

Chapter 1

Hydrogen Bonds of Hydrides and Specific Interactions of Alkyl Compounds of Main Group Elements

1.1 Hydrogen Bond Energies of Main Group Element Hydrides

Borane molecules and alkyl boron have an equilateral planar trigonal structure, with an angle of 120° between ligands. Based on the comparative analysis by Cvitaš et al. of the electron structure of isostructural molecules of diborane and ethylene molecules based on the photoelectron spectra and nonempirical calculations [1], Nefedov and Vovna [2] remark that significant differences are present in the nature of the MO for the $1b_{2u}$ orbital, the orbital of π -type ethylene, and bridgehead B–H $\rightarrow$ B in the diborane molecule. Observed changes in the binding type of the $1b_{2u}$ orbital are accompanied by its stabilization by 4.2 eV in relation to the $1(\pi)$ molecule C_2H_4 . Shifts of the photoelectron band at the level of s -type $1a_g$ and $1b_{2u}$ at values of 3.0 and 2.1 eV, respectively, as well as the levels of p -type $1b_{2g}$, $2a_g$, and $1b_{1u}$ at 1.0, 1.5, and 2.1 eV, respectively, are correlated with the energy change due to ionization of the 2s and 2p electrons of carbon and boron atoms. As described by Bieri et al. [3], the electron population of atomic orbitals of s-3.137e, $2p_x$, $2p_y$ -0.902, $2p_z$ -0e, and hydrogen 1s-1.20e in molecules of BH_3 , points to the insignificant negative charge at the hydrogen atom and its low donor properties in the formation of intermolecular hydrogen bonds in crystalline and liquid borane (Fig. 1.1). The planar structure of the borane molecule with six coordinated boron atoms forms a volumetric chain structure wherein, under the influence of the formed hydrogen bonds, the boron atoms are out of the plane and located at the apex of the mild trigonal pyramid. The chains are crosslinked by the hydrogen and boron atoms of the contacting chains due to hydrogen bond formation. Breakage of the seven hydrogen bonds in the vaporization process, with the transition to the vapor state of diborane, is accompanied by a reduction in the coordinated number of boron atoms from six to four, which is reflected by the stabilization of the two remaining intermolecular hydrogen bonds DB–H $\rightarrow$ B in the structure of the diborane molecule.

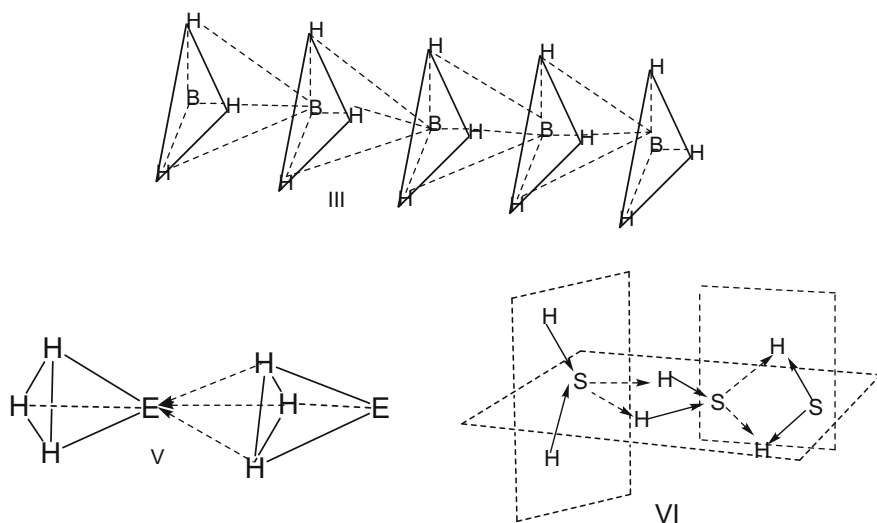
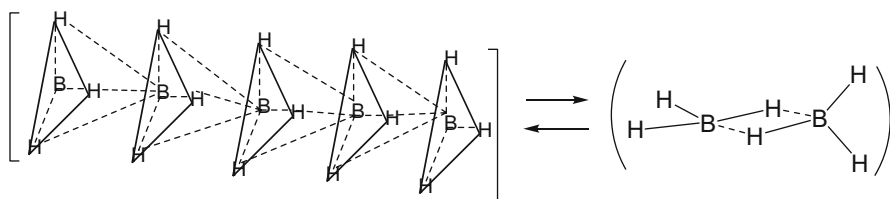


Fig. 1.1 Schematic of the crystalline and liquid structure of diborane, nitrogen, and sulfur subgroup elements with networks of hydrogen bonds



