

Preface

The nonstereotypical ideas concerning the participation of the carbon pentacoordinated atom in the formation of the specific intermolecular interaction with significantly undivided $2s^2(c)$ electron pairs of carbon atoms ($DAI \rightarrow CH_3-Al = 44.2 \text{ kJ mol}^{-1}$) have been substantiated and the phenomenon of the intramolecular reverse dative bond between carbon atoms of the methyl group of alkyl ligand and the contacting central molecule atom (in the year 1995) led to the grounded refusal from the model of sp^3 hybridization of carbon atoms, proved by the quantum chemical calculations of the methyl compounds of group IV elements. The fourth nonstereotyped idea grounded in the author's works in the period 1969–1972 is in classifying the phase transformations to the chemical processes. The values of enthalpies and entropies of the processes are connected to the number and energies of the bursting specific intermolecular interactions. The theory of alternative character and the necessity of its further development led to the formulation of the grounding of different types of hydrogen bonds and specific intermolecular interactions, and also to the methodology of the thermodynamic calculation of their energies, building on the vaporization enthalpies applicable for all series of organic compounds.

In the monograph “Specific Intermolecular Interactions of Organic Compounds” (Springer, Heidelberg/New York/Dordrecht/London; 2012), a thermodynamic analysis of the different classes of organic compounds and their series, including the ethers, ketones, alcohols, carboxylic acids, aldehydes and complex ethers, saturated and unsaturated hydrocarbons, including isostructural alkyl groups, is performed. It settles the different types of specific intermolecular interactions and hydrogen bonds, forming the networks of interactions in the liquid and crystal conditions. It outlines the theoretical problems, establishes the natural numbers of stabilization of specific interactions and hydrogen bonds, and develops the concept of the extra stabilizing effect of the isostructural methyl group. It resulted in the creation of the united system of consistent, correlated specific interactions and hydrogen bonds reflecting their nature. The development of theoretical ideas of specific intermolecular interactions and hydrogen bonds, based on the four nonstereotypical ideas, continues in the

monograph “Specific Intermolecular Interactions of Nitrogenated and Bioorganic Compounds” (Springer, Heidelberg/New York/Dordrecht/London; 2014).

Types of specific intermolecular interactions of compounds with nitrogenated and bioorganic compounds and including oxygenated hydrocarbon cycle, pentamers heterocycle, oxazoles, isoxazoles and thiazoles, oxazolines, azetidines, and aminoisoxazoles compounds with hexamers heterocycles and their derivatives, as well as compounds with the cycle of 6-caprolactam with one and two carbonyl groups are discussed in 11 of the monograph’s chapters. In the result of the implemented structural energy analysis it was created the unite system of a wide spectrum of the types of specific intermolecular interactions and hydrogen bonds, correctly reflecting their nature, and the energies were obtained and the natural numbers of their stabilization were grounded, which led to the significant development of the intermolecular interactions theory.

All preceding results of the implemented research in the field of the specificity of intermolecular interactions, including organic, nitrogenous, and compounds with two heteroatoms of nitrogen and oxygen in the molecules, provided the success in the problem solving of obtaining the energy value of the peptide hydrogen bond of all substantiated three types and the energy value of all realizing specific interactions in the formed networks in crystalline and liquid structure of peptides. Significant results in this direction are the grounding of the role of the methylene group and the fragment with the larger number of these groups, located between strong acceptors of electron density by the nitrogen atoms and carbonyl oxygen, expressing reduced ability in the formation of specific interaction in comparison with the similar fragment at the terminal part of the chain, and participation of the isostructural methyl group, connected with the marked methylene group, in the distribution of electron density in the molecule and its extra stabilizing effect to the fragment, fringing these isostructural groups, providing the introduction of additive energy contribution to the enthalpy characteristics independently from its number in peptide and protein. The obtained energy values of hydrogen bonds and specific interactions with the fifth coordinated carbon atom of peptides and deputies led to the determination of energy contribution by the conformer of chains and the value of sublimation enthalpies of dipeptide, tripeptide, and tetrapeptide chains of derivative aminoacetic acid, glycine, and L-(d)- α -alanine, aminopropionic acid. In the results, various protein secondary structures with parallel β -sheet and antiparallel β -sheet with all specific interactions and their energies are first presented.

