

Preface

The development of the molecular theory of solid and liquid conditions of organic and bioorganic compounds and their solutions is based on fundamental investigations of their structure, molecular interactions, and the dynamics of the process in the condensed phase. Of particular significance for the investigations of this development is that we have found interdisciplinary supramolecular chemistry interrelation in the molecular properties of condensed systems, as stipulated by intermolecular interactions. The solutions with specific interactions realized, analogous to hydrogen bonds, are related to associated solutions, and these are of great interest for fundamental and applied aspects. At present, scientific publications show a lot of completed systematization and we see a generalization dedicated to biophysics, and elucidation of the rules in the biological processes. However, the role of specific interactions in all identified knowledge fields is assigned to a scanty range, perhaps too restricted to mention. At the same time the absence of information on the energy of H-bonds allows us to consider only a network of hydrogen bonds, which is imperfect in physical chemistry. For organic and bioorganic compounds and their solutions the thermodynamic purposefulness of investigations is firmly established and developed. One of the basic values of this method is the possibility of its application when knowledge of the molecular structure of compounds is not sufficient. At the same time, because of this information and the thermodynamic properties of the vaporization process my well-founded principle about intercommunity of the enthalpy and entropy of evaporation and sublimation with the number and energy of dissociation bonds complete the invaluable role of the determination of the energies of specific intermolecular interactions and hydrogen bonds, which has been confirmed successfully for elementorganic and other classes of compounds. Thus, the key moment was the implementation of the critical thermodynamic analysis of the great quantity of alkyl compounds' main group elements (as I determined) that has accumulated. This analysis touches the notions of the sp^3 -hybridization model of the carbon atom valiant orbital, which had perfect attractiveness. The results of thermodynamic analysis led to the correct conclusion, a new idea about the reverse dative bond, realized between the carbon atom of an alkyl ligand and contact with the central atom of the molecule and the carbon atom,

and the ability of the end methyl ligand group to take part in the formation of specific intermolecular interactions displaying the five co-ordination stages. The fulfilled thermodynamic investigations of alkyl's aluminum substantiated the dimer molecules at the vapor phase with a stable bond (44.2 kJ mol^{-1}) formed by the five-coordinated carbon atom. The fundamental notions about the five-coordinated carbon atom, confirmed by thermodynamic investigations and, on the other side, the existence of the reverse dative bond, substantiated by the quantum-chemical calculations of methyl compounds boron, aluminum, tin, nitrogen, and oxygen resulted in a motivated refusal of the sp^3 -hybridization model of the carbon atom.

The methodological principles of substantiation of specific interaction types, formed by a five-coordinated carbon atom and hydrogen bonds and determination of its energies ensured the creation of the system of these properties coordinated by each other and reflected nature-specific interactions of different identifiable oxygenated organic compounds.

A symptomatic fact of the non-stereotypic ideas for application by the specialist, dealing with the disciplines of organic and bioorganic chemistry, resulted in the development of theoretical notions on the specific interactions and information, widening the energy data for the nitrogenated and bioorganic compounds, which is the subject treated in this monograph.

The wide spectrum of notions in the theory of hydrogen bonds is analyzed in Chap. 1, where we substantiated the specific intermolecular interactions. The term "specific interaction" unites the antiparticles' interactions with participation of the five-coordinated carbon atom with the nitrogen and oxygen atoms, respectively, without formation of stable intramolecular bonds. The network of hydrogen bonds includes only this kind of intermolecular interactions, realized in solid and liquid ammonium, for aqueous matter and hydrides of nitrogen and oxygen group elements. The nontraditional approaches of the development of theory and the methodology of the determination of the energy of various types of hydrogen bonds and specific interactions with the five-coordinated carbon atom are discussed.

The specific interactions of amines, hydrazones, hydrozines, cyanide, nitrides, amine nitrites of acyclic and aliphatic series with saturated and unsaturated alkyl ligands and the different numbers of carbon atoms at the chain were studied and we determined the energies of various types of interactions, formed by the nitrogen atom and of the hydrogen bonds. We proved the law-governed nature of stability and exposed its nature (Chap. 2).

The different types of specific intermolecular interactions and hydrogen bonds of cyclic and aromatic compounds with saturated and unsaturated hydrocarbon cycles and nitrogen atoms of the functional group are discussed in Chap. 3. The values of the energies of the hydrogen bonds and different types of specific interactions obtained accurately reflect the nature of the interactions and illustrate the natural characteristic of changing its stability at the compounds of different series depending on the influence of the intermolecular reverse dative bond.

The structural-thermodynamic analysis for a wide range of compounds of aziridines, azetidines, pentamers, and hexamers heterocycle compounds with the nitrogen atom and saturated and unsaturated hydrocarbon cycles led to the

discovery of the types of specific interactions and allowed us to reveal their nature (Chaps. 4 and 5). The idea of reverse dative bonds and the theoretical notions of specific interactions are analyzed with reference to the nitrogen atom. Located inside a cycle of availability in its one, two and three nitrogen atoms, different types of specific interactions are substantiated, their energies determined, and the levels of stability analyzed.

In Chap. 6 we consider methoxydimethylamines and *N*-(ethoxymethyl) diethylamines, methoxyacetonitriles, amides and their derivatives with hetero atoms of oxygen and nitrogen in the chain, with the network of specific intermolecular interactions and hydrogen bonds in liquid and crystal conditions and the various types of these interactions are given a basis. In the results of the thermodynamic analysis, the nature of the interactions was revealed, based on the formation of the peptide hydrogen bond by the carbonyl oxygen atom and the hydrogen atom of the amino group $\text{=C=O}\cdots\text{H-N}$ and hydrogen bond $\text{O}\cdots\text{H-N}$ corresponding to the amides and methoxymethylamines. The energies of these bonds and the different types of specific interactions for the crystalline and liquid compounds of various series were obtained and the range of values for their stabilization for compounds with the chain structure and benzene cycle was established.