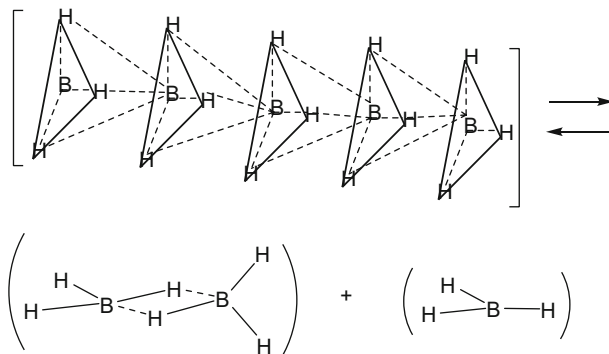
The average energy value of the ruptured hydrogen bonds, taking into account the simultaneous stabilization of the two hydrogen bonds in the diborane molecule, can be determined using the relationship of vaporization enthalpy and vaporization entropy, sublimation, and polymorphism with the number and energy of the bursting specific interactions [4–6] with the help of Eq. (1.1):

$$DB - H \bullet \bullet \bullet B = \Delta_{\text{vap}} H^0(T)/7 \quad (1.1)$$

The measured energy value of the hydrogen bond of liquid borane (Table 1.1) at 210 K has a low value. The calculated energy value of the hydrogen bond $DB \rightarrow H_D$ of liquid perdeuterated diborane is equal to 2.2 kJ mol^{-1} . Given the difference in temperature of 46 K for definition of the vaporization enthalpy of borane and perdeuterated diborane and its temperature dependence, one can assume that the limited expression of deuterium atoms is due to the stabilization of the hydrogen bonds at any given temperature.

Table 1.1 Energies (kJ mol^{-1}) of the hydrogen bonds of liquid diborane and nitrogen and sulfur subgroup elements

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K)	T (K)	$\text{DH}_3\text{B}\cdots\text{H}-\text{BH}_2$	$\text{DS} \rightarrow \text{S}-\text{H}$
Diborane	B_2H_6		12.8	210	1.83	—
Perdeuterated diborane	B_2D_6		15.3	164	2.2	—
Ammonia	NH_3		22.7	308	$\text{DH}_3\text{E}\cdots\text{H}-\text{EH}_2$ 3.8	—
			23.5	239	3.93	—
			23.4	239		—
Phosphine	PH_3		14.61 ± 0.02	185.73	2.43	—
Arsine	AsH_3		18.12 ± 0.04	210.68	3.02	—
Stibine	SbH_3		21.1 ± 2.1	254.8	3.51	—
Hydrogen sulfide	H_2S		23.2 ± 0.01	186	$\text{DH}_2\text{E}\cdots\text{H}-\text{EH}$ 5.8	—
			23.3	190		—
Hydrogen selenide	H_2Se		19.92 ± 0.21	231.8	4.98	—
Hydrogen selenide-d ₂	SeD_2		22.2	217	5.55	—
Hydrogen telluride	H_2Te		23.4 ± 1.7	271	5.68	—
Dihydrogen disulfide	H_2S_2		33.8 ± 0.1	293	8.45	—
Dihydrogen trisulfide	H_2S_3		45.5 ± 0.2	293	8.45	11.5 ± 0.2
Dihydrogen tetrasulfide	H_2S_4		56.8 ± 0.3	293	8.45	11.5 ± 0.2
Dihydrogen pentasulfide	H_2S_5		68.4 ± 0.6	293	8.45	11.53 ± 0.2



The low energy values of hydrogen bonds of diborane and perdeuterated diborane point to the fact that the given compounds are unstable at higher temperatures and that they should dissociate in pairs, with permanent shifting of the balance to the side of the partial pressure reduction of diborane and its absence at standard conditions. Therefore, reliable studies of the measurement of partial components of the diborane molecule and the borane molecule are possible only with the use of static methods.

The ammonia molecule and its derivatives phosphine, arsine, and stibine, with a trigonal pyramid and an equilateral triangle at the bottom, form a volumetric chain structure in the crystalline and liquid condition by hydrogen bonds. The chains are crosslinked with the participation of hydrogen and nitrogen atoms, or the analog of the contacting chains forming hydrogen bonds (Fig. 1.1).

The process of vaporizing liquid compounds is accompanied by the transition to vapor of monomer molecules with the rupture of six hydrogen bonds; therefore, the energies of these bonds can be determined with the help of Eq. (1.1a) [8]:

$$\text{DN} \bullet \bullet \bullet \text{H} - \text{N} = \Delta_{\text{vap}} H^0(T)/6 \quad (1.1a)$$

The energies of hydrogen bonds of hydrides of the nitrogen subgroup elements obtained at different temperatures point to the general regularity of its stabilization:

Phosphine (2.43) 185.73 K < Arsine (3.02) 210.68 K < Stibine (3.51) 254.8 K ≤ Ammonia (3.93 kJ mol⁻¹) 239 K

According to the work of Nefedov and Vovna [2], the nature of the bonds in EH₂ molecules is similar to the interaction of water molecular orbitals. The angled molecular structure of these compounds is caused by *p*-electrons and the electron populations of atom orbitals N s-3.137e, 2p_x and 2p_y-0.902e, 2p_z-1.861e, and hydrogen 1s-0.734e with great deficit provides it with high acceptor properties and, from the formation of hydrogen bonds, with increased stability compared with the nitrogen subgroup elements. The monomeric nature in the pairs of hydrides of sulfur subgroup elements causes rupture of the four hydrogen bonds during the transition of the molecules to vapor. It follows that the hydrogen bond energy

formed by the hydride molecules of sulfur subgroup elements, as for water hydrogen bonds [9], is obtained by Eq. (1.1b):

$$DS \bullet \bullet \bullet H - S = \Delta_{\text{vap}} H^0(TK)/4 \quad (1.1b)$$

The obtained energies of the hydrogen bonds of hydrides of this type of compound are described by the following equation:

$$\begin{aligned} \text{Hydrogen selenide (4.98)} \quad 231.8 \text{ K} < \text{Hydrogen selenide-d}_2 \quad (5.55) \\ 217 \text{ K} < \text{Hydrogen telluride (5.68)} \quad 271 \text{ K} < \text{Hydrogen sulfide (5.8 kJ mol}^{-1}) \\ 186 \text{ K,} \end{aligned}$$

where the increased value of the hydrogen bond in H_2S , in comparison with H_2Te , reflects the influence of the location of valence electrons at the energy level nearest the core. A more striking influence is displayed by the location of valence electrons at the second energy level of hydrogen atoms, forming hydrogen bonds with an energy of $10.99 \text{ kJ mol}^{-1}$ [9].