The present book “Specific Intermolecular Interactions of Elementorganic Compounds” accomplishes a “trilogy” dedicated to the development of a theory of specific intermolecular interactions and to enrich the system of specific intermolecular interactions and hydrogen bonds and their energies.

As the result of the implemented thermodynamic analysis of hydrides, alkyls, and alkenes (Chap. 1) of the subgroup elements of boron, nitrogen, selenium, and zinc, the energies of hydrogen bonds were determined, grounded the types of specific interactions, and their energies were obtained. It was shown that these compounds are characterized by the formation of the intermolecular reverse dative

bonds, which influence the change in stability of the specific interaction that is completed at the third carbon atom of the chain of the propyl ligand (Chap. 1). It is reasoned that only the molecule of diphenyl selenide from the series of methylphenyl–selenide–diphenyl selenide–diphenyl diselenide–diphenyl mercury compounds forms, by the two free electron pairs of selenium atom, the two specific interactions and forms one specific interaction with increased stability.

Properties of the silicon and carbon atoms analogous with essentially undivided $2s^2(C)$ and $3s^2(Si)$ electron air causes the similarity in the elements atoms in the manifestation of acceptor and donor properties, forming the hydrogen bonds and specific interactions (Chap. 2). In this connection, in the silane molecules like methane, the shifting of electron density from the hydrogen atom to the silicon atoms is accompanied by the change of differences in its positive charges, causing the formation of four hydrogen bonds $Si-H\cdots H-Si$ while preserving the four-coordinated silicon atom. With a partial substitution of hydrogen atoms in the silane molecule to the methyl, ethyl, propyl, or to the differing alkyl groups in dependence of their location, the stabilizing effect of trans influence takes place. The compounds with propyl and butyl fragments in the molecules of dipropyldi-butylsilane and propyltributylsilane form specific interactions with reduced stability compared to liquid methylpropylsilanes, and the stabilizing effect of the trans influence is within experimental error. A distinctive feature of the molecules of trisilyl of nitrogen main group elements c SiH_3 , an amino group with two or more silicone atoms of the chain, is the formation of a specific interaction with an essentially undivided $3s^2$ electron pair of silicone atom, located in the penta-coordinated condition. The specific interactions formed by the pentacoordinated silicone atom possess increased stability caused by the location of the shifted electron density at the more distant energy level in comparison with carbon. The maximum stability of the specific interaction is reached by the increasing number of silicone atoms of the chain, providing the completion of the influence of the reverse dative bond. According to the results of the implemented thermodynamic analysis of the linear silanes, oxygenated compounds, including methoxy, ethoxy, and propoxy groups, trimethoxy(methylthio)methylsilane, silacyclobutanes, and 1,1-dimethylsilacyclopentane, with benzene ring, decamethylcyclopentasiloxane, and 1,3,7,5,4-pentamethylcyclopentasiloxane, the nature of specific interactions was revealed, their energies determined, as well as that of hydrogen bonds, the natural numbers of stabilization were established, and the system of consistent energy properties was created, reflecting the nature of the organosilicon compounds.