The various types of specific intermolecular interactions of compounds with nitrogenated and oxygenated hydrocarbon cycles, pentamers heterocycles, oxazoles, isoxazoles and thiazoles, oxazolines, azetidines and aminoisoxazole compounds with hexamers heterocycles and their derivatives as well as the compounds with larger cycle 6-caprolactam with one and two carbonyl groups are analyzed in Chap. 7. In the results of the thermodynamic analysis, the nature of each type of the formed specific interaction and hydrogen bonds was revealed, obtaining its energies and the integral values of stabilization, which led to a significant development in the theory of intermolecular interactions.

The different types of hydrogen bonds formed and the specific interactions at the solid and liquid states of amine alcohols and their derivatives with the hydroxyl group are substantiated and the energies, illustrating the wide range of the change in stability were determined. The problems discussed in Chap. 8 have a straightforward relation with supramolecular chemistry and biochemistry.

The results of the analysis of thermodynamic characteristics of the low-molecular biological amino acids merit particular attention. The results of the investigations carried into biophysics the unknown and non-stereotypic notions of the types of specific intermolecular interactions, formed by the five-coordinated carbon atom with the nitrogen and oxygen atoms, respectively, and the formed structures of liquid and solid states with the network of specific interactions and participation of hydrogen bonds. The substantiated types of specific interactions with the five-coordinated carbon atom, hydrogen bonds, including the peptide hydrogen bonds, the determined values of the energies of different interactions, and the orders of their stabilization have enriched the molecular biophysics and biochemistry (Chap. 9).

All the preceding results of research in the field of specificity of intermolecular interactions, including organic, nitrogenous molecules and compounds with two hetero atoms of nitrogen and oxygen, provided success in the solving of problems on the energy value of peptide hydrogen bonds and all specific interactions in the formed networks in the crystalline and liquid structure of peptides. The significant results in this direction are the determination of the roles of the methylene group and the fragment with the larger number of these groups. These are located between strong acceptors of electron density by the nitrogen atoms and carbonyl oxygen atoms. They express the reduced ability in the formation of specific interaction compared with a similar fragment at the terminal part of the chain. We also see participation of the isostructural methyl group, connected with the mentioned methylene group, in the distribution of the electron density in the molecule and its extra stabilizing effect to the fragment, fringing these isostructural groups, leading to an energy contribution to the enthalpy characteristics independent of its number in the peptide and protein. The obtained values of the energies of the hydrogen bonds and specific interactions with the five-coordinated carbon atom of peptides and dipeptides led to the determination of the energy contribution by the conformer of the chain 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, we first presented various protein secondary structures with parallel β -sheet and antiparallel β -sheet with all the specific interactions (Chap. 10).

The application of the theory of the hydrogen bond, specific interactions, and principles of the thermodynamic analysis to urea and its derivatives, belonging to one form of the main product of a living nature metabolism, easily extracted from the organism and playing an important role in the study of the conformation stability of globular protein, illustrated the phenomenological significance of the investigations (Chap. 11). Urea with eight hydrogen bonds of two types, formed by nitrogen and oxygen atoms with combinations of their derivatives and various functional substitutes of the hydrogen atom, formed in the amine groups, allow us to trace the influence of the substitutes on the stability of hydrogen bonds and alkyl fragments on specific interactions and the arrangement of substitutes in the amine groups with regard to the stability of the intermolecular interactions formed. The new concept of the extra stabilizing effect of the isomeric methyl group for the structure and stability of molecules of organic, nitrogenated, and bioorganic compounds, amino alcohols and acids, peptides, proteins and derivatives of urea and the value of the energy of the interactions is considered in this chapter.

The research eliminated the gap created by the absence of energy values of the hydrogen bonds and specific interactions even for the simplest and most frequently occurring compounds of water and spirits in the entire field of chemistry. The volume of energy values of different types of hydrogen bonds obtained, with most of them already known and based for the first time in different types of specific interactions, which do not even include any reference, led to the creation of energy values consistent and coherent with each other, reflecting their nature accurately. On the basis of the results obtained, also for the first time, the theory of specific

intermolecular interactions was developed with the five-coordinated carbon atom; we have also undertaken the further development of the theory of hydrogen bonds, which has enriched physical chemistry, organic chemistry, biochemistry, and biophysics with fresh new ideas. The results of thermodynamic analysis of amides, compounds with nitrogenated and oxygenated hydrocarbon cycle with pentamers and hexamers heterocycles, amino acids, and peptides allow us to base the existence of several types of peptides' hydrogen bonds, explain the reasons causing the differences in their energies, and solve the problems by turning to the analysis of proteins on the basis of the values of the energies of hydrogen bonds and specific interactions. In this connection one should note the new perspective of quantum-chemical research of all the classes and series of compounds, first, of proteins, peptides, and amino acids and the necessity of obtaining the thermodynamic properties of these compounds. Special role is given to the research of alcohols and amino acids for determination of energies of hydrogen bonds of DNA.

The present book is intended to be a useful source of information for scientists, teachers, post-doctoral fellows, post graduate students, and other specialists working in the area of Chemistry, Biochemistry, Biophysics, and Chemical Technology.

In writing the book I have tried to reveal the depth of the analyzed problem and to provide its clear description remembering that "formulas are not the essence of the theory, and a real theoretician uses them sparingly expressing with words all that is possible to express in words" (L. Boltzmann).

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