Molecules of dihydrogen disulfide form the structure of the liquid condition with a network of hydrogen bonds (Fig. 1.2a). The presence in the molecule of two sulfur atoms and two hydrogen atoms causes the increased shifting of electron density from the hydrogen atoms, which provides it with an increased positive charge and acceptor properties. In turn, the sulfur free electron pairs create the possibility to shift the increased electron density to the hydrogen atom, which is accompanied by stabilization of the formed hydrogen bonds. The energies of these interactions are determined by the division of the vaporization enthalpy by the number of formed hydrogen bonds with the help of Eq. (1.1b). The obtained energy of the hydrogen bonds is given in Table 1.1.

The molecules of dihydrogen trisulfide, dihydrogen tetrasulfide, and dihydrogen pentasulfide, with one to three sulfur atoms, form four hydrogen bonds and, by the sulfur atoms, one, two, and three specific interactions $D-S \rightarrow S-$, respectively (Fig. 1.2b). This allows the energy of specific interactions to be calculated from Eq. (1.1c), taking into account the energy contribution of the four hydrogen bonds and the corresponding energies of the $D-S \rightarrow S-$ interactions contributed by the

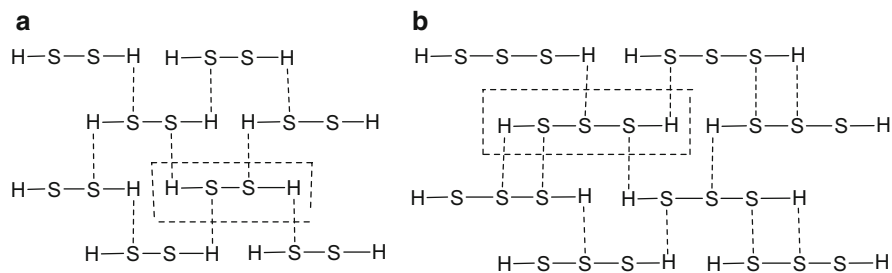


Fig. 1.2 Schematic of the liquid structure of dihydrogen disulfide (a) and dihydrogen trisulfide (b) with networks of hydrogen bonds

appropriate number of sulfur atoms of the molecule to the enthalpy characteristic, where n is the number of sulfur atoms in the molecule forming specific interactions:

$$D - S \rightarrow S- = (\Delta_{\text{vap}}H^0(TK) - 4DS \bullet \bullet \bullet H - S)/n \quad (1.1c)$$

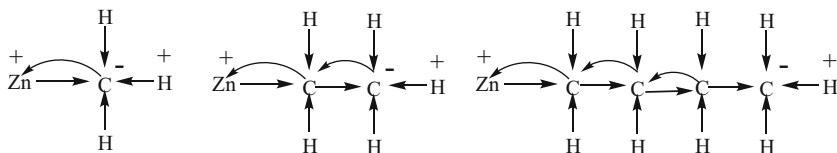
Vacant electron pairs of the sulfur atoms in the molecule of dihydrogen disulfide (8.45 kJ mol^{-1}) provide increased stability to the hydrogen bonds in comparison with the formed molecule of hydrogen sulfide (5.8 kJ mol^{-1} , 190 K). Thus, the energy value of the hydrogen bonds can be used to determine the energy of the specific interaction $D-S \rightarrow S-$ with the help of Eq. (1.1c). The obtained constant energy value of this type of specific interaction (11.5 kJ mol^{-1}) with dihydrogen trisulfide, dihydrogen tetrasulfide, and dihydrogen pentasulfide reflects the real behavior and the correctness of the concept of specific interactions.

1.2 Specific Interactions of Alkyls of Zinc Subgroup Elements

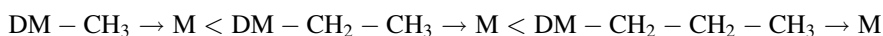
1.2.1 Zinc Alkyls

The electron configuration of MMe_2 molecules of zinc subgroup elements is rather complex. Two lower MOs are C 2s electrons, splitting the energy level, which, in the case of Cd atoms, is equal to 0.53 eV. Two C–H connecting pseudo-orbitals $1\pi_u$ and $2\pi_g$ give a single broad band at 12–14 eV according to the photoelectron spectra [10–14]. Based on the same spectra, it is shown that the molecular orbitals $3\sigma_g$ cause a binding sequence of C $2p_z$ with M- ns orbitals and a $2\sigma_u$ sequence C $2p_z$ with M- np_z orbitals. The information obtained in the photoelectron spectra allow establishment of the sequence of $d_{s/2}$ subshell levels, which proved the electrostatic nature of splitting and the small contribution of a covalent component.

The electron structures of atoms of the sulfur subgroup elements and the carbon atom in alkyl molecules have distinct differences in the donor and acceptor properties, providing shifting of the electron density from the element atom of this group to the essentially undivided $2s^2$ electron pair of the carbon atom of the alkyl chain [9]. An additional excess of the negative charge of carbon atoms is a result of the shifting of electron density from the related hydrogen atoms.