The conducted thermodynamic analysis of the compounds with tetrahedral structure of the molecules of alkyls, alkylhydrides of germanium, tin and lead, and germanium alkyl compounds with the metal–metal bonds (Chap. 3) illustrate the analogue of the interaction with siliconorganic compounds with the corresponding alkyl ligand and practically unchanged energy value of the hydrogen bonds. It is shown that the energy value of hydrogen bonds formed by the hydrogen atom in the trans position has small changes following the substitution of four hydrogen atoms in the compounds of 1,1,2,2-tetramethyldigermane and 1,1,1,2,2-tetramethyldigermane to the methyl groups. The energies were determined of the

specific interactions formed by pentacoordinated germanium atom in liquid triethyl (diethylamino)germane, methylthiogermane, hexamethyldigermoxane and methoxygermane, and ethoxygermanes, with the network of specific interactions and justified the numbers of their stabilization. Due to the obtained energy parameters of specific interactions formed by benzene ring of the crystalline compounds of tetraphenylgermane, tetraphenyltin, and tetraphenyllead, it was reasoned that the interaction of carbon atoms of benzene ring with the element atom with low coordinating ability and low donor properties is accompanied by the reduction of differences in the charges of the carbon atoms and the stability of the formed specific interactions.

It was reasoned that the intramolecular interaction of the reverse dative bond at the sulfur organic compounds with the completion of influence to the stabilization of the specific intermolecular interaction at the propyl ligand of the chain and at the six carbon atoms in the heterocycle. The types of specific interactions and hydrogen bonds were revealed (Chap. 4), forming the structure of liquid and crystalline conditions with the bonds network. The energies of the large number of specific interactions and hydrogen bonds of the various homological series were determined: sulfides and disulfides, with symmetrical and asymmetrical structure of the normal structure and with the isostructural methyl group, saturated and unsaturated ligands, and cyclic compounds including heteroatoms and thiols, cyclothiols, benzenethiols, and dithianes. The natural numbers of stabilization of the various types of specific interactions and hydrogen bonds were substantiated.

The result of the implemented thermodynamic analysis of sulfur, oxygen, and nitrogenated organic compounds is the reasoning of the types of specific interactions and determination of their energy parameters of the wide spectrum of the oxygenated and nitrogenated compounds: carbonyl sulfides and disulfides, dimethylsulfoxides and divinylsulfoxides, diacetylsulfides, 1-(methylthio)-2-(vinylloxy)ethanes, alkyl thiolactates and 1,3-dithiol-2-one, 1,3-dithiole-2-thione, sulfones with the linear, cyclic structure and benzene ring, *p*-tolyl sulfones, and diphenyl sulfone, dibenzyl sulfone (Chap. 5). The thermodynamic analysis of sulfur and nitrogenated compounds revealed information on the types and energies of specific intermolecular interactions of thiocyanates, isothiocyanates and phenyl isothiocyanate and thioacetamide and dithiooxamide, thiosemicarbazide, thiocarbohydrazide and thiobenzamides, thiazole, its derivatives and benzothiazole, and (methylthio)pyridines, which results in the substantiation of the numbers of regularities change of the energies of specific interactions and the creation of a consistent system of energy properties of sulfonated compounds, correctly reflecting the nature of the intermolecular compounds.

The result of the performed theoretical studies based on the experimental thermodynamic parameters and structure data revealed a large number of hydrogen bonds with differing and identical stability of specific intermolecular interactions with the participation of pentacoordinated carbon atom and silicone atom, formed by the essentially undivided $2s^2(c)$ electron pair. A theory of hydrogen bonds and specific intermolecular interactions with the element atoms of the main groups was developed and the energies for a large number of compounds were determined. The

result of the implemented studies is the creation of a system of corresponding energy values of hydrogen bonds and specific interactions of the organic, nitrogenated bioorganic and elementorganic, including siliconorganic and sulfonated, compounds with the participation of pentacoordinated atoms of carbon, silicon and nitrogen, sulfur, and other atoms of the main subgroup elements, adequately reflecting their nature.

Realizing that, over time, the volume of experimentally obtained vaporization enthalpies will increase, including enhanced accuracy at the standard conditions, the author considered it useful to suggest the calculations procedure and its use in the calculations of thermodynamic characteristics with a large number of experimental errors and significantly differing from the standard conditions.

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