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Preface

Since the time of discovery of noncovalency bonds the energy of the hydrogen bond in water remains the reliably measured value. Yet quite a number of versatile organic compounds have been synthesized; certain success is attained in the field of structural studies, in measuring intramolecular bonds energies, in carbohydrates, nucleic acids, and proteins chemistry, and in the development of the chemistry of organoelemental compounds. The lack in the scientific publications of the information on the energy of hydrogen bonds and specific intermolecular interactions between the simplest organic compounds (methane, ethane, ethylene, methyl ether, and formic acid) provides special difficulties in their investigation. This impedes the progress in the development of the theoretical concepts of the solution chemistry, in the establishment of correspondence between the structure and energy in various classes of organic compounds, the understanding of the solvates structure, and the specific features of interspecies interaction. Even more difficulties exist in the development in the field of solution chemistry of an independent supramolecular chemistry, the chemistry of intermolecular bonds corresponding to the association between two or more chemical species of large size. A vigorous development is observed in the physical chemistry of organoelemental compounds serving as a certain bridge connecting the inorganic and organic chemistry where frequently appear concepts contradicting the current notions existing in these fields, but which are key points for creating hypotheses, new ideas, and developing of theories inadequate to the existing ones. Let us mention here the statement of Sidgewick that the molecules with the electronic configuration of a noble gas are incapable of association, whereas our investigation established the existence in the vapor of dimers of carbonyl compounds of the elements from the subgroup of chromium, iron, and nickel.

In the physical chemistry of organic compounds and their solutions is firmly established and successfully developed the concept of the correspondence between the structure and the energy, determined by the investigation of molecular structures, of the condensed states, and of the distribution of electrons and charges on the atoms in the molecule, and by measuring the thermodynamic properties. One of the advantages of the thermodynamic methods consists in the successful application of the notion of the bond vacancies even at the lack of the sufficient information on the molecular structure and the distribution of the charge on the functional groups of the molecule. The discovery of the nature of the hydrogen bonds and specific intermolecular interactions, establishment of new previously unknown types, and their energies makes it possible to solve practical problems; in particular, it opens further opportunities in the development of the chemistry of biologically important substances and in the understanding of the empirical correlations between the thermodynamical properties and molecular parameters measured by various methods.

The key problem elaborated in the monograph is the concept that a carbon atom in the four-valency state not only is capable but actually forms the fifth coordination in the intermolecular interactions with an energy comparable with the energy of the hydrogen bond in water. The unique feature of the behavior of the carbon atom with an essentially unshared $2s^2$(c)-electron pair is its ability to act as a donor or an acceptor depending on the properties of the element participating in the interaction, to take part in the formation of solvate structure, and in the formation of specific interaction. These qualities are also inherent to molecules of amino acids, carbohydrates, and proteins.

We do not plan to consider comprehensively in this monograph all the problems of hydrogen bonds and the specificity of intermolecular interaction involving the pentacoordinate carbon atom, in all classes of organic and organoelemental compounds. We limit the scope of the discussion to the principal organic compounds: ethers, ketones, alcohols, carboxylic acids, and hydrocarbons, which always stimulated the appearance of new hypotheses and development of theories, essentially necessary for all classes of organic, organoelemental compounds, hydrocarbons, amino acids, and peptides. The information on fundamental aspects of this monograph may be obtained from its table of contents. At the same time the special importance of the theory of the hydrogen bonds and of specific intermolecular interaction, in substantiation of their types and energy determination, should be stressed. The refining of the current concepts in the field of hydrogen bonds and specific interactions in liquid and crystalline organic compounds, solutions of nonelectrolytes, of the theoretical regularities are necessary for the understanding of phenomena in organic and complex biologic systems and for further purposeful development of the key problems of the specific interactions and hydrogen bonds in the biologically important substances.

The critical analysis of the total scope of thermochemical and thermodynamic properties of alkyl derivatives of elements of the II–VI main groups established in the investigations of the author inevitably infringes on the views regarding the classical model of the sp^3-hybridized valence orbitals of the carbon atom whose attraction prevented the doubts in its imperfection (Chap. 1). As a result of this analysis the phenomenon of the reverse dative bond between the carbon atoms of the alkyl chain and the contacting central atom of the molecule was substantiated and also the capability of the terminal methyl groups to participate in the specific intermolecular interactions revealing the pentacoordinated state. These fundamental statements led to the founded rejection of the model of the sp^3-hybridized carbon atom based on the quantum-chemical calculations of the methyl derivatives of the elements of subgroups of boron and tin, and methyl compounds of nitrogen and oxygen, additionally confirming the capability of a pentacoordinate carbon to take part in the formation of the specific interaction. The implementation of these concepts into the theoretical footing of organic and inorganic chemists may be somewhat inertial due to the unconventional ideas and the approach to the theory of the hydrogen bonds and specific interaction. But the fact that here are compiled the self-consistent energies of the hydrogen bonds of various types and specific intermolecular interactions adequately reflecting their nature, the data, which are highly necessary for the specialists, gives a hope that they will be gratefully acknowledged.

The scientific idea of the reverse dative bond in organoelemental compounds with a hydrocarbon group confirmed with the quantum-chemical calculations in its development underlies the new concepts on the nature of the bonds in the alkyls of nontransition elements and in organic compounds with a heteroatom. This idea ensures the understanding of the chemistry of liquid solvents and liquid and solid nonelectrolytes (Chap. 2). The results of thermodynamic calculation are attractive for they provide an unambiguous solution of the problem of measuring the energy of the hydrogen bonds and the specific intermolecular interactions whose quantitative value remained unknown and even unestimated approximately. The growing number of carbon atoms in the alkyl chain results in more stable specific interactions formed by the terminal methyl group of the propyl fragment (Chap. 3). This fact is due to the weakening of the influence of the reverse dative bond on the terminal methyl group with the growing number of carbon atoms in the alkyl chain. From the large number of the established rules of the energy changes in the specific interactions of the saturated and unsaturated cyclic ethers and organic cyclic oxides, we report one among them regarding the regular decrease in the energy of low-stability hydrogen bonds between the hydrogen atoms of the CH_2 groups and the oxygen atom of the oxides with the growing number of the methylene groups in the molecular ring.

The alternative character of the theory and the necessity of its further development prompted the elaboration of the principles of proving various types of hydrogen bonds and specific intermolecular interactions and the procedures of thermodynamic calculation of their energies based on the enthalpies of vaporization that were suitable for all classes of organic compounds. These principles are reported in Chap. 3 and are elaborated in the successive chapters.

In Chap. 4, thermodynamic analysis is performed of the structural and thermodynamic characteristics of liquid and solid symmetric and unsymmetrical ketones with saturated and unsaturated alkyl chains, cyclic ketones, diketones, and oxyketones. As a result the self-consistent energy values were obtained for the specific intermolecular interactions and the H-bonds of low stability formed by the oxyketones. An important attention is paid to the new conception in the theory of the structure and stabilization of the molecules of ketones, alcohols, to the extrastabilizing effect of the isostructural methyl groups ensuring their reduced values of the enthalpy characteristics in the vaporization processes and the equal contribution into the enthalpy characteristic of the vaporization of four CH_2 groups with contiguous methyl groups. This principle is valid for various classes of organic compounds and reflects the analogy of the structural fragments at the number of CH_2 groups exceeding eight in ketones, alcohols, and obviously in more complex organic substances with the heteroatoms in the molecules and in the complex biological systems. A special attention is paid to the thermodynamic investigation of saturated and unsaturated ketones with a large number of carbon atoms and isostructural methyl groups.

In Chap. 5, various types of hydrogen bonds and specific intermolecular interaction were substantiated and their nature was revealed in liquid and solid monohydric and polyhydric alcohols with saturated and unsaturated chains, with the open and cyclic structure and isostructural alkyl groups. Theoretical problems are discussed and the regularities in the stability series of bonds are substantiated. The results obtained impelled to carry out thermodynamic investigation of isostructural and acetylene alcohols, and their solutions with polyatomic saturated and unsaturated ketones. The findings obtained confirmed the developed concept of the stabilizing effect of the isostructural methyl group.

In Chaps. 6 and 7, the theory of the hydrogen bond finds further development and are extended the theoretical notions and rules to liquid and solid aldehydes, esters, and carboxylic acids. The performed thermodynamic analysis of the enthalpy and structural entropy characteristics of vaporization of carboxylic acids associated in vapor resulted in valid energy values of various types of hydrogen bonds and specific intermolecular interactions of saturated and unsaturated mono- and dibasic acids, acids with an isostructural methyl group, hydroxycarboxylic acids, methoxy- and ethoxycarboxylic acids, peroxycarboxylic acids, and cyclic carboxylic acids. The established array of valid self-consistent energies of various types of hydrogen bonds and specific intermolecular interactions is illustrated by the regular series of their stabilization.

Chapter 8 illustrates the application of the developed theory of specific interactions to alkanes and alkenes and the established regularities of the specific interactions existing in their condensed state.

In writing the book the author 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). The author is deeply grateful to Professor Josef Barthel (Regensburg University, Editor-in-Chief of the Journal of Molecular Liquids) for his suggestion and demand of the author to write a monograph basing on the theme of the article submitted to the *Journal of Molecular Liquids*. The ideas reported in this article underlie the development of the thermodynamic theory of the hydrogen bond and the specific interactions originating from the pentacoordinated carbon atom.

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Synopsis

The book presents the development of the thermodynamic theory of specific intermolecular interactions, nonstereotypic ideas, and approaches to the theory of H-bonding and specific interactions involving motivated concepts on a five-coordinated carbon atom based on the discussion of a wide spectrum of compounds (ethers, ketones, alcohols, carboxylic acids, and hydrocarbons). New types of hydrogen bonds and specific interactions are substantiated and on the basis of elaborated methodology their energies are determined and the system of interconnected quantitative characteristics of a stability of specific intermolecular interactions, reflecting both their nature and law-governed changes, is created. A new conception of the extra stabilizing effect of isostructural methyl group is considered in the theory of a structure and stability of molecules of organic compounds and in the energy of interactions.