Realization of the reverse dative bond, caused by the partial transfer of electron density from the carbon atom to the element atom of the sulfur subgroup, reduces its positive charge. The shifting of electron density from the element atom of the sulfur subgroup to the essentially undivided $2s^2$ electron pair of the carbon atom of the methyl group in the dimethyl compound of the elements of this group provide it with donor properties and the ability to form a specific intermolecular interaction $DZn-CH_3 \rightarrow Zn$ or, in the general case, $DM-CH_2-CH_3 \rightarrow M$, $DM-CH_2-CH_2-CH_3 \rightarrow M$. The completion of the influence of the reverse dative bond at the third or fourth carbon atom provides the maximum difference in the corresponding positive and negative charge at the carbon atom of the terminal methyl group of the propyl or butyl compound and the metal atom. Thus, stabilization of the specific interaction due to an increase in the length of the alkyl chain occurs:



The relationship between the vaporization enthalpy and vaporization entropy, sublimation, polymorphic transformation, and melting and the number and energy of the bursting specific interactions causes the expressed dependence of the corresponding thermodynamic property on the number of carbon atoms of the alkyl chain [9]. A clear distinction in the dependence of the vaporization enthalpy of zinc alkyls (Fig. 1.3) on the number of carbon atoms for compounds $Zn(CH_3)_2$ to $Zn(C_3H_7)_2$ and $Zn(C_4H_9)_2$ to $Zn(C_7H_{15})_2$ is caused by the completion of the influence of the reverse dative bond at the third carbon atom of the chain. Further increase in the enthalpy characteristic reflects the contribution of the increasing number of methylene groups. This dependence allows us to refine the value of the vaporization enthalpy of dipentylzinc (53.5 kJ mol^{-1}), given in the literature without information on temperature and error.

Zinc alkyls with a linear molecular structure form a network in the crystalline and liquid conditions that is formed by specific intermolecular interactions with the

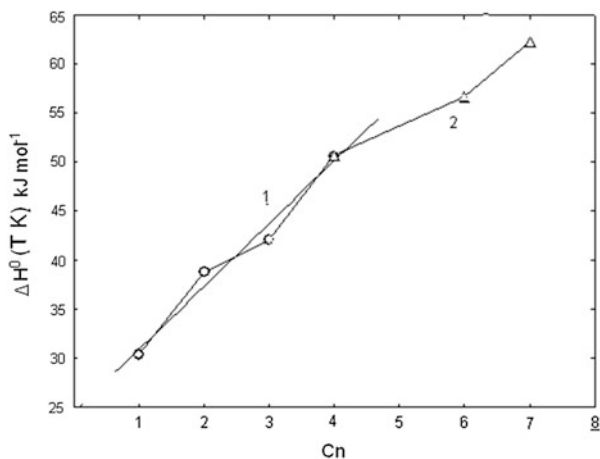


Fig. 1.3 Dependence of vaporization enthalpy of zinc alkyls on the number of carbon atoms (C_n) in the chain: 1 influence of reverse dative bond, 2 contribution of energy of CH_2 groups

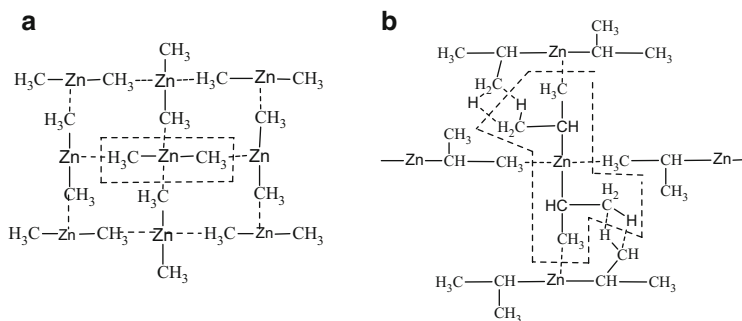
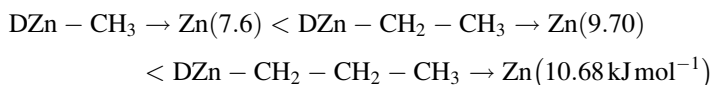


Fig. 1.4 Schematic of the liquid structure of dimethylzinc (a) and diisopropylzinc (b) with networks of specific interactions

participation of the pentacoordinated carbon atom of the methyl, propyl, butyl, or alkyl ligand and the four-coordinated zinc atom (Fig. 1.4a). Consequently, the vaporization process is accompanied by the transition to vapor of the monomer molecules with the rupture of four specific interactions, whose energy is determined using Eq. (1.2):

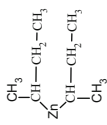
$$\text{DZn} - (\text{CH}_2)_n - \text{CH}_3 \rightarrow \text{Zn} = \Delta_{\text{vap}} H^0(T)/4 \quad (1.2)$$

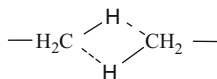
In calculating the energy of specific interactions, the most correct values of the vaporization enthalpies of the compounds were used, obtained with the help of a static measuring method of vapor pressure in vacuum with a low error level. Table 1.2 gives the energy values of specific interactions, which are described by the sequence of stabilization:



The energy of specific interaction of dipropylzinc is close to the energy of a hydrogen bond of liquid water ($10.99 \text{ kJ mol}^{-1}$). The energy contribution of methylene groups to the vaporization enthalpy of alkyls with the largest number of carbon atoms in the chain is the difference between the vaporization enthalpy of the neighboring alkyl compound in the series or the value obtained as the difference between the vaporization enthalpy of the compound and the enthalpy of dipropylzinc (Table 1.2). The isostructural methyl group of zinc alkyls participates in the formation of the network of specific interactions (Fig. 1.4b) and forms two specific interactions of low stability with a similar group of contacting molecules via the hydrogen atom in the *trans* position to the chain carbon atom.

