheless, along with the inevitable differentiation and divergence rising from the variability of subjects under investigation and of special approaches to their description, high integration potential occurs in quantum chemistry alike in the whole chemistry, the basis for which being underlined by the unique chemical form of the matter movement and, as a consequence, the unified general methodology of the matter knowledge.

The information potentialities of quantum chemical methods (even taking into account the restrictions, which are well-known and allow evaluations of the computations accuracy) are essentially greater, than of the experimental ones [134].

Quantum chemical computations enable one to determine simultaneously the assemblage of principal characteristics of molecules and substances, which can not be extracted from any experimental method [134]. Among the above properties are geometry, symmetry point group, electron density distribution (including charges on atoms, bond orders) (for the systems with open shells - also spin density distribution), topology of electron density (bond path, location of bond critical point, electron density in the latter, Laplacian of the above value, ellipticity, other parameters of AIM-analysis), dipole, quadrupole, octapole, hexadecapole moments, polarisability, hyperpolarisabilities, composition, hybridization, population, symmetry and energies of molecular orbitals, characteristics of natural bond orbitals (NBO), superdelocalisabilities, electrostatic potential of molecule, total energy, thermodynamic functions and their components, heat of formation, entropy, free energy of formation, proton affinity, ionization energy (potential), electron affinity, rotational constants, frequencies and intensities of bands in vibrational spectra, wavelengths and oscillator strengths of bands in electronic spectra, chemical shifts and spin-spin coupling constants in NMR spectra of various nuclei, parameters of NQR and Mössbauer spectra, hyperfine constants in EPR spectra, *et al.* By means of quantum chemical methods, the data of X-ray and ultraviolet photoelectron spectroscopy, Auger spectroscopy, mass spectrometry, gas electron diffraction, *etc.*, are interpreted.

On the basis of quantum chemical considerations, one could judge on the reactivity of different positions of molecules in the charge-controlled and frontier-controlled processes, when the reaction rate is determined by the charges on atoms and the electron density of frontier orbitals, respectively. There is a possibility to reveal the character of chemical bonds, different intra- and intermolecular interactions, charge transfer, to calculate the thermodynamic parameters of reactions, to compute the transition states, to evaluate the reaction barriers, to study the topology of potential energy surface and to construct the reaction paths. Along with the aforesaid, the effect of medium on all the calculated characteristics becomes possible to be taken into account.

The information provided by the quantum chemical methods is substantially multidimensional. In this sense, among the experimental methods, approaches and techniques, those are only partially similar to the Hyphenated Techniques created on the basis of methods of separation and diagnostics.

Sometimes [134] the quantum chemical methods are referred to as being comparable with NMR in their information-supply ability. As Professor Boris A. Ershov (Faculty of Chemistry, St. Petersburg State University) tells, “NMR could make everything”.

Like any science and methodology, quantum chemistry encounters problems in connection with both its own internal development and application of the corresponding methods.

Nevertheless, in the same sense as for NMR, the quantum chemistry should be referred to as capable of “making everything” even more reasonably at present. There are no doubts that quantum chemistry will answer any challenge and will overcome possible difficulties at the steps of further development.

Quantum chemistry determines, to a considerable extent, a progress of the whole chemistry as a science, which moves in the course of its development toward the sophistication of both the research methods (physical, mathematical ones) and the subjects mentioned above, the contemporary knowledge of the chemistry of the latter being impossible without the quantum chemical treatment.

For realizing the quantum chemical methods, any unambiguous and unclear-in-sense constants are not required usually. The methods of quantum chemistry ([2, 86, 105, 134-144] *et al.*) either do not use the postulates outside the scope of fundamental points, principles and mathematical tools of quantum mechanics, theoretically substantiated approximations of quantum chemistry (adiabatic, single-electron, MO LCAO), procedures for taking into account the relativistic, non-adiabatic effects and electron correlation, strict rules of composing the basis sets (*ab initio*), or exploit the simplified non-empirical schemes involving the effective core potential (ECP), or pseudopotential (ECP method), or use the reasonable approach of zero differential overlap, consider in the explicit form the valence electrons only, and introduce the parameters, which already prove their efficiency for predicting different properties (semiempirical ones). Besides, the parameters could be fitted for solving the given problems (*e.g.*, [102, 103]). The promising package of essentially hybride methods, that combines the strict non-empirical computations with the semiempirical account for the electron correlation energy, is based on the Density Functional Theory (DFT) [138]. For computing the large systems, including high-molecular compounds, biopolymers, the approaches QM/MM and ONIOM have been developed [139]. The principally novel general avenue of inquiry in computer-assisted quantum chemistry, compared to the methods MO and VB, free of requiring computational mega resources, is presented by the method of multiparticle wavefunctions using the hypothesis of equipotential surfaces prohibition (Professor Eugeny A. Smolenskii and Professor Nickolai D. Chuvylkin, N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow) [137, 140-144]. The aforesaid does not exhaust the variety of methods and approaches of the current quantum chemistry.