Contents

Abbreviation

DA	Donor–acceptor bond
DE-Me	Dissociation energies of bond
Ddis.dim	Dissociation energies of dimmer molecule
$\begin{tikzcd} \mathrm{M} \arrow[r] & \mathrm{CO}\text{ -} \arrow[l, bend right] \end{tikzcd}$	Reverse dative bond on metal carbonyl
$\begin{tikzcd} \mathrm{Al} \arrow[r] & \mathrm{C} \arrow[l, bend right] \end{tikzcd}$	Reverse dative bond AlR_3
(η^E)	Dynamic viscosity
Pa (kPa)	Vapor pressure at Pascal
$T_{m.p.}$	Melting point
$T_{b.p.}$	Boiling point
$\Delta_{vap}H^0(298)$	Vaporization enthalpy
$\Delta_{vap}H^0(298)$ alc	Vaporization enthalpy of alcohols
$\Delta_{vap}H^0(298)$ cyc.c	Vaporization enthalpy of cyclic hydrocarbon
$\Delta_{vap}H^0(298)$ bz	Vaporization enthalpy of benzene
$\Delta_{vap}H^0(298)$ der.bz	Vaporization enthalpy of derivative of benzene
$\Delta_{vap}H^0(298)$ к. iso	Vaporization enthalpy of compounds with the number (*k*) isostructural fragments
$\Delta_{vap}H^0(298)$ c n	Vaporization enthalpy of compounds with normal structure
$\Delta_{vap}H^0(T)$ cyc.pr.	Vaporization enthalpy of cyclic propyl
$\Delta_{vap}H^0(T)$ pr	Vaporization enthalpy of propyl
$\Delta_{vap}H^0(T)$ c.bu.	Vaporization enthalpy of cyclic butane
$\Delta_{vap}H^0(298)$ frag	Contribution’s energy of fragment at enthalpy
$\Delta_{vap}H^0(T)$ hc.a	Vaporization enthalpy of hydroxy carboxylic acids
$\Delta_{vap}H^0(T)$ po.a	Vaporization enthalpy of peroxy carboxylic acid
$\Delta_{vap}H^0(T)$mtc.	Methoxypropionic acid
$\Delta_{evop}H^0(T)$	Evaporation enthalpy
$\Delta_{evap}H^0(T)$ c.a.	Evaporation enthalpy of cyclic carboxylic acid
$\Delta_{evap}H^0(T)$ bz.a	Evaporation enthalpy of benzoic acid
$\Delta_{melt}H^0(T)$	Melting (heat) enthalpy

$\Delta_{pol}H^0(T)$	Enthalpy of polymorphic transformation
$\Delta_{sub}H^0(298)$	Sublimation enthalpy
$\Delta_{sub}H^0(T)$mbz.a.	Sublimation enthalpy of methylbenzoic acid
$\Delta_{sub}H^0(T)$ mbz.a	Sublimation enthalpy of methoxybenzoic acid
$\Delta_{sub}H^0(T)$ etbz.a	Sublimation enthalpy of ethylbenzoic acid
$\Delta_{sub}H^0(T)$ hbz.a	Sublimation enthalpy of hydroxylbenzoic acid
$\Delta_{sub}H^0(T)$ *iso*	Sublimation enthalpy of isostructural compound
$\Delta_{sub}H^0(298)$ d.i.p.	Sublimation enthalpy of diisopropyl
$\Delta_{sub}H^0(298)$ d.e.	Sublimation enthalpy of diethyl ether
$\Delta_{sub}H^0(T)$bz.a.	Vaporization enthalpy of benzoic acid
$\Delta_{sub}H^0(T)$mbz.a.	Sublimation enthalpy of methylbenzoic acid
$\Delta_{sub}H^0(T)$ebz.a	Sublimation enthalpy of ethylbenzoic acid
$\Delta_{sub}H^0(T)$ipbz.a	Sublimation enthalpy of isopropylbenzoic acid
$\Delta_{sub}H^0(T)$hbz.a	Sublimation enthalpy of hydroxybenzoic acid
$\Delta_{sub}H^0(T)$mtbz.a	Sublimation enthalpy of methoxybenzoic acid
C_n	Number of carbon atoms at alkyl chain
E.E.C.	Endoeffect coordination
Ddest. E	Destabilized effect
AN	Acetonitrile
FA	Formamide
AC	Acetone
NMF	*N*-methylformamide
DMF	*N*,*N*-dimethylformamide
DMSO	Dimethyl sulfoxide
Me	Methyl
Et	Ethyl
Pr	Propyl
Bu	Butyl
iso-p	Isopropanol
Et. al.	Ethanol
iso.m. bu.	*iso*-Methylbutanol
1-Bu	1-Butanol
1-al	1-Alcohol
iso-CH_3	Isostructural methyl group

Contribution's Energy at Enthalpy

DCH_3	*iso*-CH_3
DCH_2	CH_2-group
DCH	CH-group

Energies of Specific Intermolecular Interaction of Pentacoordinate Carbon Atom

$N{-}CH_3{\leftarrow}N{-}$	$N(CH_3)_3$
$N{-}CH_2{-}CH_3{\leftarrow}N$	$N(C_2H_5)_3$

Energy of Specific Interaction of Saturated Alkyl Series (Fragment)

$D{-}O{\rightarrow}CH_3$	Methyl
$D{-}O{\rightarrow}CH_3{-}CH_2{-}$	Ethyl
$D{-}O{\rightarrow}CH_2{-}CH_2{-}$	Ethylene
$D{-}O{\rightarrow}CH_3{-}CH_2{-}CH_2{-}$	Propyl
$D{-}O{\rightarrow}CH_3{-}(CH_3){-}CH$	Ligand with a *iso*-CH_3-group
$D{-}O{\rightarrow}CH_2{-}(CH_2)_n{-}$	Fragment of alkyl chain
$D{-}O{\rightarrow}CH_3{-}(CH_2)nC{-}$	Alkyl chain of ketone
$D{-}O{\rightarrow}C{=}O$	Carbonyl group
$D{-}CH_2{-}CH_3{\rightarrow}CH_2{-}CH_3$	Hydrocarbon
$DH_3C{\rightarrow}H{-}CH_2$	*iso*-CH_3
$DH_2C{\rightarrow}H{-}CH$	Methylene group
$DH{-}C{\rightarrow}H{-}C$	CH group

Energy of Specific Interaction of the Alkene Series Unsaturated Ligand (Fragment)

$D{-}O{\rightarrow}CH_2{=}CH{-}$	$CH_2{=}CH{-}$ fragment
$D{-}O{\rightarrow}CH_3{-}CH{=}CH{-}$	Propylene
$D{-}O{\rightarrow}CH_2{=}CH{-}CH_2{-}$	Propylene
$D{-}O{\rightarrow}CH_2{=}CH{-}CH_2{-}$	Propylene
$D{-}O{\rightarrow}CH_2{=}(CH_2)_n{-}$	Alkene chain
$DH{-}O{\rightarrow}CH{\equiv}C{-}CH_2$	Chain with the triple bond – $C{\equiv}C$
$D{=}HC{-}H_3C{\rightarrow}CH_2{=}CH{-}$	Unsaturated hydrocarbon (fragment)

Energies of Specific Intermolecular Interaction of Alkyl Series with Carbonyl Oxygen

$D{=}O{\rightarrow}CH_3{-}$	CH_3
$D{=}O{\rightarrow}CH_3{-}CH_2{-}$	C_2H_5
$D{=}O{\rightarrow}CH_3{-}CH_2{-}CH_2{-}$	C_3H_7
$D{=}O{\rightarrow}CH_3{-}(CH_2)_n{-}$	$CH_3{-}(CH_2)_n{-}$ alkyl series

Energies of Specific Intermolecular Interaction of Alkene Series with Carbonyl Oxygen

$D{=}O{\rightarrow}CH_2{=}CH{-}CH_2$	Propylene
$D{=}O{\rightarrow}CH_3{-}CH{=}CH$	Propylene

Energies of Specific Intermolecular Interaction of Ketone Series

$D{=}O{\rightarrow}CH_3{-}C{-}$	Acetonic form
$D{=}O{\rightarrow}CH_2{-}CH_2{-}C{-}$	Saturated fragment ketone
$D{=}O{\rightarrow}CH_3{-}CH(CH_3){-}C{-}$	Fragment with isostructural CH_3 group
$D{=}O{\rightarrow}CH_3{-}(CH_2)_n{-}C{-}$	Alkyl chain of ketone

Energies of Specific Intermolecular Interaction of Ketene Series

$D{=}O\rightarrow CH_2{=}CH{-}C{-}$	Propene
$D{=}O\rightarrow CH_3{-}CH{=}CH{-}C{-}$	Butene

Energy of Hydrogen Bond of Etheric Oxygen

$DH{-}O\cdots H{-}O{-}$	Alcohol, acid
$D{-}O\cdots H{-}C{-}$	CH group
$D{-}O\cdots H{-}C{-}H$	CH_2
$D{-}O\cdots H{-}CH_2$	CH_3
$D{-}O\cdots H{-}N$	Amino group
$DN{-}H\cdots N{-}H{-}$	NH_3
$D{-}O\cdots H{-}C{=}$	H–C= with double bond

Energy of Hydrogen Bond with Carbonyl Oxygen

$D{=}O\cdots H{-}C{-}$	CH
$D{=}O\cdots H{-}CH{-}$	CH_2
$D{=}O\cdots H{-}CH_2$	CH_3; *iso*-CH_3
$D{=}O\cdots H{-}N{-}$	Amino group

Chapter 1
Reverse Dative Bond in Organic Compounds, Molecular Complexes and Inconsistency of the sp^3-Hybridization Model with Respect to Carbon Atom

1.1 Introduction

Extensive investigation of organometallic and organoelemental compounds in various aggregate states resulted in the establishment of the thermodynamic properties of the vaporization process and enthalpy of formation, and simultaneously of their dissociation energies. The results of performed calorimetric measurements were accompanied with deep critical analysis of the methodological approach leading to reliability of the data of the thermodynamic studies. The rich experience of the calorimetric investigations shows that the final thermodynamic findings for the same compounds obtained by various research teams [1–3] are well consistent.

In many events, the established thermochemical properties and dissociation energies of organic complexes remain the only physicochemical characteristics of molecules providing the information on the features of intramolecular and intermolecular interactions. However, unlike the thermochemical properties of inorganic compounds the analogous experimental data of organoelemental compounds, in particular, of alkyl derivatives of nontransition elements, were not subjected to the critical analysis and the reasons remained unclear, and the reasons leading to inadequate character of the variation in the average cleavage energy of the chemical bonds at growing number of the carbon atoms in the alkyl chain. Analogous inconsistencies with the current concepts originating from the results of the study of inorganic and organic compounds are not isolated instances. However, the most important inconsistency corresponds to the fulfillment of the critical analysis of the total array of thermochemical and thermodynamic properties of alkyl compounds necessarily related to the classical conception of the model of the sp^3-hybridization of the valency orbitals of a carbon atom whose attractiveness prevented the doubts regarding its imperfection.

Here should be mentioned a fundamental paper of V.L. Talroze and A.L. Lubimova where for the first time cation CH_5^+ was described with a hypercoordinated structure [4]. However, these results remained unclaimed for over

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40 years. In recent decades, fundamental works appeared on the developing nontraditional chemistry of hypercoordinated carbon [5] and nonclassical structures of organic compounds [6]. In the latter publications, the prediction approach was analyzed of isolobal relations by R. Hoffmann for considering nonclassical organic and organometallic structures.

In this chapter, the reliably established thermodynamic and thermochemical properties of organoelemental compounds are analyzed and the contradiction of these data is revealed with the forecasts based on the model of the sp^3-hybridization. As a result of the analysis, the phenomenon of a reverse dative bond is substantiated between the carbon atoms of the alkyl group and the contacting central atom, the inconsistency of the sp^3-hybridization model is proved, and the capability of the carbon atoms of terminal methyl groups to take part in the specific intermolecular interaction is revealed. The scientific conception of the phenomenon of the reverse dative bond in organoelemental compounds with the saturated and unsaturated hydrocarbon substituent in its development should underlie new notions on the bond nature in alkyls of nontransition elements and organic compounds containing a heteroatom and provide the understanding of the chemistry of liquid nonelectrolytes.