Table 1.2 Energies (kJ mol⁻¹) of specific interactions of liquid zinc alkyls

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K)	References	T (K)	DZn $\rightarrow$ CH ₃ -(CH ₂) _n	DH ₃ C $\rightarrow$ H-CH ₂
Dimethylzinc	ZnC ₂ H ₆	H ₃ C-Zn-CH ₃	30.4 $\pm$ 0.2	[15]	298	$n=0$ 7,6	—
Diethylzinc	ZnC ₄ H ₁₀	C ₂ H ₅ -Zn-C ₂ H ₅	38.8 $\pm$ 0.4	[15]	298	$n=1$ 9,70	—
Dipropylzinc	ZnC ₆ H ₁₄	C ₃ H ₇ -Zn-C ₃ H ₇	42.7 $\pm$ 0.4	[16]	345	$n=2$ 10,68	—
Diisopropylzinc	ZnC ₆ H ₁₄		41.8 $\pm$ 0.5	[16]	324	$n=1$ 9,70	1.6:4 = 0.4
Dibutylzinc	ZnC ₈ H ₁₈	C ₄ H ₉ -Zn-C ₄ H ₉	50.7 $\pm$ 0.3	[17]	342	$n=2$ 10,68	Σ DCH ₂ = 4.0 $\times$ 2
Di-sec-butylzinc	ZnC ₈ H ₁₈		40.9 $\pm$ 0.2	[17]	330	9.82	1.6:4 = 0.4
Diisobutylzinc	ZnC ₈ H ₁₈		44.6 $\pm$ 0.2	[17]	330	$n=2$ 10,68	1.9:4 = 0.5
Di-tert-butylzinc	ZnC ₈ H ₁₈		44.3	[17, 18]	—	$n=1$ 9.45	6.5:8 = 0.8
Dipentylzinc	ZnC ₁₀ H ₂₂	C ₅ H ₁₁ -Zn-C ₅ H ₁₁	53.5	[7]	342	12.7	Σ DCH ₂ = 2.7 $\times$ 4
Dihexylzinc	ZnC ₁₂ H ₂₆	C ₆ H ₁₃ -Zn-C ₆ H ₁₃	56.2	[7]	—	10.68	Σ DCH ₂ = 2.25 $\times$ 6
Diheptylzinc	ZnC ₁₄ H ₃₀	C ₇ H ₁₅ -Zn-C ₇ H ₁₅	62.3	[7]	—	10.68	Σ DCH ₂ = 2.45 $\times$ 8



Taking into account that the ethyl group of diisopropylzinc contributes equivalently to the similar group of diethylzinc, the energy contribution to the vaporization enthalpy of four specific interactions of low stability formed by the two isostructural methyl groups can be obtained from the difference in the vaporization enthalpies of these compounds:

$$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2 = (\Delta_{\text{vap}}H^0(T\text{K})_{\text{ipz}} - \Delta_{\text{vap}}H^0(T\text{K})_{\text{et}})/4 \quad (1.2a)$$

Similarly, we define the energies of specific interactions of this type in diisobutyl zinc by the difference between the vaporization enthalpies of diisopropylzinc and dipropylzinc:

$$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2 = (\Delta_{\text{vap}}H^0(T\text{K})_{\text{ipz}} - \Delta_{\text{vap}}H^0(T\text{K})_{\text{pz}})/4 \quad (1.2b)$$

Correspondingly, double the number of formed specific interactions of the same type, formed in liquid di-*tert*-butylzinc, can be obtained from the difference in the vaporization enthalpies of diethylzinc and di-*tert*-butylzinc:

$$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2 = (\Delta_{\text{vap}}H^0(T\text{K})_{\text{tbz}} - \Delta_{\text{vap}}H^0(T\text{K})_{\text{etz}})/8 \quad (1.2c)$$

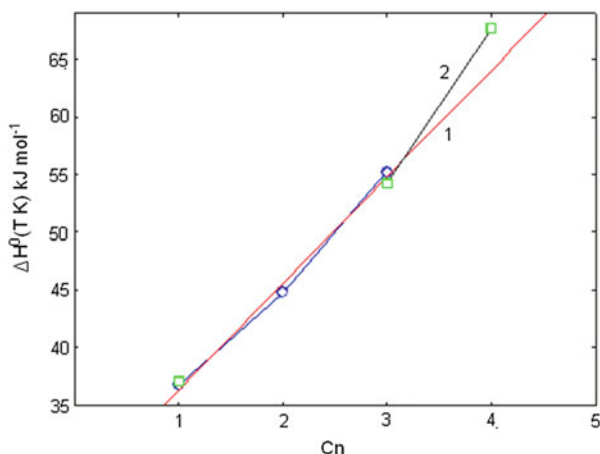
$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2$: Diisopropyl zinc (0.4) = Diisobutyl zinc (0.5) < Di-*tert*-butyl zinc (0.8 kJ mol⁻¹)

The low values for the energies of the specific interactions reflect some stabilization of liquid di-*tert*-butylzinc. The energy contribution of the formed specific interactions of low stability of the isostructural methyl groups of di-*sec*-butylzinc can be taken as equal to that for the similar diisopropylzinc. This allowed the specific interaction energies of the formed propyl group of compounds to be obtained (Table 1.2).