The experience shows that commonly the properly selected semiempirical methods, provided that each of those corresponds to a sufficiently adequate model of definite-kind-molecules and describes a part of molecular properties, are not worse, in respect to efficiency, than one complicated method. That obeys the law of technical systems development: the efficiency of instrument increases with the increase in degree of its narrow specialization.

Up to the present, for solving the numerous interpretational problems of chemistry, the semiempirical quantum chemical methods hold true an importance.

Their use with respect to "classical" systems may be tolerated provided that those are capable of explaining and predicting the most important features of structure and reactivity of large molecules, macromolecules, periodic structures, crystal lattices, aggregates of molecules, clusters, therewith capable also of reproducing the physicochemical properties of molecular systems (microspecies) and substances (assemblages of microspecies) from the test-kit. At least for the preliminary estimations followed by the considerations at a higher level of theory, their application is encouraged.

The semiempirical methods would apparently find their further application for modeling the specific and non-specific solvent effects, as well as for computation of electronic spectra when it is necessary to involve thousands or even millions configurations to CI.

In order to justify the economical reasoning and expended time required for the establishment of predictive quantitative structure - property relationships aimed at the molecular design of chemical compounds, such the relationships should be obtained sufficiently simply and fast, and in this respect semiempirics also finds its "niche".

At the same time, for studying the electronic structure of molecular systems in fine detail, the electronic effects in molecules, the nature of chemical bonds, dispersion and other weak interactions, adsorption, catalysis, for analyzing the potential energy surfaces of the majority of reaction types, the *ab initio* and DFT methods are required. Moreover, these methods allow the highly-precise simultaneous computations for the whole complex of properties to be done. As applied to "non-classical" systems (with non-standard stereochemistry, hypercoordination, *etc.*), the use of sophisticated approaches for solving any problems necessitating the quantum chemical consideration, is alternativeless.

As for the term "non-classical systems", *e.g.*, for the organic compounds, non-classical structures are defined according to the presence of non-tetrahedral tetracoordinated or/and hypercoordinated carbon atoms in their molecules or ions [145, 146].

The future of applied quantum chemistry may undeniably lie with the rigorous, sophisticated methods. A considerable progress in solving the various problems of chemistry, biology and interdisciplinary areas at high level of theory (*ab initio*, DFT) will be favoured by the further development of computing devices, including the improvement of workstations-supercomputers, fast-operating clusters, which realize the distributed parallel computations, as well as by a probable appearance, within near-future, of the quantum computers with an about terabyte memory and a rate of data transfer at a gigabyte level.

It should be remembered, however, that the appearance, development and fruitfulness of the semiempirical methods of quantum chemistry follow inevitably from the fundamental principle of complementarity (Niels H.D. Bohr), in consequence of which the clarity of knowledge and description of the molecular objects properties is accomplished by means of model insight and imagines [147].

Ab initio computational methods are not in fact deduced completely "from the first principles", but are also essentially semiempirical, the empirics being transferred to the level of basis choice [147]. The empirics is intrinsic, even to a greater extent, in hybrid DFT methods, that are not at a disadvantage in relation to *ab initio* and often superior in their potentialities.

No the most perfect experimental and theoretical methods allow one to overcome the accuracy limits of determination of molecules' parameters: 10^{-2} Å for the geometric parameters, 2-3 degrees for valence angles, $(2\text{-}3)\cdot10^{4}$ cm^{-2} for force constants [147]. An experience of *ab initio* computations application in molecular spectroscopy has shown that the resulting values of parameters could be used only as the initial approximations to be refined by means of the inverse tasks [147].

As Professor Lev A. Gribov (V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow) [148] notes, semiempirical and *ab initio* approaches and methods are not mutually exclusive, but complement each other, and the most rational avenue of the further development of quantum chemistry lies in searching a "golden middle".

In our mind, the latter would be achieved on solving the interpretational chemical problems (including those described in the present chapter) by means of the quantum chemical methods provided that: i) the methods of different hierarchy and theory level are adequate to the problems to be solved; ii) the hybrid methods of Density Functional Theory (DFT) are used.