1.2 Some Problems of Liquid Molecular Complexes and Solutions

The contemporary trends in the investigation of molecular liquids are restricted to the study of organic compounds, characterized by the variety of hydrogen bonding. It is alcohols, organic acids, functional solvents, amines, and amino acids. The availability of the spatial structure in the liquid state with a three-dimensional network structure containing the chain and ring fragments [7–10] with the common donor–acceptor nature of the intermolecular hydrogen bonding is regarded as a very important special feature of these compounds. Different compounds of the homological series with the hydroxyl group are characterized by the chain intermolecular hydrogen bonding extended to long-range environment. As result of this longer range of the solvation at methyl alcohol and formic acid it is higher considerably than at ethyl, *n*-butyl alcohols and acetic acid with the characteristic for their ring structure of dimers [11]. However, an examination of the nature of the intermolecular interaction in liquid ketones, ethers rouses great difficulties. The understanding of the structure of the solvents and their solutions with the complicated molecules are becoming more problematical. That is why a liquid state of many classes of organic compounds is liable to oblivion. The nature of intermolecular interactions of these compounds is not examined on the following reasons. Firstly, historically an opinion existed that liquid organic compounds participated in the universal (nonspecific) interactions and consequently the investigation of these was complicated. Secondly, simplicity of perception and attractiveness of the comprehensive

sp^3-hybridization model of electron configuration of carbon atom at saturated hydrocarbons, alkyl compounds could not be questioned and discussed severely. However, it is not in conformity with the notion about saturated hydrocarbons as the compounds with universal intermolecular interactions are characterized by the values of the vaporization enthalpy more than 20 kJ mol^{-1}. It shows a necessity to develop new idea which will explain the nature of intermolecular interactions of liquid organic compounds identically. Demand for the new ideas is of the general interest for the examination of alkyl compounds, ketones, ethers, alcohols, and other more complicated compounds with functional groups. The reliably established experimental thermodynamic properties of the alkyl compounds are not corresponding to foretold values by sp^3-hybridization model of an electron configuration of carbon atom. This model cannot explain the reasons causing the increase in the vaporization enthalpy in the homological series, for example, of gallium alkyls compounds [12].

Compounds	$GaMe_3$	$GaEt_3$	$Ga(n\text{-}Pr_3)$	$Ga(n\text{-}Bu_3)$
$\Delta_{vap}H^0$ (298) kJ mol^{-1}	32.6 ± 0.1	43.1 ± 0.5	46.6 ± 0.5	51.6 ± 1.6

The regularities in the variation of the vaporization enthalpy are often ascribed to the growth in the molecular mass [10]. However, this suggestion is only a superficial description of the phenomenon and prevents revealing the nature of the intermolecular interaction. These regularities are observed in the homologous series of saturated and unsaturated hydrocarbons. The inconsistency of this common view is illustrated by the data on the vaporization enthalpy of various organic compounds (Table 1.1) demonstrating the lack of correlation between the molecular mass and the enthalpy characteristics, energies of the donor–acceptor bonds. Note that water possessing stable hydrogen bonds corresponds to the middle position among the compounds mentioned in Table 1.1.

Therefore, the new concepts should provide a possibility to describe from the general viewpoint the nature of the intermolecular interactions in molecular liquids and solutions applying the thermodynamical properties of the processes of vaporization and sublimation and employing them to the estimation of the energy of the hydrogen bonds and of the specific interactions of organic compounds.

Table 1.1 Vaporization enthalpy $\Delta_{vap}H^0$ (T) (kJ mol^{-1}) and energy of donor–acceptor bonds (kJ mol^{-1}) [12, 13]

Compounds	$\Delta_{vap}H^0$ (T)	DA	Compounds	$\Delta_{vap}H^0$ (T)	DA
n-Propane	18.77	–	2,2,2-Tri-fluoroethanol	43.97	13.5
n-Butane	22.39	–	Water	43.99	20.7
n-Pentane	25.77	–	*N*,*N*-Dimethylformamide	47.51	17.8
Acetone	29.0	7.0	*n*-Decanone	51.08	–
Tetramethyltin	32.0	–	Tetraethyllead	51.39	–
Acetonitrile	32.9	9.0	Dimethyl sulfoxide	52.88	24.1
Tetramethyllead	37.1	–	Formamide	64.98	24.1
Methanol	37.43	19.7	–	–	–

1.3 Contradiction of Thermodynamic Properties of Organoelemental Compounds to the sp^3-Hybridization Model

Organoelemental compounds forming a certain connecting bridge between inorganic and organic chemistry can be described both from the viewpoint of the utmost general conceptions and in the framework of the specially developed notions.

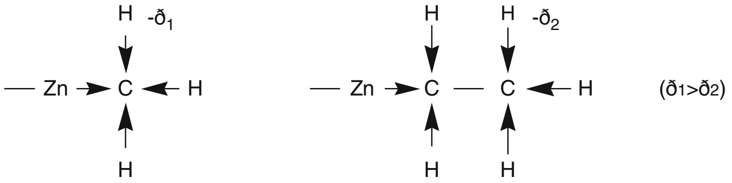
The synthesis of sandwich cene and then dibenzene, monocyclic, and polycyclic organoelemental compounds considerably shifted the direction of the studies of structures and the bonding therein. The performed simultaneously with the theoretical considerations of the intramolecular interactions experimental studies of physicochemical properties and thermodynamic characteristics made necessary an analysis of the nature of the intermolecular interactions present in various aggregate states and in the solutions of organoelemental compounds. Evidently, first in this respect were the studies on the metal carbonyls [14–16]. The discovery of strong intermolecular interactions in the solid and the liquid state and the proof of the presence of dimeric molecules in the vapor of nickel, iron, molybdenum, and tungsten carbonyls disproved the Sidgewick statement that the compounds with the 18-electron configuration of metal atoms were incapable of association. The latter statement contradicted the actual values of vaporization enthalpy of alkyl compounds of all nontransition elements. For quite a number of inorganic compounds, the nature is already established of the interaction in various aggregate states, of specific and nonspecific interactions in water and nonaqueous solutions. However, analogous investigations of organoelemental compounds were only at the beginning of development, and the obtained experimental findings were not analyzed or were treated superficially without establishing the causes and consequences, for instance, stating that heavier molecules were less volatile.

The fact that the models of sp-, sp^2-, and sp^3-hybridization explained the structure of molecules is incontestable. However, the sp^3-hybridization model for carbon atom in alkyl compounds prevents the possibility to understand a trivial fact of high volatility of methane, methyl compounds of nontransition elements as compared, e.g., with the ethyl analogs [13, 16]. The existing now wide range of experimental data on the thermodynamic properties of nonelectrolytes solutions corresponding to the mixing enthalpy [17, 18] was not discussed at all. At the same time, the extremal point on the diagrams of mixing heats with any combination of alkyl compounds of nontransition elements is used as a proof for the formation of a stable complex in the system based on the fact of the existence of a stable and volatile complex of the composition R_3MAsR_3 in alkyl compounds of the elements of the third and fifth groups. In solutions where the solvent and the solute are organic components with established types of specific intermolecular interactions still are conserved the hydrogen bonds and heterobonds in the molecular complexes [19–21].

Yet an attempt was made to explain the association in such systems by the formation of the carbenium ion [22]. Evidently, the key to the understanding of the features of the intermolecular interactions in alkyl groups and alkyl compound lies in the features of the electron density distribution in the molecules of these compounds. The calculations of the electron density distribution in alkyls B $(CH_3)_3$ and $N(CH_3)_3$ [23] performed using extended Hueckel method [24] showed within the limits of assumed approximations the different direction of the shift of the electron density. Its distribution in the methyl compounds of boron and nitrogen corresponds to the following charges on atoms [19, 25] $B(CH_3)_3$ – B(0.704), C (−0.525), H(0.097), $N(CH_3)_3$ – N(0.024), C(−0.113), H(0.035) and on methyl groups −0.234e and −0.008e, respectively. In the calculations of Gallais et al. [25] for the electron density distribution in a dialkyl ether, a negative charge is located on the oxygen (−0.228) and a positive charge on the methyl group (+0.114e).

The mentioned data for these compounds show that the methyl groups at boron and oxygen possess the charges of opposite signs, and in the series B–N–O the positive charge on the boron changes to a negative charge on the oxygen atom. This is governed by the fact that the acceptor properties of the central atom in the alkyls of elements in subgroups of zinc, boron, and silicon change to donor qualities in the elements of subgroups of nitrogen and oxygen in their alkyl compounds.

If it is valid that the increased energy of the M–C bond dissociation in going from $M(C_2H_5)_n$ to $M(CH_3)_n$ is caused by the chemical bond stabilization at increased shift of the electron density from the metal to carbon atom, then the presence of a strong bond in a methyl compound, for instance, of zinc ($Zn–CH_3$) should also involve the increased shift of the electron density to the carbon atom from the hydrogen and zinc resulting in an increased negative charge on the methyl group compared to an ethyl analog.



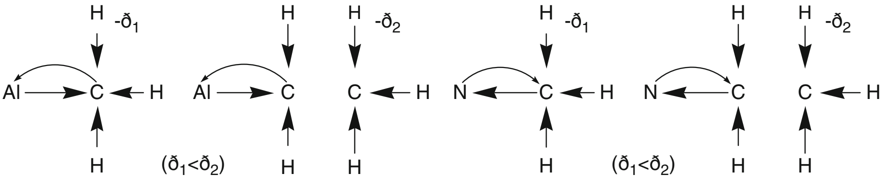
Consequently, the intermolecular interaction in the liquid dimethylzinc should be very strong and therefore the vaporization enthalpy of its methyl derivative being the integral characteristic of all existing intermolecular interactions [26] also should be essentially larger than the vaporization enthalpy of the ethyl and propyl analogs. This is a necessary conclusion of the consideration of the compounds of the elements of all main groups. However, these logical considerations based on the sp^3-hybridization model contradict the experimental values of the vaporization enthalpy, namely (Table 1.2):

$$\Delta_{vap}H^0(T)_,(ZnMe_2)<\Delta_{vap}H^0(T),(ZnEt_2)<\Delta_{vap}H^0(T),(Zn\,n-Pr_2).$$

Table 1.2 Dissociation energies (kJ mol^{-1}) of metal–carbon bond [1, 2] and vaporization enthalpy (kJ mol^{-1}) of alkyl compounds [12, 16]

Compounds	DE–Me	DE–Et	$\Delta_{vap}H^0$ (T)	
			EMe_n	EEt_n
ZnR_2	186.4	145	30.4 ± 0.2	38.8 ± 0.4
CdR_2	148.5	110.6	37.1 ± 0.07	46.0 ± 0.4
HgR_2	130.0	102.7	36.7 ± 0.1	–
AsR_3	238.4	185.9	27.7 ± 0.2	38.5 ± 0.7

This means that the dissociation energy of the bond Zn–C (E–C), the charge on the carbon atom of the methyl and ethyl group, and the evaporation enthalpy are not governed exclusively by the shift of the electron density from the zinc atom to carbon or from carbon atom to oxygen. Let us pay attention also to the fact that the visible correlation between the shift of the electron density in the molecule and the bond dissociation energy, for instance, Zn–C (E–C) in alkyls does not result in the correlation of each of these properties with the vaporization enthalpy in the homologous series of the element (Table 1.2). This makes it possible to conclude that the charge on the carbon atom of these alkyl groups and the charge on the zinc atom or the atom of the element of II–IV and V–VI groups is governed not only by the shift of the electron density, but by one more important property of the carbon atom that is not taken into consideration. This property is its capability to take part in the formation of the reverse dative bond at the expense of the essentially unshared $2s^2$-electron pair that significantly changes its charge and the charge of the atom of the metal or element contacting with this carbon in the molecule.