1.2.2 Alkyls of Cadmium and Mercury

In the work by Nefedov and Vovna [2], it is noted that the values of exciton binding (Eb) for the internal Hg 4f 7/2 level with an energy of 107.14 eV and for the C 1s level with a value of 289.6 eV in comparison with the values of 107.1 eV for the mercury atom and 290.7 eV for C₂H₆ point to the insignificant positive charge of the Hg atom in the molecule of Hg(CH₃)₂. In this connection, the small difference in the vaporization enthalpies (Fig. 1.5) and, consequently, the low energy

Fig. 1.5 Dependence of the vaporization enthalpy of liquid zinc alkyls on the number of carbon atoms in the chain: 1 mercury alkyls, 2 cadmium alkyls



difference of specific interactions of $\text{Cd}(\text{CH}_3)_2$ and $\text{Hg}(\text{C}_2\text{H}_5)_2$ point to the low positive charge at the cadmium atom. Interrelation of the vaporization enthalpy and sublimation enthalpy with the energy and number of bursting specific interactions is equal for cadmium and mercury alkyls with the same number of carbon atoms and the sharp increase in the values of the enthalpy characteristic of the alkyl elements (Fig. 1.5) indicates the significant shifting of electron density from the metal atoms to the end methyl group with an increasing number of carbon atoms in the chain. The measured charges reported in the literature [11–14] for the mercury atoms in $\text{Hg}(\text{Alk})_2$, changing from +0.023 in $\text{Hg}(\text{CH}_3)_2$ to $-0.070e$ in molecules of $\text{Hg}(i\text{-Bu})_2$, are caused by the participation of isostructural methyl groups in the redistribution of electron density in the molecules of isobutylmercury. As shown in Fig. 1.5, the dependency of the alkyl vaporization enthalpy on the number of carbon atoms in the chain was used to clarify the value of the enthalpy characteristic of diethylcadmium (Table 1.3), used in the determination of the energy of specific interactions. The analogy of linear molecules of cadmium alkyls and mercury alkyls with the structure of zinc alkyl molecules, provides a similarity in the structure of their liquid and crystal conditions with the network of specific interactions, respectively, a normal structure and with the isostructural group (Fig. 1.5). The energy calculations of specific interactions of liquid cadmium and mercury alkyls of a normal structure, using Eq. (1.2), illustrate their stabilization (Table 1.3) with an increasing number of carbon atoms in the chain. High energies of the compounds with propyl ligands indicate significant differences in the positive charge of the metal atom and the negative charge of the carbon atom of the end methyl group. Note that the maximum stability of specific interactions occurs for the compounds with butyl ligands. The calculated energy contribution of the isostructural methyl group of diisopropylmercury and the formed specific interaction of low stability $\text{DH}_3\text{C} \rightarrow \text{H}-\text{CH}_2$ (1.9 kJ mol^{-1}) using Eq. (1.2b) points to its

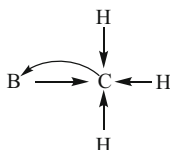
Table 1.3 Energies (kJ mol^{-1}) of specific interactions of liquid cadmium alkyls

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K) [7]	References	T (K)	$\text{DM} \rightarrow \text{CH}_3-(\text{CH}_2)_n$	$\text{DH}_3\text{C} \rightarrow \text{H}-\text{CH}_2$
Dimethylcadmium	CdC_2H_6	$\text{H}_3\text{C}-\text{Cd}-\text{CH}_3$	37.10 ± 0.07	[18, 19]	324	9.27	—
Diethylcadmium	$\text{CdC}_2\text{H}_{10}$	$\text{C}_2\text{H}_5-\text{Cd}-\text{C}_2\text{H}_5$	46.0 ± 0.4	[18, 19]	324	11.5	—
Dipropylcadmium	$\text{CdC}_6\text{H}_{14}$	$\text{C}_3\text{H}_7-\text{Cd}-\text{C}_3\text{H}_7$	54.2 ± 0.4	[19]	342	13.6	—
Dibutylcadmium	$\text{CdC}_8\text{H}_{18}$	$\text{C}_4\text{H}_9-\text{Cd}-\text{C}_4\text{H}_9$	67.7 ± 9.2	[18, 19]	356	16.75	—
Dimethylmercury	HgC_2H_6	$\text{H}_3\text{C}-\text{Hg}-\text{CH}_3$	36.7 ± 0.1	[18]	321	9.18	—
Diethylmercury	$\text{HgC}_4\text{H}_{10}$	$\text{C}_2\text{H}_5-\text{Hg}-\text{C}_2\text{H}_5$	44.8 ± 1.7	[18]	—	11.2	—
Dipropylmercury	$\text{HgC}_6\text{H}_{14}$	$\text{C}_3\text{H}_7-\text{Hg}-\text{C}_3\text{H}_7$	55.2 ± 1.3	[7, 18]	—	13.8	—
Diisopropylmercury	$\text{HgC}_6\text{H}_{14}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{Hg} \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	53.6 ± 1.7	[7]	—	11.2	$7.6:4 = 1.9$

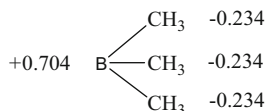
significant stabilization in comparison with that in liquid diisopropylzinc (0.4 kJ mol^{-1}).

