

## Electronic structure of planar-quasicycled organic molecules with intramolecular hydrogen bond

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**Abstract:** By means of the HF/6-311G(d,p) method, the electronic structure of the series of organic molecules, among which are malonaldehyde, acetylacetone, thiomalonaldehyde, the derivatives of aniline 2- $\text{XC}_6\text{H}_4\text{NH}_2$ , phenol 2- $\text{XC}_6\text{H}_4\text{OH}$ , benzenthio 2- $\text{XC}_6\text{H}_4\text{SH}$  ( $\text{X} = \text{CHO}, \text{COOH}, \text{COO}^-, \text{NO}, \text{NO}_2, \text{OH}, \text{OCH}_3, \text{SH}, \text{SCH}_3, \text{F}, \text{Cl}, \text{Br}$ ), 8-hydroxyquinoline, 8-mercaptoquinoline, tropolone, has been studied. The intramolecular hydrogen bond (IHB) has been established to lead to a local electron redistribution in quasicycle, and primarily to the electron density transfer between the direct IHB participants – from the hydrogen atom toward the proton-acceptor atom. On forming the IHB of the S–H $\cdots$ O type, the electron density in general decreases on the sulphohydril hydrogen atom and increases on the sulphur atom.

**Keywords:** intramolecular hydrogen bond, electronic structure, organic compounds with planar quasicycle, quantum chemical *ab initio* study, dipole moment.

### INTRODUCTION

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.<sup>1–10</sup> 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,<sup>1,4,5,8,9,11</sup> being promising building blocks for constructing the supramolecular structures with the specific receptor properties. For the planar quasicyclic systems, the

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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 isomer 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 interaction being the same as those in the molecule with IHB.<sup>12,13</sup>

The aim of the present work consists in obtaining the direct information about the IHB effect on the electronic structure of molecules by means of quantum chemical study of the electron density redistribution in the molecules when forming IHB.

Using as the reference objects (for comparison) the conformers with a 180°-rotation of the X–H bond in respect to the rotamers with a hydrogen-bonded quasicycle, as well as the corresponding *para* isomers, we have studied the IHB effect on the electronic structure of molecules with planar quasicycle, as well as the corresponding *para* isomers. For the substituted anilines, *para* isomers are the only available reference compounds. In the case of other compounds the regularities of the IHB influence on the electronic structure have been stated using more adequate references – rotamers.

#### COMPUTATIONAL METHOD

The quantum chemical computations were performed *ab initio* by the Hartree – Fock (HF)<sup>14</sup> method with the 6-311G(d,p) basis set<sup>15,16</sup> using the program from the Hyper Chem package [HyperChem (TM), Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA] with the complete geometry optimization (Polak – Ribiere conjugate gradient algorithm).<sup>17</sup> That theory level (HF/6-311G(d,p)) is sufficient for the overview of tendency in electron density redistribution on the IHB formation in the series of compounds. Such a statement is confirmed by the computations at higher theory levels for 8-hydroxyquinoline<sup>18</sup> and 8-mercaptoquinoline.<sup>19</sup>

#### RESULTS AND DISCUSSION

The objects of investigations (Fig. 1) were:

1. Malonaldehyde (**I**) and acetylacetone (**II**) in the enolic form, thiomalonaldehyde (**III**) in the thioenolic form.

2. The derivatives of aniline 2- $\text{XC}_6\text{H}_4\text{NH}_2$ : 2-aminobenzaldehyde (**IV**, X = CHO), 2-aminobenzoic (anthranilic) acid (**V**, X = COOH), 2-aminobenzoate anion (**VI**, X =  $\text{COO}^-$ ), 2-nitrosoaniline (**VII**, X = NO), 2-nitroaniline (**VIII**, X =  $\text{NO}_2$ ), 2-aminophenol (**IX**, X = OH), 2-methoxyaniline (*ortho*-anisidine) (**X**, X =  $\text{OCH}_3$ ), 2-aminobenzenethiol (**XI**, X = SH), 2-methylmercaptoaniline (**XII**, X =  $\text{SCH}_3$ ), 2-fluoroaniline (**XIII**, X = F), 2-chloroaniline (**XIV**, X = Cl), 2-bromoaniline (**XV**, X = Br).