This means that the shift of the electron density from an atom, e.g., of aluminum to carbon on its 2s-orbital is accompanied with the subsequent transition of the part of the electron density on the 3p_z-orbital of the aluminum atom. As a result the dissociation energy of the Al → CH_3 bond is stabilized. In the ethyl compound, the second carbon atom of the ethyl group impedes the shift of the electron density from the carbon atom contiguous to the aluminum, therefore the dissociation energy Al → CH_2–CH_3 is stabilized to a lesser degree than in the trimethylaluminum. It follows that the difference in the transmittance of the electron density from the carbon atoms of methyl and ethyl groups provides different stabilizing effect on the Al → C bond and increased negative charge ($-\delta_1 < -\delta_2$) on the methyl carbon atom of the ethyl group. Consequently, the latter methyl group forms a more stable specific intermolecular interaction, and the integral enthalpy characteristic of the ethyl compound is always larger than that of the methyl compound of the same element.

In the alkyl compounds of the elements from nitrogen and oxygen subgroups in connection with its electronegativity the shift of the electron density occurs along the alkyl chain occurs from the 2*s*-orbital of the carbon atoms of the alkyl group contacting with these elements to the orbitals of the atoms of these elements. The interacting carbon atoms of the chain in the ethyl, propyl, and other alkyl groups hamper the shift of the electron density from the carbon atom of the terminal methyl group. Consequently, the reverse transmission of the electron density occurs mainly on the contiguous carbon atom, and the carbon atom of the terminal methyl group in the ethyl and propyl substituent possesses a decreased negative charge and therefore has an increased acceptor power. As a result the bonds $N \leftarrow C$, $O \leftarrow C$ are destabilized, and the specific intermolecular interactions $N–CH_3 \leftarrow N$, $N–CH_2–CH_3 \leftarrow N$ are stabilized, and the enthalpy of vaporization and sublimation of ethyl and propyl compounds grows.

Just the increased integral value of vaporization enthalpy indicates the increased donor properties of the carbon atom of the terminal methyl in the ethyl, propyl, and butyl groups ($ZnMe_2$ – 30.4, $ZnEt_2$ – 38.8, $Zn(n\text{-}Pr)_2$ – 42.1, $Zn(n\text{-}Bu)_2$ – 50.7 kJ mol^{-1}) in the alkyls of the elements of the II–IV groups and the increased acceptor properties in the alkyls of the elements of the V–VI groups [27].

The understanding of this problem requires the rejection of the sp^3-hybridization and adoption of the formation of the dative bond between the carbon atom of the alkyl group and the donor-metals or elements-acceptors contacting with it and belonging, respectively, to II–IV and V–VI groups.

The essence of this hypothesis consists in the notion that the dative bond is formed by hydrocarbon substituents with the atoms of all nontransition elements; it stabilizes complexes AR_k and affects their physicochemical properties.

Actually, the sp^3-hybridization model is inconsistent already because due to its universalism it cannot explain the intramolecular bonds in organoelemental compounds, regularities in the changes of the thermodynamic parameters, and the specificity of the intermolecular interactions.

1.4 Reverse Dative Bond in Organometallic and Organoelemental Compounds

The versatile structures of organoelemental compounds are manifested in diversity of the intramolecular interactions. In the founder of the sandwich compounds of ferrocene with equal the interatomic distances Fe–C on conditions that of the ring C_5H_5 into the formation of the $Fe–C_5H_5$ bond is restricted by the π-shell three types of bonds are presumed to be involved: covalent, donor–acceptor, and dative [28]. This originates from the fact of the presence in the C_5H_5 of an unpaired π-electron, two vacant π-orbitals, and two unshared pairs of π-electrons. Semiempirical and ab initio calculations showed that the effective charge was distributed as $Fe^{+\delta}(C_5H_5)_2{}^{-\delta}$. Although the charge value depends on the calculation procedure and varies in the range $\delta = 0.6 - 1.3$ [28] no experimental data contradict to this scheme.

In the dibenzenechromium $Cr(C_6H_6)_2$, covalent bonds are lacking and only donor–acceptor and dative bonds are present. According to quantum-chemical calculations, the dominant role belongs to the dative bonds and the charge distribution is like $Cr^{+\delta}(C_6H_6)_2^{-\delta}$. The study of bonds Cr–C polarity in symmetrical sandwiches $Cr(C_6H_6)_2$ and $Cr(C_5H_5)_2$ confirmed the low polarity in the mixed sandwich $Cr(C_5H_5)(C_6H_6)$. This is caused by the close location of the energies of interacting electronic levels at the dative interaction Cr–C_6H_6, therefore the considerable charge transfer along this dative bond is facilitated. An analogous close location of the energy levels is observed in $Cr(CO)_6$, where the acceptor character of the $(CO)_3$ fragment is more pronounced than that of C_6H_6. The strong acceptor properties of the CO group are manifested in the cyclopentadienyl carbonyl complexes of manganese and iron. The positive charge on the metal atom grows in going from $Mn(C_5H_5)_2$ to $Mn(C_5H_5)(CO)_3$ simultaneously with the growing charge on the carbon in the C_5H_5 ring. The π-acceptor nature of the carbonyl ligand is the most pronounced. The main bond energy values in gaseous carbonyls and carbon monoxide [28] showed that at the coordination of the CO molecules, the energy both of electrons C(1*s*) and O(1*s*) decreased because the CO ligand acted as a strong electron acceptor and at the formation of the dative π-bond M → CO significantly more electron density was transferred on the antibonding π-orbital of the ligand than was shifted to the metal atom at the formation of the donor–acceptor σ-bond M ← CO.

The M–CO bonds in the carbonyl compounds are fairly strong and belong to the strongest bonds in organometallic compounds. This is seen from the values of the average dissociation energy (DM–CO) and the energy of the cleavage of one CO group (D_1) [29] (Table 1.3).

At the same time the formation of dative bonds M → CO due to the transfer of the *d*-electron density from the metal atom to the carbonyl group does not exclude the strong association of metal carbonyls in the condensed state and the stability of gaseous dimers $M_2(CO)_{2n}$ owing to the formation of metal–metal bonds [29]

Table 1.3 Dissociation energies (kJ mol^{-1}) of M–CO bond and of dimer molecules of metal carbonyls [29]

Metal carbonyls					
Dissociation energy	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	$Fe(CO)_5$	$Ni(CO)_4$
DM–CO	105	149	176	116	144
$D_1(CO)_{n-1}$ M–CO	152	167	190	171	102
Ddis. dimer $M_2(CO)_{2n}$	25.9	29.7	33.9	32.3	23.9

if non-two-electron type. The mentioned concise list of the well-based examples of organoelemental compounds with a dative bond does not include the compounds containing saturated hydrocarbon groups.

In the series of ligands with the π-acceptor properties $CO > C_2H_2 > C_2H_4 > PPh_3$ the latter belongs to weaker π-acceptor. It is obvious that the appearance of the π-dative bond in the presence of a σ-bond occurs in the organometallic compounds in the case of ligands containing double bonds. With respect to energy the strength of the dative bond decreases at the replacement of the triple bond in the molecule C_2H_2 by the double bond in the molecule C_2H_4. In event of a dative bond involving a methyl group, its contribution into the stabilization of M–C bonds would be less significant.

$$\begin{tikzcd} M \arrow[r] & C \arrow[l, bend right] \end{tikzcd}$$

The present idea that is not consistent with the current conceptions has not been formulated before not on account of the absence of experimental data. These data were abundant, but they contradicted the theory of the hybridization of valence atomic orbitals. However, it was suggested [28, 30] to extend both the hybridization theory and the theory of hypervalence bonds to the molecules where the coordination number of the central atom was ≤4, therewith for the hybridization only of the sp^3 type and for the nontransition elements of the first half of the period. The quantum-chemical calculations show [28] that the energy of the 2*s*-orbital of the carbon atom in methane is located considerably lower than the 1*s*-orbitals of hydrogen, and consequently in the CH_4 molecule two electrons $2s^2$(c) form an essentially unshared electron pair, and the C–H bonds arise mainly at the expense of the interactions 2*p*(C)–1*s*(H) [28]. Therefore, the C–H bonds in CH_4 belong to the type of orbital-deficient hypervalence and not to common covalence ones and the tetrahedral structure of the methane molecule is not due to sp^3-hybridization [28].

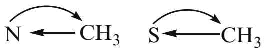
Therefore, the essentially unshared $2s^2$-electron pair of carbon atom is capable of formation of additional bonds, but these are less strong bonds than those formed by ethylene and especially acetylene with metal atoms. The general difference between acetylene, ethylene, and methane consists in the presence in the former of occupied (π) and vacant (π*) levels twice as much as in the ethylene, and the single carbon atom in methane (group CH_3 or R) possesses an essentially unshared electron pair. As a consequence, the acetylene and the ethylene form dative bonds with the atoms of transition metals having sufficiently large number of electrons (Pt, Ag). Inasmuch as the CO molecule possesses even more pronounced ability to form the dative bond $\begin{tikzcd} M & C \arrow[l, bend right] \end{tikzcd}$, its interaction with the atoms of transition elements extends to the elements with d^4-electrons (Cr, Mo, W). The presence of the given two types of bonds stabilizes the energy of the intramolecular interaction $\begin{tikzcd} M \arrow[r] & CO \arrow[l, bend right] \end{tikzcd}$. However, the elements of the zinc subgroup (d^{10}-electrons) do not form such bonds. The difference consists in that the latter metals belong to the nontransition elements whose energy levels of *nd*-orbitals are situated by 10–15 eV higher, and the energies of p^3-orbitals by 10–20 eV lower as compared to the energies of valence *nd*-orbitals, the most important for binding the ligands. In other words, in the atoms of nontransition elements the energies *nd*–*np* and *np*–*ns* are widely separated, often by over 10 eV (in elements of V–VIII groups), and the difference in energies grows with the group number [30]. In typical ligands, the energies of the valence orbitals are as a rule somewhat lower than the energies of the valence *np*-orbitals of the elements of the main V–VIII groups. The vacant *nd*-orbitals of the central atom in the molecules of the coordination compounds of nontransition elements proved to be located at the orbitals of ligands. In the case of compounds of the fourth group elements, germanium, tin, and lead exist reliable data that their *nd*-orbitals take part in binding the ligands [28].