1.3 Specific Interactions of Alkyls of Boron Subgroup Elements

The calculation results [20] for the electron density distribution in molecules of B (CH_3)₃, performed using an improved version of the method of Huckel [21] with various approximations, indicate shifting of the electron density from the boron and hydrogen atoms to the carbon atom of the methyl group.



A part of the charge ($\sim 0.3e$) is transferred from the carbon atom to the $3p_z$ orbital of the boron atom as the reverse dative bond, stabilizing the intermolecular interactions. The result of the electron density redistribution are the charges on the boron atom and the methyl group [22], forming specific interactions in liquid and crystal conditions.

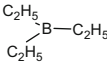
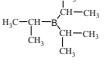


Alkyl boranes with a planar molecular structure in the crystal and liquid conditions show similarity to boranes with respect to the volume of the network of specific interactions with the six-coordinated boron atom (Fig. 1.1). The vaporization process is accompanied by the transition to vapor in practically the monomer condition, which allows the energy calculation to be performed using Eq. (1.3):

$$\text{DB} - (\text{H}_2)n - \text{CH}_3 \rightarrow \text{B} = \Delta_{\text{vap}} H^0(T\text{K})/6 \quad (1.3)$$

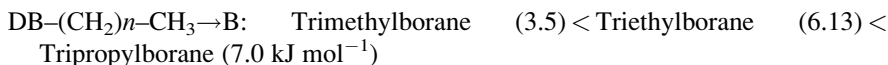
Taking into account the equivalent energy contribution by the ethyl fragments of triethylborane and triisopropylborane, the energy contribution of the three isostructural methyl groups to the vaporization enthalpy of triisopropylborane or the contribution of the six specific interactions formed by the isostructural methyl groups, can be determined from the difference between the vaporization enthalpies of the compound and triethylborane (1.3a):

Table 1.4 Energies (kJ mol^{-1}) of specific interactions of liquid borane alkyls

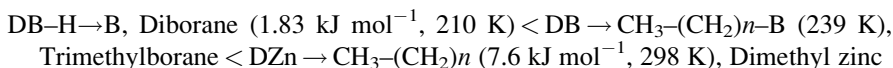
Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K) [7]	T (K)	DB $\rightarrow$ CH ₃ – (CH ₂) _n –B	DH ₃ C $\rightarrow$ H– CH ₂
Trimethylborane	BC ₃ H ₉		20.9 ± 0.1	239	3.5	–
Triethylborane	BC ₆ H ₁₅		36.8 ± 0.4	298	6.13	–
Tripropylborane	BC ₉ H ₂₁		41.8 ± 1.3	–	7.0	–
Triisopropylborane	BC ₉ H ₂₁		41.8 ± 1.3 40.0	–	6.13	5.9:6 = 0.8

$$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2 = (\Delta_{\text{vap}}H^0(\text{K})_{\text{tipb}} - \Delta_{\text{vap}}H^0(\text{K})_{\text{teb}})/6 \quad (1.3a)$$

The calculation results (Table 1.4) indicate that the general pattern of stabilization of specific interaction energies formed by the alkyl ligand with an increasing number of chain carbon atoms is caused by the relative increase in electron density shift and also by reduction in the influence of the reverse dative bond:



This draws attention to the low stability of the hydrogen bonds of liquid diborane in comparison with the energy of specific interactions of liquid trimethylborane and dimethylzinc, formed by the pentacoordinated carbon atom, reflecting the ability of the carbon atom of the methyl group to shift the electron density:



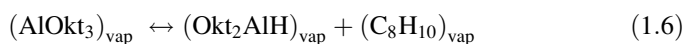
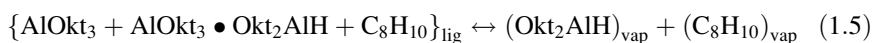
Aluminum alkyl compounds are the only representatives of alkyl elements of the third to sixth group of the periodic system that are characterized by the association in pairs. However, inconsistency in the results of thermodynamic studies on them demanded significant changes in the type and quality of the experimental approaches. Research [18, 23–25] using the static method using zero gauge glass with a substance vacuum distillation system and filling of the membrane chamber, measuring of the vapor pressure with an error of ± 0.1 torr, the possibility of the determination of molar mass, and the study of the related processes in the vapor phase has ensured accurate qualitative measurement. The obtained data on the vapor composition, substantiated by the presence of vapor molecules in dimeric form over the liquid trimethylaluminum and triethylaluminum with proportions of 88.8 and 30.1%, respectively, at around 320 K and decreasing with increasing temperature, provided their thermodynamic properties [26, 27].

Detailed studies of the thermal behavior of trialkylaluminums showed that the mechanism of thermal decomposition of $\text{Al}(\text{C}_2\text{H}_5)_3$, including the generation stage

and the open circuit, is a sequence of free-radical processes. Thus, the process of decomposition belongs to the radical and olefin–hydride mechanism. The obtained information on the thermal behavior of AlEt_3 , AlBu_3 [24, 25], and AlOkt_3 [23] substantiated the tendency to the olefin–hydride process in a series of trialkylaluminums with a normal structure and an increasing number of atoms in the ligand. It complies with the results given by Korneev [28]: $\text{AlMe}_3 > \text{AlEt}_3 > \text{AlPr}_3 > \text{AlBu}_3$.