3. The derivatives of phenol 2- $\text{XC}_6\text{H}_4\text{OH}$ : 2-hydroxybenzoic (salicylic) aldehyde (**XVI**, X = CHO), 2-hydroxybenzoic (salicylic) acid (**XVII**, X = COOH), salicylate anion (**XVIII**, X =  $\text{COO}^-$ ), 2-nitrosophenol (**XIX**, X = NO), 2-nitrophenol (**XX**, X =  $\text{NO}_2$ ), 1,2-dihydroxybenzene (pyrocatechol) (**XXI**, X = OH), 2-methoxyphenol (guaiacol) (**XXII**, X =  $\text{OCH}_3$ ), 2-hydroxybenzenethiol (**XXIII**, X = SH), 2-methylmercaptophenol (**XXIV**, X =  $\text{SCH}_3$ ), 2-fluorophenol (**XXV**, X =

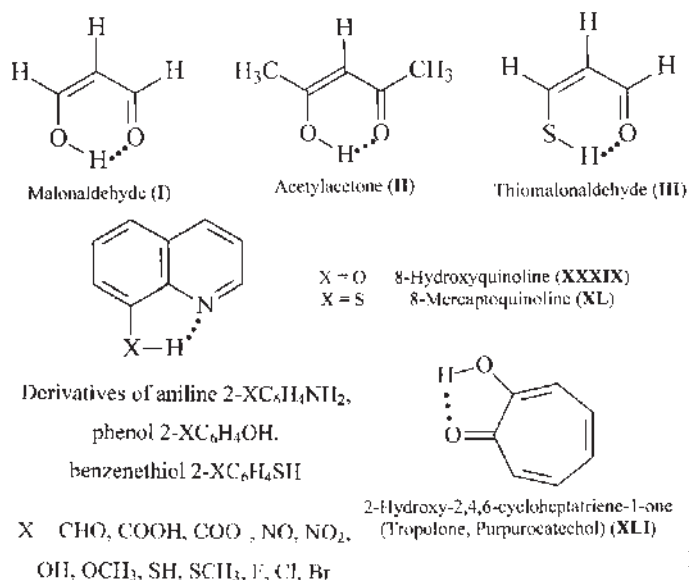


Fig. 1. Objects under study.

F), 2-chlorophenol (XXVI, X = Cl), 2-bromophenol (XXVII, X = Br).

4. The derivatives of benzenethiol 2- $\text{XC}_6\text{H}_4\text{SH}$ : 2-mercaptobenzoic (thiosalicylic) aldehyde (XXVIII, X = CHO), 2-mercaptobenzoic (thiosalicylic) acid (XXIX, X = COOH), thiosalicylate anion (XXX, X = COO<sup>-</sup>), 2-nitrosobenzenethiol (XXXI, X = NO), 2-nitrobenzenethiol (XXXII, X = NO<sub>2</sub>), 2-methoxybenzenethiol (XXXIII, X = OCH<sub>3</sub>), 1,2-dimercaptobenzene (dithiocatechol) (XXXIV, X = SH), 2-methylmercaptobenzenethiol (XXXV, X = SCH<sub>3</sub>), 2-fluorobenzenethiol (XXXVI, X = F), 2-chlorobenzenethiol (XXXVII, X = Cl), 2-bromobenzenethiol (XXXVIII, X = Br).

5. 8-Hydroxyquinoline (XXXIX), 8-mercaptoquinoline (XL).