CH_4	4.3	NH_3	4.07	OH_2	4.79
CF_4	5.1	NF_3	2.9	OF_2	2.17

However, it corresponds to more fine contributions of the *nd*-orbitals. The same reasons sometimes impede the involvement of the valence s^2-electrons of the central atom into the bond formation: their energy frequently proves to be too low as compared to the energy of the valence orbitals of ligands [30]. However, another pattern is observed in compounds of carbon with fluorine. This is due to the fact that the energy level of the 2*ps*-orbital of fluorine is closer to the energy of 2*s*-orbitals of carbon, whereas the level of the 1*s*(H) is significantly higher than the energy level 2*s* of the carbon atom. Therefore, in the CF_4 molecule also $2s^2$-valence electrons of the carbon take part in the formation of bonds with fluorine, and thus the CF_4 molecule contains four covalent C–F bonds. Based on the growth of the mean energy (eV) of the two-center bond in going from CH_4 to CF_4, Korol'kov [30] concluded on transition from the hypervalent molecular structure in CH_4 to CF_4 structure with four covalent and respectively stronger bonds. The important point here is that the energy levels of 2*p*-orbitals of the nontransition elements are located far nearer to the carbon 2*s*-orbital than the energy levels of 1*s*(H) and 2*s*(C) orbitals. Inasmuch as in the carbon atom of the methyl group, $2s^2$-electron pair remains essentially unshared, depending on the direction of the electron density shift in the bonds M–C and E–C the carbon atom is capable to act as a donor or an acceptor due to the relative deficit or excess of the electron density. For instance, in methyl compounds of the elements of subgroups of zinc, aluminum, or germanium a significant shift of the electron density to the carbon atom should occur. In the formation of these compounds, the carbon atom of the methyl group obtaining an excess of electron density by the bond Al → C transfers a part from $2s^2$-electron pair to the free p_z-orbitals of the atoms of the elements $\mathrm{Al}\overset{\curvearrowleft}{\longrightarrow}\mathrm{C}$ forming a reverse dative bond. To the distribution of the electron density in the molecule of $B(CH_3)_3$ corresponds a negative charge on the carbon (−0.525e) and positive charge on the boron (0.704e), whereas in the $O(CH_3)_2$ molecule the negative charge is on the oxygen atom (−0.228), and positive one on each methyl group (0.114) [19, 23].
Similar situation should occur in the methyl compounds of all elements of the zinc, boron, and silicon subgroups, and also in compounds of oxygen and nitrogen with

the distinction that the definite involvement of the essentially unshared $2s^2$-electron pair of carbon should be different.

As mentioned earlier, in going to the elements of the fifth and sixth groups the electronegativity of the element atoms increased, and therefore the essentially unshared $2s^2$(c)-electron pair of the methyl group acts as an acceptor in the formation of the reverse dative bond.



However, based on the value of the charge on the nitrogen atom (+0.024e) [23] or on oxygen (−0.228e) [24] it is not possible to estimate the contribution of the reverse dative bond into the strengthening of the N–CH_3, O–CH_3 bonds since the number of the transferred electrons is unknown. Yet the fact of the positive charge on the nitrogen atom indicates the considerable contribution of the reverse dative bond into the value of the dissociation energy of the N–CH_3 bond.

Hence, the reverse dative bond in the alkyls of the elements of the main groups is essentially different from the existing bond of analogous nature in the acetylene and ethylene compounds with the transition elements.

Limiting ourselves to the above description concerning the studied electronic structure of certain organometallic and organoelemental compounds we shall in the next section turn to a more detailed analysis of the results of quantum-chemical calculations of a number of methyl compounds of the elements from the aluminum and silicon subgroups.

1.5 Electronic Configurations of Alkyl Compounds and Inconsistency of the sp^3-Hybridization Model

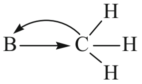
The first reliable quantum-chemical calculations of the electron density of the $2s$, $2p_x$, $2p_y$, $2p_z$, and $3s$, $3p_x$, $3p_y$, $3p_z$-orbitals of boron and aluminum in the molecules AR_k were performed by Hückel method [31] using the modification developed by Hoffmann [32, 33]. In this method, the orbital is regarded as a linear combination of atomic orbitals of all valence electrons of the atoms in the molecule. Obviously, this version of the Hückel method does not utilize the hybridization and the orientation of the orbitals. The results of these calculations have a fundamental importance for they contain the necessary information on the electronic population of the p_z-orbital of the boron and aluminum atoms (Table 1.4).

Table 1.4 Electronic populations of atomic orbitals of central atom in molecules AR_k [23]

Orbital	BH_3	AlH_3	$B(CH_3)_3$	$Al(CH_3)_3$
s	0.912	0.812	0.812	0.505
p_x, p_y	0.825	0.497	0.552	0.206
p_z	0.0	0.0	0.140	0.111

The zero electronic population of the p_z-orbitals of the boron and aluminum in the hydrides AH_k reveals that the hydrogen atom is incapable or nearly incapable to transfer the electron density to this orbital. Consequently, in the molecule BH_3 and AlH_3 the $2p_z$ and $3p_z$-orbitals of the boron and the aluminum remain unpopulated [34], and the reverse dative bond does not operate apparently due to the considerable energy difference between these levels and the 1*s*-level of the hydrogen atom. However, the electronic population of the p_z-orbital of the boron and aluminum in the AR_k molecule is 0.149 and 0.111 electron, respectively. This result shows the ability of the carbon atom of the methyl group to take part in the formation of the reverse dative bond, and this ability is incomparable with that of the hydrogen atom. Later quantum-chemical calculations [35] taking into account all electrons of the boron atom in the BH_3 molecule found some electronic population of the p_z-orbital of the boron atom (0.029), although lower than in the $B(CH_3)_3$ molecule. The high electron-acceptor property of boron and aluminum atoms is usually ascribed to the nearly unpopulated p_z-orbital atoms of these elements and the presence there of a high positive charge. The occupancy of the p_z-orbital of the boron (0.140) and aluminum (0.111) atoms in the molecules of $B(CH_3)_3$ and $Al(CH_3)_3$ shows the donor property of the carbon atom of the methyl group and the lower acceptor quality of aluminum atom compared to boron. These results raise doubts of adequacy of description of the nature by the model of the sp^3-hybridization of the carbon atom.

Hence the reverse dative bond of the carbon atom of the methyl group is substantiated by the calculations of the electron density distribution in the molecules of $B(CH_3)_3$ [23] and $Al(CH_3)_3$ [36]. In the $B(CH_3)_3$ molecule the boron atom operates as a strong π-acceptor, the boron p_z-orbital in $B(CH_3)_3$ acquires 0.3 electron, and the source of this charge is predominantly the carbon atoms of the methyl groups, namely, a covalent [19] and a reverse dative bond form.



As a result the bond in $B(CH_3)_3$ is stabilized, and the excess charge on the methyl group is reduced. Consequently, the carbon atom of the methyl group possesses a weaker dative property (and the boron, a weaker acceptor property) in the formation of intermolecular bonds $B–CH_3 \rightarrow B$ in the liquid trimethylboron. In the trimethylaluminum, the p_z-orbital of the aluminum atom obtained 0.111 electrons from the carbon atoms of the methyl groups, and the reverse dative and covalent bonds are also formed.

The important feature of the performed quantum-chemical calculations [35] consists in the statement that the electron density distribution in the BH_3CO molecule is accompanied by the transfer of about 0.23 electrons from the carbon atom of the carbon monoxide to the proper p_z-orbital of the boron atom in the BH_3 molecule decreasing thus its positive charge. The electron transfer occurs mainly through an essentially unshared 2*s*-electron pair of the carbon atom to the p_z-orbital

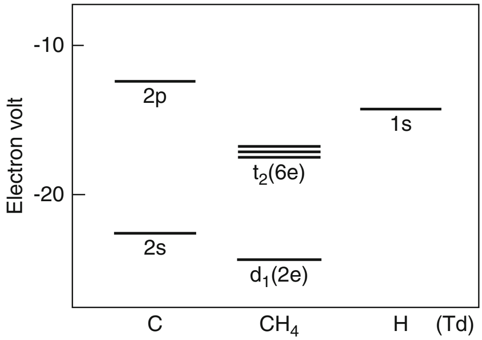


Fig. 1.1 The arrangement of 2s-, 2p-levels of carbon atom and 1s-level of hydrogen atom

of boron. Due to the electron transfer the carbon atom acquires a positive charge, and the boron atom, a large negative charge ensuring the reverse dative bond and a stable B–C bond.

The quantum-chemical calculations of the electronic structure of methane [28] showed that the 2*s*-level of the carbon atom was localized significantly lower than the 1*s*-level of hydrogen, therefore the $2s^2$-electron pair of the carbon atom remained essentially unshared (Fig. 1.1). Therefore, the bonds in the methane molecule formed as a result of the interaction $2p_C$–$1s_H$ and consequently the C–H bond belongs rather to the orbitally deficient hypervalent than to the common covalent bonds [28]. Since at the interaction of σ-orbitals of equivalent hydrogen atoms in the CH_4 molecule with three *p*-orbitals (Cartesian) the tetrahedron configuration is more feasible, the existing geometry of the CH_4 molecule is not necessarily connected with the sp^3-hybridization. Therefore, the essentially unshared 2*s*-electron pair of the carbon atom is capable of additional interaction alongside the four valence bonds providing the five-coordinated state of the carbon atom.

The lack of more informative quantum-chemical calculations of the electronic structures of AR_k molecules required more extensive research with the use of the modern approaches [37–44]. Nonempirical quantum-chemical calculations of the electronic structures of the trimethyl derivatives of nontransition metals $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$, of $Al_2(CH_3)_6$ dimer, and $[Tl(CH_3)_3]_4$ tetramer [37] were performed with the use of two methods: restricted Hartree–Fock (RHF) and Becke–Lee–Yang–Parr (B3LYP) that was a version of the density functional theory (DFT) based on three-parameter functional including exchange and correlation contributions (local and nonlocal). Ab initio calculations by RHF method in the bases MINI and 6-31G* were carried out by GAMESS program [45, 46], and the ab initio calculations by B3LYP method were performed in the bases 6-31G* and LanL2DZ using GAUSSIAN-94 software [47].

The estimation of the accuracy of the results of the quantum-chemical calculations was done by evaluation of the internuclear distances between the metal and the carbon and the bond angles in $A(CH_3)_3$, $A(CH_3)_4$. The values of *R* (A–C) and bond angles calculated in all the three atomic bases were fairly consistent with the experimental data for all investigated methyl derivatives. Therewith obviously the theoretically established geometrical structure of each compound was the same as found experimentally, for instance, symmetry point group C_{3v} for $Al(CH_3)_3$. The performed quantum-chemical calculations of $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$, dimer $Al_2(CH_3)_6$, tetramer $[Tl(CH_3)_3]_4$, and methane CH_4 provided the most important characteristics of the electronic structure: total energy (E), one-electron energies of the valence MO(ε), efficient atomic charges (q) corresponding to the overall electronic population of the valence orbitals of the atoms (V), multiplicity indices of two-center bonds (W), spatial distribution of the valence electron density. The values calculated by different methods are in good agreement; in total, RHF data and B3LYP data for three different bases (MINI, 6-31G*, LanL2DZ) are similar. The data obtained by the RHF method in different atomic bases are very close, those obtained by B3LYP method in bases LanL2DZ and 6-31G* are lesser and greater than the RHF data respectively, therefore we further use in the discussion the RHF data.