As for solving the given scientific problems requiring the quantum chemical methods application, so the most intriguing and promising results should be expected within the interdisciplinary areas of science, when the work is conducted in cooperation, by theoretically- and experimentally-oriented researchers (spectroscopists, electrochemists, photochemists, radiochemists, plasmachemists, cryochemists, syntheticians, analyticians, material scientists, astronomists, astrophysicists and cosmochemists, geochemists and geologists, lithologists, hydrologists, oceanologists, limnologists, agrochemists, soil scientists, biochemists, enzymologists, immunochemists, biophysicists, biologists, microbiologists, biotechnologists, pharmaceuticians, pharmacologists, toxicologists, medicians, ecologists, specialists in stereochemistry, structural chemistry, thermodynamics, phase equilibria and transitions, kinetics, chemistry of combustion, shock compression, detonation and explosion, chemistry of high energies and extremal attacks (reactions in plasma, in the course of photolysis and radiolysis, under the action of shock waves, of high temperatures and pressures, of electric and magnetic fields, in electric discharge, under the electro thermal conditions, under the effect of high-frequency electromagnetic vibrations, ultrasound, electrohydraulic hammer, *etc.*), in catalysis, solution chemistry, physics and chemistry of disperse systems, condensed states, in surface phenomena, topochemistry, physics of semiconductors, dielectrics, segnetoelectrics, piezoelectrics, ferromagnetics, auxetics, supercritical and non-Newton fluids, in the problems of superfluidity and fermionic condensates, Bose - Einstein condensates, supersolids, high-temperature superconductivity, in magnetochemistry, dielectrometrics, optics, laser chemistry, electrooptics, acoustooptics, electronics, spintronics, optoelectronics, photonics, vacuum engineering and instrumentation, photographic chemistry, chemistry of crystals and crystallography, mineralogy, physics and chemistry of surface, films and coatings, adhesion, corrosion and protection against it, mechanochemistry and rheology, tribochemistry and tribology, sonochemistry, electrohydraulic effect, radiation and nuclear chemistry, biophysical chemistry, molecular biology, bionics, genomics, transcriptomics, proteomics, metabolomics, in environmental science, in extraction, flotation, adsorption and sorption at all, ion exchange, chromatography, diffusion, electromigration, membrane processes, chemical engineering, metallurgy, powder technique, welding, nanochemistry and nanotechnology, chemical and electrochemical energetics, including chemical, biochemical current sources and energetic substances, diffraction and ionization research methods in chemistry, *etc.*).

Therewith the peculiarities of experimental methods, the data of which are subject to treat by means of quantum chemistry, should be taken into consideration.

Every physical method has its own characteristic time.

Besides, the methods of direct determination of the molecules geometry (X-ray structure analysis, neutron diffraction, gas electron diffraction, microwave spectroscopy) yield, strictly speaking, values of spatial parameters different-in-sense (distinct are r_e-, r_0-, r_z-, r_s-, r_g- and another types of structures) [149].

How should the data from different physical methods be adjusted to a unified basis, and what could the values computed by the quantum chemical methods be referred to?

As seen from the list of scientific fields presented above, the quantum chemistry is applicable for interpreting the results of experimental studies and for prognosis at both microscopic and macroscopic levels.

One could separate the following approaches to the quantum chemical description of processes and phenomena capable of being registered at a macroscopic level [2, 86, 105, 135, 136].

1) Heats [136] and free energies of formation, heat capacities, entropies are inherent to the assemblages of species. However, the semiempirical methods of quantum chemistry estimate these quantities with a rather well accuracy, considering the isolated molecules [136]. That is related to the compensation for the affecting leap “molecule - assemblage of species” by means of the appropriate parameterization. For instance, the formula for heat of formation is contributed from the enthalpies of atoms formation - the values gained from experiments [150]. The relevant expressions have been also chosen for computing the potentials of core-core repulsion [150].
2) For improving the adequacy of models underlying the basis of quantum chemical computations, the latter are performed not for the separate molecules, but for voluminous clusters (supermolecules, nanostructures), to simulate the real or near-real state of substance.
3) The alternative to the second approach is indirect account for surrounding within the framework of continuum models.
4) There are discrete-continuum approaches involving the essential features of the points 2 and 3.

Presented above are the examples of all the four mentioned approaches realization.

We believe that the development in the century XXI lies ahead primarily in the fields among which are computer-assisted chemistry (quantum chemistry, molecular dynamics, molecular design), the study of mechanisms of chemical and electrochemical reactions in inorganic and organic chemistry, chemical material science, ecological chemistry [151]. Our assessments coincide sometimes with the commonly accepted ones. Thus, in questionnaire [151], the first ten of scientists-chemists of the century XX included John A. Pople, who was soon awarded (along with Walter Kohn) with Nobel Prize-1998 in chemistry [152] for a fundamental contribution to the development of quantum chemical methods. The Nobel Prize-1999 in chemistry was gained by Ahmed Zewail for his fundamental works in the field of femtochemistry, that open up possibilities for studying the course of reactions in real-time mode, for obtaining the direct information on the transition states, for providing the selectivity of yields of the desirable reaction products [153].

The further development of the scientific avenue discussed in this chapter is planned as being related to the studies of fine peculiarities of the molecules electronic structure, the reactivity in chemistry and biology, the mechanisms of action of analytical reagents, the molecular drug design. Therewith in accordance with the whole-world tendency, the role of the *ab initio* and DFT quantum chemical methods increases, the same is true for molecular dynamics, QSAR (QSPR) modeling, molecular docking, *de novo* design.

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