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

The charges on atoms of the molecular system I-XLI, with IHB as well as of the reference compounds (another conformers of the molecules and the corresponding *para* isomers), were obtained within the framework on the analysis of orbital occupancies by Mulliken.<sup>20</sup>

The electron distribution in molecule defines its dipole moment. Therefore, the correctness of the results of our quantum chemical computations is indirectly confirmed by the good reproduction of experimental dipole moments of molecules of the studied and reference substances (Fig. 2). Even for the so exotically constructed compound as tropolone XLI, the value of dipole moment we calculated, 3.608 D\*, agrees with the value of 3.71 D measured by the second Debye method in benzene at 25 °C with the data extrapolation to the infinitely low concentration.<sup>21</sup>

Moreover, the relationship between the experimental and computed values of dipole moments is of linear character: the number of compounds  $m = 38$ ,  $\mu_{\text{exper}} =$

\* To obtained the values in Cm multiply by  $3.33564 \times 10^{-30}$ .

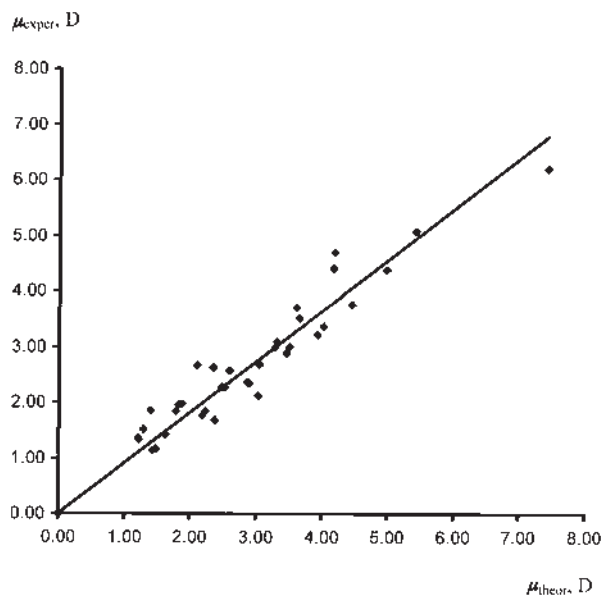


Fig. 2. Dependence between the experimental and computed values of the dipole moments.

$b\mu_{\text{theor}}$ , where  $b = 0.9111 \pm 0.0374$ , therewith the correlation coefficient is sufficiently high:  $r = 0.9601$ . The correlation equation obtained could be used for evaluating *a priori* the dipole moments in the cases, when the experimental estimation is complicated, as well as for predicting the dipole moments of molecules of the compounds not synthesized yet.

The analysis of the results obtained has allowed to formulate the following tendencies of the IHB effect on the electronic structure of molecules.

1. In the molecules of 2-nitroaniline **VIII**, 2-methoxyaniline **X**, 2-aminophenol **XIV** and 2-methoxyphenol (guaiacol) **XXII**, IHB leads to the electron density transfer between the direct participants of binding, *i.e.*, from the mobile hydrogen atom toward the proton-acceptor oxygen atom. In the same group of compounds is 2-methylmercaptobenzenethiol **XXIV**, where on the IHB formation, the charge on proton-acceptor sulphur atom decreases by 0.043 (24.6 %) compared to the conformer without IHB.

2. In the system, **I**, **II**, **IV–VII**, **XV–XXI**, **XXV–XXVII**, **XLI** on the IHB formation, the local electron redistribution in quasicycle takes place (Fig. 3 serves as an example). Therewith, analogously, to Paragraph 1, the electron density is transferred from the hydrogen atom to the acceptor atom – IHB participant. The exception is 2-fluorophenol **XXV**, in the molecule of which the charge on mobile hydrogen atom remains practically unchanged on forming IHB, whereas the negative charge on fluorine atom increases by 0.021 (6.84 %). In the molecule of malonaldehyde **I** enolic form, on forming IHB the negative charge on carbonyl atom of oxygen increases considerably (by 0.088, or 22.1 %).