The directly calculated characteristics of the valence electronic structure of the trimethyl derivatives $A(CH_3)_3$ show the presence of the contribution from the configuration originating from the hypervalent interactions in the $A–CH_3$ fragment alongside the configuration of the covalent interactions corresponding to the sp^3-hybridization scheme of the valence orbitals of the carbon atom in CH_3. Consequently, in the valence electronic structure of $A(CH_3)_k$ one of the electron pairs of each fragment $A–CH_3$ is localized predominantly on the C atom and thus the possibility exists of the formation in the subsequent intermolecular interactions of the dative bond $C(2e) \rightarrow A(0e)$. In the valence electronic structure of compounds $[A(CH_3)_k]_n$ with bridging CH_3 groups, e.g., in the dimer $Al_2(CH_3)_6$ and tetramer $[Tl(CH_3)_3]_4$, the multiplicity indices of the two-center bonds $A–C_b$ between the atoms A and bridging carbon atoms C_b are nearly the same as the multiplicity indices of the two-center bonds $A–C_t$ with the terminal carbon atoms C_t (in particular, $W_{Al–C(b)} = 0.87$, $W_{Al–C(t)} = 0.89$). It means that in the three-center fragment $A–C_b–A$ one two-center bond is formed in the same way as that with the terminal CH_3-group ($A–C_t$) (Fig. 1.2), and another one is the mentioned dative bond $C(2e) \rightarrow A(0e)$.

Therefore, the results obtained show that in the electronic structure of dimeric and tetrameric derivatives $[A(CH_3)_k]_n$ including bridging CH_3 groups the dative bonds under discussion are really existing.

Dative bond between the carbon atom C of the alkyl group R and the central atom A in compounds AR_k $C(2e) \rightarrow A(0e)$ may form involving, on the one hand, the valence electron pair of the carbon atom (in particular, $2s^2$(c)-electron pair), more properly, by the electron pair of the alkyl group R localized prevailingly on the carbon atom, and on the other hand, involving the vacant orbital localized

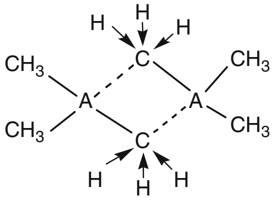


Fig. 1.2 Dimer molecule of trimethylaluminum

predominantly on atom A. In the form of the latter may appear, firstly, unoccupied one-center valence orbital of atom A or, secondly, the free multicenter orbital of compound AR_k, for instance, the free valence MO nonbonding or weakly antibonding with respect to the bonds A–R with the sufficiently low energy. These assumptions are based on the following statements. Firstly, even in the CH_4 molecule the valence $2s^2$-electron pair remains essentially localized on the C atom, and only two electrons (of the four valence electrons) of the C atom on its three valence AO $2p_x$, $2p_y$, $2p_z$ effectively take part in the hypervalent (electron-deficient) C–H bonds with all four hydrogen atoms (for the tetrahedron symmetry point group it is fully consistent with the group theory requirements). Therefore, it is probable that the same feature (the conservation of the pseudoatomic $2s^2$(c)-electron pair) is also characteristic of the electronic structure of the methyl group attached to atom A (A–CH_3) where the carbon atom forms four bonds (one C–A and three C–H) also employing two electrons on its three valence AO $2p_x$, $2p_y$, $2p_z$, moreover, due to the fact that the orbital negativity of the A atom at least does not exceed that of the hydrogen atom. Secondly, the electronic structure of carbonium cation $[CH_5]^+$ may be the most easily described by the combination of the hypervalent bonds like in the methane CH_4 between the carbon atom and four H atoms with the fifth dative bond of carbon with a hydrogen cation (formally) formed by the valence electron pair of the C atom and the vacant orbital of the hydrogen cation. Analogous structures belong to the other complexes of the pentacoordinate carbon discovered in the recent decade. Thirdly, the proper existence of methyl derivatives with the bridging (μ_2) CH_3 groups in the classic example of the $Al_2(CH_3)_6$ requires the presence in their structure, same as in the carbonium cation, of the pentacoordinate carbon atom. In the electronic structure of the bridging μ_2CH_3 group linked simultaneously to two A atoms, the carbon atom formed four bonds (with its three H atoms and one A atom) in the same way as does the terminal CH_3 group bonded to a single A atom, namely, using only two of its electrons on its valence AO $2p_x$, $2p_y$, $2p_z$. The fifth bond with the second A atom the carbon atom of the bridging μ_2CH_3 group formed apparently by the dative mechanism at the expense of its valence $2s^2$-electron pair and the vacant orbital of this A atom. Inasmuch as the tetrahedron configuration is the most feasible for the interaction of the σ-orbitals of the four equivalent substituents with the three Cartesian p-orbitals of the central atom, the considered geometry of CH_4 is not at all connected with the sp^3-hybridization [33]. Finally, fourthly, the constantly revealed experimentally efficient intermolecular interactions in alkyl (in particular, in methyl) compounds of the nontransition elements are fundamentally underlain by the same phenomena [38–44].

The energy of the interaction involving the pentacoordinate carbon atom in the $Al_2(CH_3)_6$ dimer proved to be high. We measured it from the dissociation enthalpy of the process $Al_2(CH_3)_6 = 2Al(CH_3)_3$ where two bridging bonds Al–CH_3–Al were broken (Fig. 1.3). Their energy of 44.2 ± 0.9 kJ mol^{-1} [48, 49] is four times larger than the energy of the hydrogen bond in liquid water. The revealed effective intermolecular interactions in the liquid alkyls of the elements of the main groups and their energies measured by thermodynamic properties are underlain by the operation of the essentially unshared $2s^2$-electron pair of carbon atom. The energy

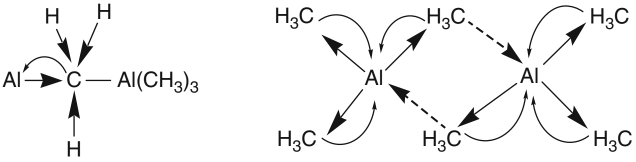


Fig. 1.3 Reverse dative bonds in dimer molecule of trimethylaluminum

of the intermolecular interactions significantly depends on the reverse dative bond existing in the molecules of the alkyl compounds (Fig. 1.3).

The divergence of the regular variations in the experimentally measured thermodynamic characteristics of the main groups elements from the properties predicted by the model of the sp^3-hybridization, the involvement of the essentially unshared $2s^2$-electron pair of the carbon atom in the dative bond and in the formation of stable specific interactions with the participation of the pentacoordinate carbon atom, the existence of dimer molecules and of the reverse dative bond in the alkyl molecules demonstrate the inconsistency of the above mentioned model [12].

Proceeding from the theoretical investigations C.A. Coulson regarded the model of the sp^3-hybridization not as a real phenomenon in the same way as the resonance structures. The advantage of the hybridization concept consisted in the conservation of the notion of a localized bond and of the coupling of two atoms involved into the formation of the bond [50]. The rejection of the sp^3-hybridization model is the route to the theory of the specific interactions in liquid and solid state, of molecular solutions; it leads to the development of the theory of the dative bond in organic and organoelemental compounds, in functional solvents. The thermodynamic aspects of the reverse dative bond were developed in [51–58].

1.6 Reverse Dative Bond and Steric Effect in Alkyls and Molecular Complexes

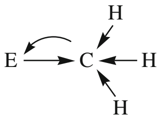
The notion of the dative bond in alkyl compounds [52, 59–61] confirmed by the quantum-chemical calculations of the electron density distribution finds its support and development in the mean dissociation energies of the element–carbon bond in the alkyl compounds obtained from the experimentally measured enthalpies of formation (Table 1.5). The maximum capability to the formation of a reverse dative bond should belong to the alkyl compounds with a methyl group, therefore they possess the highest mean dissociation values (Table 1.5). The replacement of the methyl by an ethyl group with a C–C bond affects the capacity of the carbon atom in contact with the atom of the nontransition element for the electron transfer from the $2s^2$ orbital of this carbon to the p_z-orbital of the atoms of the elements of the third and fourth groups and from the p_z-orbital of the atoms of the elements of the fifth

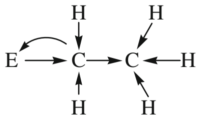
Table 1.5 Dissociation energies (kJ mol^{-1}) of element–carbon bond in alkyl compounds of II–VI groups [3, 16]

Compounds	DE–CH_3	DE–C_2H_5	Δ = DE–CH_3 − DE–C_2H_5
CdR_2	146 ± 4	113 ± 4	33.0
BR_3	379.9	344.5	29.4
AlR_3	283.3	272.6	10.7
GaR_3	256.4	224.9	31.5
GeR_4	258.2	242.9	15.3
SnR_4	226.4	194.7	31.7
PbR_4	161.4	129.6	31.7
NR_3	311.8	296.7	15.1
PR_3	285.5	230.2	55.3
AsR_3	238.4	185.9	52.5
SbR_3	223.5	179.8	43.5
OR_2	362.9	358.7	4.2
SR_2	303.6	293.5	10.1

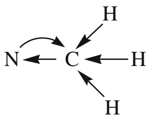
and sixth groups to the $2s^2$ orbital of the carbon. Therefore, in these molecules the mean dissociation energies of the bond element–ethyl are always less than the mean dissociation energies of the bond DE–CH_3 (Table 1.5). Consequently, the difference Δ = DE–CH_3 − DE–C_2H_5 may be taken as a measure of the energy contribution of the reverse dative bond stabilizing the dissociation energy E–CH_3 in $E(CH_3)_n$ and E–C_2H_5 in $E(C_2H_5)_n$. This value of the stabilization energy of the E–CH_3 bond may be regarded as the relative value of the contribution of the reverse dative bond comparable for all alkyl compounds.

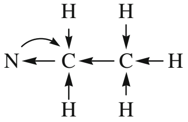
It is difficult to draw a clear distinction between the distribution of the electron density in the molecules of alkyl derivatives from the atoms of the elements of the II and IV groups and the reverse dative bond from the carbon atom, and also





from the atoms of element of the V and VI groups to the carbon atom since these effects supplement each other.





Nonetheless, the differences in the dissociation energies of the bonds E–CH_3 and E–C_2H_5 reflect the influence of the second carbon atom of the alkyl group on the participation in the dative bond of the essentially unshared $2s^2$ electron pair of the carbon atom contacting with the atom of the corresponding element.

The lesser difference in the dissociation energies DE–Me – DE–Et in the nitrogen alkyls compared with the alkyls of phosphorus and arsenic (Table 1.5) is due to the weaker reverse dative bonds in the nitrogen compounds because of its lower donor ability. The low positive charge instead of negative one on the nitrogen atom (+0.024) and negative charge on each methyl group (−0.008) suggests the insignificant difference in the electronic occupancy in the triethylamine molecule. Even lesser difference in the dissociation energies of oxygen alkyls (4.2 kJ mol^{-1}) suggests the conclusion that the electron density distribution in dimethyl ether and diethyl ether differs insignificantly. Just this fact prevented obtaining reliable information in the framework of the approximations of the Gallais method [32] for the charges on oxygen, carbon, and hydrogen in the molecules of these compounds. On the contrary, significant difference in the electron density distribution is expectable for the methyl and ethyl compounds of phosphorus, arsenic, and also of antimony, tin, lead, boron, and gallium. The growth of the donor ability in the pair oxygen–sulfur is manifested in the difference in the energies of dissociation of bonds DS–Me − DS–Et = 10.1 kJ mol^{-1} compared to 4.2 kJ mol^{-1} in analogous oxygen compounds. Therefore, the large values of the dissociation energy of O–R bonds are caused by the shift of the electron density from the carbon atom to the oxygen. Inasmuch as the energy difference of the $2s^2$ level of the carbon atom and the *p*-orbitals of the elements grows in the series P–As–Sb, O–S–Se–Te, consequently the role of the reverse dative bond diminishes in going from arsenic to antimony.

Hence the difference in the dissociation energies of DS–Me and DS–Et is subjected to the influence of opposite effects. Its growth in going from NR_3 to PR_3 indicates the prevailing role of the reverse dative bonds, whereas the decrease in this value shows the essential diminishing influence of the dative bond due to the

Table 1.6 Dissociation energies (kJ mol^{-1}) of element–carbon bond in alkyl compounds of zinc, boron, and germanium subgroup elements

Compounds	DE–R		
	Zn–R	B–R	Ge–R
$M(CH_3)_n$	182 ± 1	371 ± 4	258.2 ± 3
$M(C_2H_5)_n$	151 ± 4	353 ± 2	242.9 ± 4
$M(C_3H_7)_n$	165 ± 12	360 ± 4	242 ± 2
$M(C_4H_9)_n$	162 ± 12	356 ± 2	247 ± 8
$M(C_6H_{13})_n$	–	343 ± 8	–
$M(C_7H_{15})_n$	–	343 ± 8	–
$M(C_8H_{17})_n$	–	343 ± 8	–
	Hg–R	Te–R	Sn–R
$M(CH_3)_n$	125 ± 1	217 ± 6	222 ± 4
$M(C_2H_5)_n$	109 ± 1	195 ± 6	192 ± 4
$M(C_3H_7)_n$	106 ± 1	199 ± 5	197 ± 8
$M(C_4H_9)_n$	–	195 ± 5	197 ± 4
$M(C_5H_{11})_n$	–	198 ± 5	–

increased difference between the energies of the *p*-orbitals of P $>$ As $>$ Sb and the energy of the $2s^2$-orbital of carbon.

The next important statement demonstrates that in going from methyl to ethyl and further to *n*-propyl, *n*-butyl compounds the mean dissociation energy M–R (E–R) decreases to the values negligibly varying after a distinct "*n*" index value (number of the carbon atoms in the alkyl group) (Table 1.6).

This fact indicates directly that, firstly, the growth of the number of carbon atoms in the alkyl group after a certain number (no more than three) virtually does not affect the electron density distribution between the central atom and carbon atom (and hydrogen) contacting with it, and secondly, that the growth of the number of carbon atoms in the alkyl group after a certain number (no more than three) virtually does not affect the change in the dissociation energy and the contribution of the reverse dative bond into the vaporization enthalpy and consequently into the energy of the intermolecular interaction. It should be here taken into consideration that the displacement of the electron density in an alkyl chain depends on the presence in the middle of the chain of an even and odd carbon atom [29]. This factor should affect the dissociation energy of the A–R bond as seen to a certain extent from the data in Table 1.6. However, in this case we mean finer effects masked by the accuracy in the determination of the dissociation energies of the A–R bonds. We shall consider this problem further by the example of the intermolecular interactions in the liquid alkyl compounds. The comparison of mean bond dissociation energies in the series of alkyls of the same element (Table 1.6) leads to a conclusion that their values decrease in going from the methyl to the ethyl compound and further to propyl, butyl, and up to octyl derivatives these values remain virtually constant.

The dissociation energies in propyl, butyl, and more complex compounds are not different to such extent that we would not be able to assume the equal contribution of the reverse dative bond in all these compounds into the dissociation energy. Therefore, it becomes clear that the length of the alkyl chain with more than three carbons does not affect the dissociation energy of the A–C bond. Consequently, the growing length of the carbon chain of the alkyl group does not produce a steric effect and does not affect the stability of the compound. Since the decrease in the dissociation energy in going from the methyl to the ethyl compound is accompanied with the weakening of the reverse dative bond, the steric effect may exist only between the carbon atoms contacting with the central atom of the compound AR_k. In other words, the notion of the influence of the steric effect at the growing number of the carbon atoms in the alkyl chain on the decrease in the dissociation energy in the series $Zn(CH_3)$–$Zn(n\text{-}C_4H_9)$, $Sn(CH_3)_4$–$S(n\text{-}C_4H_9)$, $Te(CH_3)_2$–$Te(n\text{-}C_4H_9)$ is incorrect. We illustrate these statements by the examples reflecting the fundamental difference in the mean values of the dissociation energy of A–C bond, selecting a molecule with a smaller radius of the central atom.

Figure 1.4 demonstrates the endoeffect of coordination at the successive increase in the number of hydrogen atoms in BH_3 whose covalent radii according to Pauling [62] amount to 0.34 and 0.30 Å. The dashed line drawn from the origin through the dissociation energy of the first hydrogen atom located in the flat structure of

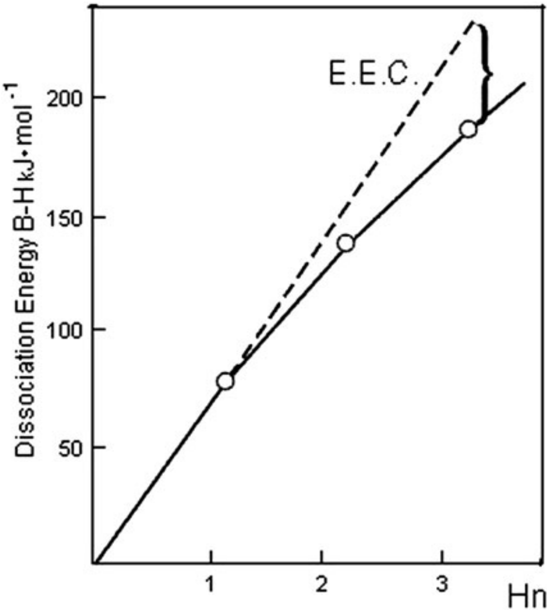


Fig. 1.4 Dependence of the dissociation energy B–H from the number of hydrogen atom in molecule BH_3

an equilateral triangle illustrates the changes in the dissociation energy in the series $BH > BH_2 > BH_3 > BH_4$ at the absence of the steric effect. Therefore, the difference between the extrapolated values (dashed line) and the experimentally obtained dissociation energies of B–H bonds (continuous line) corresponds to the magnitude of the coordination endoeffect in this case of hydrogen atoms.

The endoeffect value at the successive addition of two and three hydrogen to boron atom resulting in a flat triangular structure amounts to 8 and 22 kJ mol^{-1}, respectively, and at the addition of the fourth hydrogen atom, 35 kJ mol^{-1}.

In a flat molecule of trimethylboron at the same covalent radius of boron and the radius of the carbon atom of 0.77 Å, the coordination effect increased twice compared with analogous effect in the BH_3 molecule and amounts to 18 and 48 kJ mol^{-1} in $B(CH_3)_2$ and $B(CH_3)_3$, respectively. It means that the increased radius of the coordinated carbon atom directly interacting with boron results in growing of the Coulomb interaction between the carbon atoms of the methyl groups. Consequently, the distance between the coordinated atoms and the central boron grows from $r_{B\text{–}H} = 1.16$ Å to $r_{B\text{–}C} = 1.578$ Å [63]. The successive addition of the second, the third, and the fourth methyl group to the nitrogen atom with a covalent radius 0.70 Å resulted in the growth of the coordination endoeffect from 19 to 50 and 115 kJ mol^{-1}, respectively. Thus, the double increase in the radius of nitrogen compared to boron and reduced interatomic distances in the trimethylamine molecule $r_{N\text{–}C} = 1.451$ Å [63] practically does not lead to any difference in the coordination endoeffect of the methyl groups in the trimethylboron and trimethylamine.

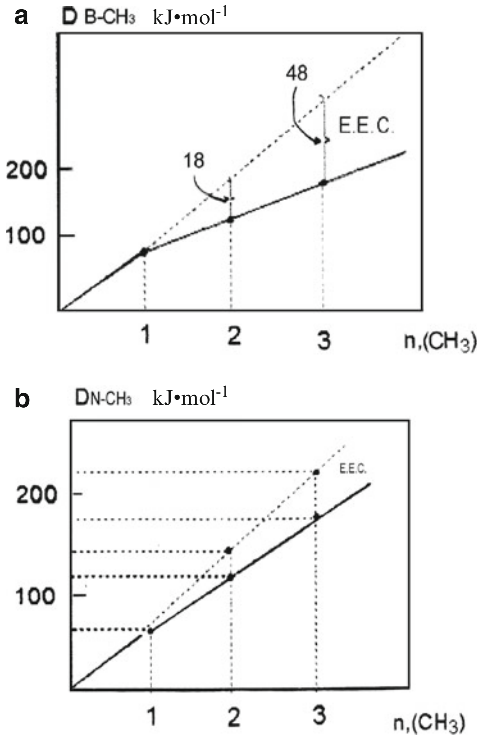


Fig. 1.5 Dependence of the dissociation energy B–CH_3 (**a**) and N–CH_3, (**b**) in molecules $B(CH_3)_3$, $N(CH_3)_3$ on the number of methyl groups, and the coordination endoeffect

An important fact consists in the equal value of the endoeffect in a flat molecule of $B(CH_3)_3$ and a trigonal pyramid of $N(CH_3)_3$ with the location of the methyl groups in the base forming a equilateral triangle. In these molecules are also different interatomic distances $r_{B–C} = 1.578$ Å and $r_{N–C} = 1.451$ Å. These facts lead to a conclusion that in the steric effect are involved only the atoms directly linked to the boron or nitrogen, hydrogen atoms in the BH_3, and only carbon atoms of methyl groups in the trimethylboron and trimethylamine (Fig. 1.5).

Hence the mean values of the dissociation energies of alkyl compounds listed in Table 1.6 include the steric effect contributed by the carbon atom contacting with the central atom of the compound AR_k.

The decrease in the donor properties of the carbon in the ethyl group of triethylamine originates from the effect of the second carbon atom of this group, therefore the cleavage energy of the ethyl group should be lower than the dissociation energy of the methyl group in the trimethylamine. In its turn the coordination endoeffect of the ethyl groups situated in the equilateral trigonal base of a pyramid structure additionally contributes to the value of the dissociation energy. Consequently, the donor properties of nitrogen atoms should decrease in the series $N(CH_3)_3$, $N(C_2H_5)_3$, and $N(C_3H_7)_3$. It follows from the analysis of the dissociation energy of the N–R bond (Table 1.6) that starting with the propyl compound these values vary insignificantly and therefore the propyl, butyl, and more complex

Table 1.7 Dissociation energy of bond B–N (kJ mol^{-1}) in alkyl complexes

Bond	Complexes				
	$H_3BN(CH_3)_3$	$(CH_3)_3BNH_3$	$(CH_3)_3BNH_2(CH_3)$	$(CH_3)_3BNH(CH_3)_2$	$(CH_3)_3BN(CH_3)_3$
DB–N	136.8	57.8	73.7	80.8	73.7

alkyl groups are characterized by hardly differing donor properties and ensure the equivalent electron density distribution in the NR_3 molecules. By the same reasons the steric effect observed in the base of the trigonal pyramidal structure of these molecules originating from the carbon atoms contacting with nitrogen should not interfere with the interaction of NR_3 molecules with the acceptor molecules BR_3. The high energy of the donor–acceptor bond in the complex $H_3BN(CH_3)_3$ should be attributed also to the high positive charge on the boron atom in BH_3. The energy of the donor–acceptor interaction between BR_3 and NR_3 is also due to the donor properties of nitrogen in the triamines which are partially consumed in overcoming the endoeffect of the fourth ligand coordination, in this case, of the nitrogen atom of the triamine, in the forming complex (Table 1.7).