The IHB formation in the molecules of 2-aminobenzaldehyde **IV**, 2-amino-

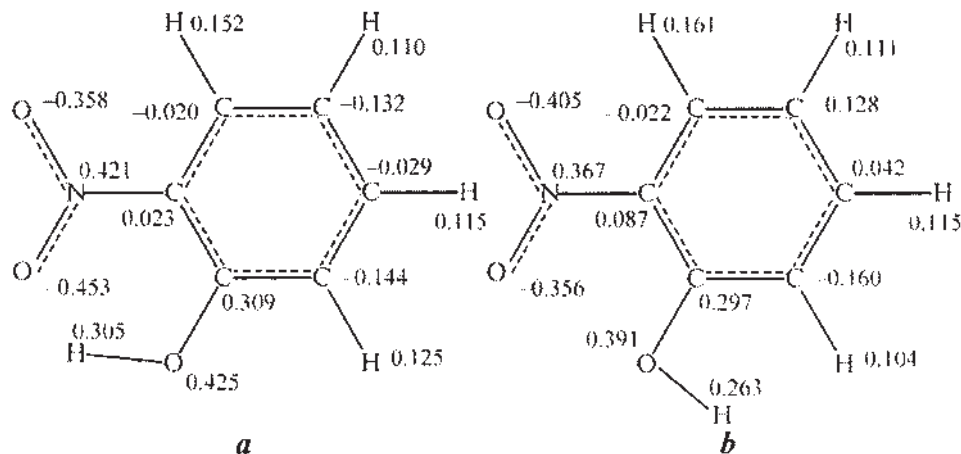


Fig. 3. Charges on atoms in the molecule of 2-nitrophenol **XX**: *a*-conformer with IHB, *b*-conformer without IHB.

benzoic acid **V**, 2-aminobenzoate anion **VI**, 2-nitrosoaniline **VII** and 2-nitrophenol **XIX** is accompanied by the electron density flow from the NH proton toward the atoms of amine nitrogen and oxygen, as well as from the carbon atom (nitrogen of nitroso group) toward the oxygen atom within the carbonyl (carboxylate) group or nitroso group.

Because of the IHB formation in 2-bromoaniline **XV**, the negative charge on nitrogen atom becomes 0.068 (11.7 %) lesser (in comparison with the *para* isomer). Similarly to that, in 2-chlorophenol **XXVI** the negative charge on chlorine atom increases by 0.041 (83.7 %); greater by 0.036 (13.9 %) becomes the negative charge on carbon atom bound to chlorine (as compared with the conformer without IHB). In the molecule of 2-bromophenol **XXVII** in going from the conformer without IHB to the hydrogen-bound rotamer, the negative charge on bromine atom increases by 0.039 (433 %).

In the molecules **XVI–XVIII**, **XX**, **XXXIX–XLI**, the electron density transfer from the hydrogen atom involved in IHB to the both heteroatoms (the atom carrying this proton and the atom – acceptor of proton in IHB) is observed. Therewith for salicylic aldehyde **XVI**, the increase in positive charge on carbon atom of the aldehyde group and in negative charge on carbon atom bound to it is peculiar. In salicylic acid **XVII** on forming the IHB, the polarization of C=O bond and the increase in negative charge on the carbon atom bound to carboxyl group take place. Salicylate anion **XVIII** is characterized by the polarization of carboxylate group bonds when IHB is formed. Both the positive charge on carbon atom at the *ipso* position in respect to OH group, and the negative charge on C-atom bound to the COO<sup>-</sup> group, increase. In the case of 2-nitrophenol **XX**, the general tendency described in Paragraph 2 of electron density redistribution in quasicycle, does not refer to carbon atom bound to the carboxyl group. In the molecule of pyrocatechol

**XXI** on forming IHB, the increase in negative charge by 0.060 (13.8 %) and the proton-acceptor atom of oxygen occurs. For 8-hydroxyquinoline **XXXIX**, the principal change in electron distribution is on nitrogen atom, the negative charge on which increases by 0.093 (24.0 %). In the molecule of 8-mercaptoquinoline **XL**, the most remarkable electron density redistribution is within the SH group, according to the Paragraph 3. As for the molecules **XXXIX**, **XL**, the tendencies in IHB effect on the electron structure of molecules revealed in the present work coincide with those found at the higher theory levels: B3LYP/6-31G(d,p), B3LYP/6-31+G(2d,2p), B3LYP/6-311++G(d,p), MPW1K/6-31+G(2d,2p), MPW1K/6-311++G(d,p), MPW1K/6-311++G(2d,3p)/MPW1K/6-311++G(d,p), BH&HLYP/6-311++G(d,p), G96LYP/6-311++G(d,p), including the use of natural bond analysis (NBO).<sup>18,19</sup> The latter testifies to the correctness of the results of the present work.

3. Provided that IHB forms with a participation of the S–H bond in the molecules **III**, **XXIII**, **XXVIII–XXXII**, **XXXVII**, **XXXVIII**, the electron density is transferred mainly within the S–H group from the hydrogen atom toward the sulphur atom (in Fig. 4 an example is presented).

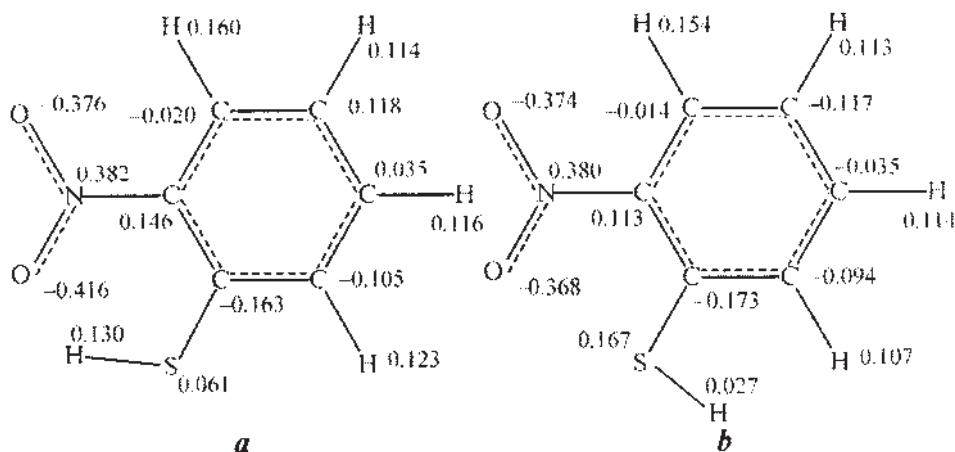


Fig. 4. Charges on atoms in the molecule of 2-nitrophenol **XXXII**: *a*–conformer with IHB, *b*–conformer without IHB.

In the case of 2-hydroxybenzenethiol **XXIII**, the latter statement is valid also with respect to the O–H...S IHB. Probably, such character of electron redistribution in sulphur-containing molecules is caused, to the considerable extent, by a high polarizability of sulphur atom.<sup>22,23</sup> Along with the aforementioned general tendency, one could point to the particular peculiarities for some compounds. Thus, in thiosalicylate anion **XXX** on forming IHB, the redistribution of charges in carboxylate group takes place. In the molecule of 2-nitrobenzenethiol **XXXII**, the charge transfer from SH proton toward the oxygen atom of nitro group occurs; besides, the positive charge on carbon atom bound to nitro group increases. Therefore, the compound **XXXII** can be equally assigned to the group of substances described in the Paragraph 2.

4. In the molecules of 2-aminobenzenethiol **XI**, 2-methylmercaptoaniline **XII**, 2-fluoroaniline **XIII**, 2-chloroaniline **XIV**, 1,2-dimercaptobenzene (dithiocatechol) **XXXIV**, 2-methylmercaptobenzenethiol **XXXV**, 2-fluorobenzenethiol **XXXVI**, the electron density redistribution is not substantial as compared to the reference systems. That is due to the fact that the distance between the acidic hydrogen atom and the proton-acceptor centre (Table I) is close to the boundary distance among a hydrogen bond and a van der Waals interaction.<sup>24–29</sup>

TABLE I. Distances between atoms participating in intramolecular hydrogen bond: computed at the HF/6-311G(d,p) theory level and boundary<sup>24–29</sup> among the specific and van der Waals interactions