The comparison of the energy levels of the core and valence electrons of the H_3BAR_k complexes showed that in the reaction of BH_3 with NH_3 and $N(CH_3)_3$ occurred a strong σ-interaction. It was demonstrated by the X-ray electron spectroscopy that the replacement of the hydrogen atom in NH_3 by the methyl group resulted in an insignificant decrease in the electron density on the nitrogen atom [64]. Nonetheless, the change of a single hydrogen for a methyl group in the NH_3 molecule sharply stabilized the complex, and that should be attributed to the shift of the electron density on the p_z-orbital of the boron atom governing the B–N in this complex. The replacement of the second hydrogen atom in the NH_3 molecule by a methyl group affects to a lesser extent the complex stabilization, and the substitution of the last hydrogen results in a slight destabilization. Thus, the destabilization of the B–N bond is due to the increased coordination endoeffect of carbon atoms in the fragment $N(CH_3)_3$ of the $(CH_3)_3BN(CH_3)_3$ complex in the base of the pyramidal structure of the trimethylamine and to the lower ability of the methyl group of this fragment to transmit the electron density as compared to the hydrogen atom. This resulted in a certain decrease in the charge on the nitrogen atom. At the replacement of three hydrogen atoms in the ammonia molecule by methyl groups, the positive charge on the nitrogen in $N(CH_3)_3$ amounts to +0.024e [25, 65, 66] (Fig. 1.6).

Due to the formation of the complex $(CH_3)_3BN(CH_3)_3$ the positive charge on the nitrogen grows by 0.792e. The charge on the boron atom decreases by 0.441e, and 0.293e is located on its p_z-orbital [19]. The electron density distribution in the complex is characterized by the location of 0.25e on the p_z-orbital of boron.

A special attention attracts the complexes with NH_3 where one hydrogen is replaced with alkyl groups with the normal or branched structures. The insignificant difference in the dissociation energies of the trimethylboron complexes with primary amines NH_2R containing methyl, ethyl, isopropyl, and *sec*-butyl groups illustrate the trend in their variation. This trend in its turn reveals the stabilization of the complex at the replacement of the methyl group by ethyl in the molecule of the

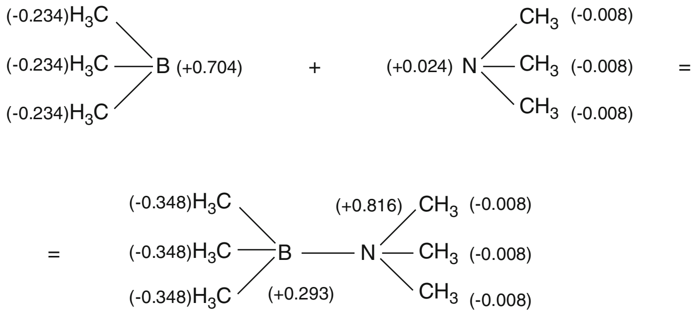


Fig. 1.6 Charge distribution in complexes $(CH_3)_3BN(CH_3)_3$, $N(CH_3)_3$, and $B(CH_3)_3$

Table 1.8 Dissociation energy of bond B–N (kJ mol^{-1}) at isostructural alkyl complexes

Complex	Bond DB–N	Complex	Bond DB–N
$(CH_3)_3BNH_2(CH_3)$	73.7	$(CH_3)_3BNH_2(i\text{-}C_4H_9)$	72.4
$(CH_3)_3BNH_2(C_2H_5)$	75.3	$(CH_3)_3BNH_2(tert\text{-}C_4H_9)$	52.4
$(CH_3)_3BNH_2(i\text{-}C_3H_7)$	72.8	–	–

primary amine due to the shift of relatively larger electron density from the ethyl group to the nitrogen atom as compared to the effect of the methyl group in the $(CH_3)_3BNH_2(CH_3)$. However, the replacement of the ethyl group by the isopropyl in the complex $(CH_3)_3BNH_2(i\text{-}C_3H_7)$ containing also same as ethyl two-carbon chain results in the decrease in the dissociation energy. Further replacement of the isopropyl group by the isobutyl moiety with the increase of the chain length to three carbon atoms is not accompanied with the larger shift of the electron density in the three-carbon chain, and the dissociation energy of these complexes remains unchanged. The location of two methyl groups on the carbon atom in contact with the nitrogen in the *tert*-butyl moiety of the complex $(CH_3)_3BNH_2(tert\text{-}C_4H_9)$ results in the reduction of the donor properties of the two-carbon chain to a great extent leading to a decrease in the dissociation energy by 22.9 kJ mol^{-1}. Thus, the isostructural methyl groups of the isopropyl, isobutyl, and *tert*-butyl moieties hamper the shift of the electron density to the nitrogen along two-carbon and three-carbon alkyl chains resulting in the decrease in the negative charge and donor properties (Table 1.8).

The comparative analysis of the electronic structure of trimethylaluminum and trimethylboron [64] by the method Xά-PB showed insignificant contribution of the Al $3p_z$-orbital into the π-MO and a large charge on the aluminum atom [64]. This contribution originates from the participation of the reverse dative bond in the aluminum alkyls AlH_2R, and its decrease in the series $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$ originates from the reduction in the energy of the dissociation complexes of alkylaluminum with alkyls of nitrogen and oxygen (Fig. 1.7) up to the propyl derivative. The virtually constant value of the energy of dissociation of complexes from tri-*n*-propylaluminum till tri-*n*-octylaluminum can be governed only by the constant charge of the aluminum atom and the electron density on its p_z-orbital.

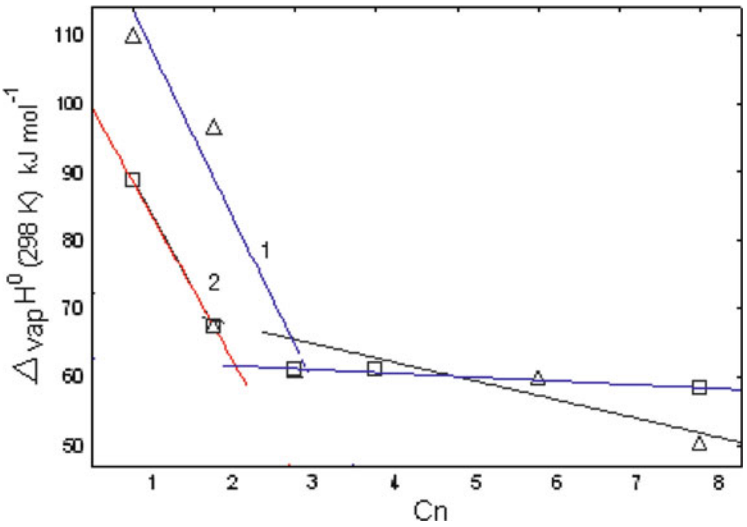


Fig. 1.7 Dependence of the dissociation energy of the donor–acceptor bond Al–O (1) and Al–N (2) in the molecular complexes $R_3AlO(C_4H_9)_2$ and $R_3AlN(C_2H_5)_3$ on the number of carbon atoms in the alkyl chain of AlR_3

Table 1.9 Dissociation energy of bond Al–N (kJ mol^{-1}) at alkyl complexes

Complex	Bond DAl–N	Complex	Bond DAl–N
$(C_3H_7)_3AlN(C_2H_5)_3$	61.1	$(C_3H_7)_3AlO(C_2H_5)_2$	65.0
$(i\text{-}C_3H_7)_3AlN(C_2H_5)_3$	75.3	$(i\text{-}C_3H_7)_3AlO(C_2H_5)_2$	71.2
–	–	$(i\text{-}C_4H_9)_3AlN(C_2H_5)_2$	93.6

The dependences shown in Fig. 1.7 permit reliable interpolation for the estimation of dissociation energy of the complexes $(C_5H_{11})_3AlN(C_2H_5)_3$, $(C_6H_{13})_3AlN(C_2H_5)_3$, and $(C_7H_{15})_3AlN(C_2H_5)_3$ equal, respectively, 60.5, 59.5, and 59.0 kJ mol^{-1}. These data show that independent of the flexible carbon chain up till the octyl group in the trigonal flat structure of the AlR_3 molecule the steric effect exists only between the carbon atoms contacting with the aluminum. The characteristic feature of the alkylaluminum complexes is their high stability in the case of branched alkyl groups (Table 1.9).

This fact in its turn indicates that the isostructural position of the methyl group governs the shift of the electron density in the carbon alkyl chain. The presence of an isostructural methyl group in the isobutyl moiety provides the stability of complex close to that of trimethylaluminum. Thus, the aluminum atoms in $Al(CH_3)_3$ and $Al(i\text{-}C_4H_9)_3$ have similar positive charges, and their $3p_z$-orbitals contribute similarly into the π-MO. This is confirmed by the effective charges of mercury in $Hg(Alk)_2$ varying from +0.023e in $Hg(CH_3)_2$ to −0.070e in $Hg(i\text{-}C_4H_9)_2$ [64]. The insignificant positive charge on the mercury atom in $Hg(CH_3)_2$ is also confirmed in [67]. Note that the majority of published results of the experimental investigations on the dissociation energies of the donor–acceptor complexes compiled in [19] are reported without indicated accuracy and are obtained in different solvents and by different methods, therefore in our analysis we relied on the most trustworthy data obtained by one procedure.

Thus, the thermodynamic analysis of a series of similar alkyl complexes of boron and aluminum with alkyl compounds of the elements from the fifth and sixth groups involving the data of quantum chemistry made it possible:

- To reveal the role of the reverse dative bond in the compounds AR_k, its part in the formation of the charges on the atoms of elements of subgroups of boron, nitrogen, and oxygen, to explain the fact of the presence electrons on the p_z-orbitals at the expense of the reverse dative bond
- To substantiate the appearance of the coordination endoeffect in alkyl compounds AR_k due to the carbon atoms of alkyl groups contacting with the central atom
- To reveal the special role of the isostructural methyl group in the stabilization of complexes, the shift of the electron density in the fragment of the molecule
- To understand the effect of the reverse dative bond on complex stabilization

The reported trends in the changes of the dissociation energies of alkyl compounds with the normal and branched structure of the alkyl groups refute the sterical effects obtained in [68] based on linear correlations for C_3H_7(1.38), i-C_3H_7(1.59), C_4H_9(1.59), and i-C_4H_9(1.69).

The significant result of the performed thermodynamic analysis is the fact that the compounds with the branched alkyl groups are insensitive to the steric effect. On the contrary, they provide more stable complexes. This fact suggests a skeptical position with respect to the correlation analysis in the chemistry of organoelemental and organic compounds considering the steric effects [68]. The true accounting for the steric effect may be based on a detailed analysis of the dissociation energy, thermodynamic properties, and the data on the electron density distribution in compounds under consideration.

The thermodynamic properties of compounds and the quantum-chemical calculations discussed in this chapter showed that the considered reverse dative bond is a fundamental property of organometallic, organoelemental compounds of the elements of main groups and of organic compounds. The reverse dative bond in alkyls stabilizes the molecules of alkyl compounds AR_k and affects all their physicochemical properties, the complexing in solutions and in vapor, their dissociation energies, and the energies of specific interactions in condensed state, in solutions of nonelectrolytes, and the solvation processes.

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