Number	Compound	Interaction	Distance/Å	
			Boundary	Computed
<b>XI</b>	2-Aminobenzenethiol	S...H	2.62	2.631
<b>XII</b>	2-Methylmercaptoaniline	S...H	2.62	2.618
<b>XIII</b>	2-Fluoroaniline	F...H	2.24	2.351
<b>XIV</b>	2-Chloroaniline	Cl...H	2.67	2.597
<b>XXXIV</b>	1,2-Dimercaptobenzene (Dithiocatechol)	S...H	2.62	2.509
<b>XXXV</b>	2-Methylmercaptobenzenethiol	S...H	2.62	2.533
<b>XXXVI</b>	2-Fluorobenzenethiol	F...H	2.24	2.341

The results obtained can be discussed in the connection with reactivity of organic compounds in the reactions initiated by electrostatic interaction. Among those are many complexing reactions with a participation of donor oxygen atom of a ligand. From the viewpoint of hard and soft acids and bases concept,<sup>30–32</sup> the oxygen is a hard reactive centre.<sup>22,23</sup>

With the metal cations (hard Lewis acids), the charge-controlled hard–hard interaction is realized. The reactivity indices are therewith the charges on atoms and electrostatic potentials (ESP) of the molecules. The latter is determined by both the electron distribution and the geometry of molecules. On cleavage of the IHB, no substantial change in ESP could occur from the sides of carbonyl and phenolic oxygen atoms – the possible reactive centres of complexing, since in going from one conformation to another, the changes in both the electron distribution and molecular geometry are minimal.

The latter is valid also for the reactions, in the course of which the strong covalent bonds are formed (soft-soft interaction between the metal cations – soft Lewis acids and the sulphur-containing compounds.<sup>22,23</sup> The IHB cleavage does not influence the energy of bond between metal and donor centre.

Therefore, independently on the extent of reactant's restructuring as the reaction proceeds, IHB does not obviously effect on the mechanism of chelation. However, IHB is involved in the energetic effect of the reaction, that is of importance for the aimed design of analytical reagents.



## ИЗВОД

ЭЛЕКТРОНСКА СТРУКТУРА ПЛАНАРНИХ КВАЗИ-ЦИКЛИЧНИХ  
ОРГАНСКИХ МОЛЕКУЛА СА МЕЋУМОЛЕКУЛСКОМ ВОДОНИЧНОМ  
ВЕЗОМ

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Проучавана је електронска структура серије органских молекула, међу којима су малоналдеhid, ацетилацетон, тиомалоналдеhid, деривати анилина 2- $\text{XC}_6\text{H}_4\text{NH}_2$ , фенол 2- $\text{XC}_6\text{H}_4\text{OH}$ , тиобензен 2- $\text{XC}_6\text{H}_4\text{SH}$  ( $\text{X} = \text{CHO}, \text{COOH}, \text{COO}^-, \text{NO}, \text{NO}_2, \text{OH}, \text{OCH}_3, \text{SH}, \text{SCH}_3, \text{F}, \text{Cl}, \text{Br}$ ), 8-хидроксихинолин, 8-меркаптохинолин, трополон. Утврђено је да међумолекулска водонична веза (ИВ) води локалној редистрибуцији електрона у квази-цикличном молекулу и то примарно трансферу електронске густине између директних учесника ИВ – од водоничног ка атому протон-акцептора. У формирању ИВ типа  $\text{S}\cdots\text{H}\cdots$ , електронска густина опада водоничном сулфохидрилном атому, а повећава се на атому сумпора.

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## REFERENCES

1. G. C. Pimentel, A. L. McClellan, in *The Hydrogen Bond*, L. Pauling, Ed., W. H. Freeman, San Francisco, 1960, p. 475
2. A. A. Terent'ev, *Thermodynamics of Hydrogen Bond*, Saratov University Press, Saratov, 1973, (in Russian)
3. I. P. Gragerov, V. K. Pogorelyi, I. F. Franchuk, *Hydrogen Bond and Rapid Proton Exchange*, Naukova Dumka, Kiev, 1978, (in Russian)
4. *Intermolecular Interactions: From Diatomics to Biopolymers*, B. Pullman, Ed., New York, 1978
5. *Molecular Interactions*, Vol. 2, H. Ratajczak, W. J. Orville-Thomas, Eds. Wiley and New York, 1981
6. W. Saenger, in *Principles of Nucleic Acid Structure (Springer Advanced Texts in Chemistry)*, C. R. Cantor, Ed., Springer, New York, 1984
7. G. A. Jeffrey, W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991
8. V. M. Bilobrov, in *Hydrogen Bond and Intramolecular Interactions*, V. K. Pogorelyi, Ed., Naukova Dumka, Kiev, 1991, (in Russian)
9. S. Scheiner, *Hydrogen Bonding: A Theoretical Perspective (Topics in Physical Chemistry)*, Oxford University Press, Oxford, 1997
10. R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Clarendon Press, Oxford, 1990
11. Z. Holzbecher, L. Diviš, M. Král, L. Šůcha, F. Vlácil, *Organic Reagents in Inorganic Analysis*, SNTL-Nakladatelství Technické, Literaturní, Prague, 1975, (in Czech)
12. N. G. Golubev, G. S. Denisov, V. M. Shraiber, in *Hydrogen Bond*, N. D. Sokolov, Ed., Nauka, Moscow, 1981, p. 212, (in Russian)
13. A. El-Nahas, K. Hirao, *J. Mol. Struct. Theochem* **459** (1999) 229
14. V. I. Minkin, B. Ya. Simkin, R. M. Minyaev, *Theory of Molecules Structure*, Phoenix, Rostov-on-Don, 1997, (in Russian)
15. J. E. Dennis, R. B. Schnabel, *Numerical Methods for Unconstrained Optimization and Nonlinear Equations*, Prentice-Hall, Englewood Cliffs, New Jersey, 1983
16. A. D. McLean, G. S. Chlander, *J. Chem. Phys.* **72** (1980) 5639
17. R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **72** (1980) 650
18. A. E. Shchavlev, A. N. Pankratov, A. V. Shalabay, *Int. J. Quantum Chem.* **106** (2006) 876
19. A. E. Shchavlev, A. N. Pankratov, A. V. Shalabay, *J. Phys. Chem. A* **109** (2005) 4137



20. R. S. Mulliken, *J. Chem. Phys.* **23** (1955) 1833
21. O. A. Osipov, V. I. Minkin, A. D. Garnovsky, *Reference Book on Dipole Moments*, Vysshaya Shkola, Moscow, 1971, (in Russian)
22. J. E. Huheey, *Inorganic Chemistry. Principles of Structure and Reactivity*, Harper & Row, Publishers, New York, 1983
23. A. S. Dneprovskii, T. I. Temnikova, *Theoretical Bases of Organic Chemistry. Structure, Reactivity and Reaction Mechanisms of Organic Compounds*, Khimiya, Leningrad, 1991, (in Russian)
24. Yu. V. Zefirov, *Zhurn. Obshch. Khimii* **46** (1976) 2636
25. Yu. V. Zefirov, P. M. Zorkii, *Zhurn. Strukt. Khimii* **17** (1976) 994
26. Yu. V. Zefirov, P. M. Zorkii, *Uspekhi Khimii* **58** (1989) 713
27. Yu. V. Zefirov, P. M. Zorkii, in *Problems of Crystal Chemistry*, Issue 9, 1992, M. A. Porai-Koshits, Ed., Nauka, Moscow, 1993, p. 6, (in Russian)
28. P. M. Zorkii, in *Problems of Crystal Chemistry*, Issue 9, 1992, M. A. Porai-Koshits, Ed., Nauka Moscow, 1993, p. 188, (in Russian)
29. Yu. V. Zefirov, P. M. Zorkii, *Uspekhi Khimii* **64** (1995) 446
30. R. G. Pearson, *J. Amer. Chem. Soc.* **85** (1963) 3533
31. R. G. Pearson, in *Theoretical Models of Chemical Bonding*, Part. 2, Z. Maksic, Ed., Springer-Verlag, Berlin, 1990, p. 45
32. P. K. Chattaraj, P. v. R. Schleyer, *J. Amer. Chem. Soc.* **116** (1994) 1067.