As a result, there was an appropriate opportunity to choose the conditions for an accurate study of AlPr_3 . The vapor pressure measured in independent experiments and the molecular weights of compounds as measured in the vapor phase (165.0 c. u.) and as calculated according to the formula (156.0 c.u.), clearly indicated the presence of dimeric molecules in the vapor. The low partial pressure of dimeric molecules in the vapor of AlPr_3 , not exceeding 5.8 % at low temperatures, is connected with the reduction in the tendency to dimerization in the series $\text{AlMe}_3 > \text{AlEt}_3 > \text{AlPr}_3 > \text{AlBu}_3$.

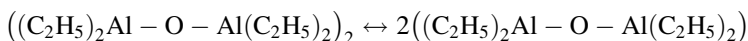
For unsaturated vapor up to the compound decomposition temperature (413 K), the change in vapor pressure with temperature corresponds to Gay–Lussac’s law; thus, for saturated vapor, the dependence $P = f(T\text{K})$ was processed according to the appropriate equations and resulted in a vaporization enthalpy and vaporization entropy of $43.0 \pm 2.0 \text{ kJ mol}^{-1}$ and $88 \pm 6 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. These values correspond to those given by Chickos and Acree [7]. According to the research results, at temperatures below the commencement of decomposition processes at 320 K, vapor up to 5 mm participates in the vaporization process with the transition to vapor of the monomer and dimer molecules of AlBu_3 . Similar results for trialkylaluminum [23] reflect the balance between the starting material and the components formed in the liquid and vapor phases:



After the complete evaporation of the starting material in the system, equilibrium of the trialkylaluminum is established and $\text{AlOkt}_3 \bullet \text{Okt}_2\text{AlH}$ (Eq. 1.5) is formed in the solution. Above 430 K in the unsaturated vapor, molecules of the two compounds are present and the vapor molecular mass calculated from the total pressure and the quantity of the starting material (in the two independent experiments) are in good agreement with each other (254 c.u.) and are consistent with Eq. (1.4) [23].

The subsequent increase in the vapor pressure at increasing temperature is caused by the balance shown in Eq. (1.4) shifting towards the more complete transformation of trialkylaluminum to dialkylaluminum hydride. At 483 K, trialkylaluminum is totally dissociated and the system presents equimolar amounts of dialkylaluminum hydride and olefin. The average molecular weight is equal to 183 c.u., and that calculated according to the Mendeleev–Clayperon equation is 193.7 c.u. At temperatures above that specified, the vapor pressure changes in

accordance with Gay–Lussac’s law, i.e., olefin present in the system is in an unsaturated state. This allowed the dependence $P = f(T)$ for Okt_2AlH and thermodynamic vaporization parameters $\Delta H^0(T\text{ K}) = 51.9$ and $\Delta S^0(T\text{ K}) = 95.5 \text{ kJ mol}^{-1} \text{ K}^{-1}$ at 388–433 K to be obtained. The obtained value of the vaporization enthalpy at 11.2 kJ mol^{-1} is lower than that established (63.1 kJ mol^{-1}) for the unbalanced conditions at 333–393 K [29]. Therefore, it is necessary to state that uncouneted overlay processes related to the vaporization of the basic substance of aluminum alkyls cause significant differences in the vaporization enthalpy values of alkyl compounds, which are irrelevant with respect to the general laws of their change with an increasing number of carbon atoms in the alkyl chain. It is not possible to determine the energy values of the formed specific interactions in the liquid aluminum alkyls. The correct values of the vaporization enthalpies of a number of compounds in the literature [24–26] were obtained under conditions that were significantly different from and incomparable with the standard conditions and, therefore, do not provide comparable values for the energy characteristics. These peculiarities take place in hydrogen and oxygen derivatives of the aluminum alkyls [18, 24, 25, 30]. However, of particular interest is tetraethylaluminoxan, in which dimeric molecular forms are stable in the vapors and undergo dissociation [30]:



Tripropylaluminum is the only trialkylaluminum with a low ability to form dimeric molecules, which provides it with properties similar to gallium, indium, and thallium alkyls. X-ray diffraction studies of trimethylindium crystals showed the presence of four indium atoms in its structure, forming square and trigonal trimethylindium units located in the plane and perpendicular to the plane of In_4 [31]. The tetrameric unit is held by the groups located in the directions of lines connecting indium atoms, and the distance $(\text{H}_3\text{C})_3\text{In}-\text{CH}_3$ ($3.1 \text{ \AA}$) indicates the formation of weak covalent bonds.

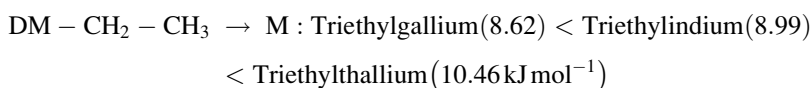
Research studies on the structure of trimethylindium and trimethylgallium crystals [32, 33] showed the formation of a distorted trigonal bipyramidal structure with coordination of the five methyl groups with $\text{In}-\text{C}$ interatomic distances of 2.06, 2.12, and $2.16 \text{ \AA}$ (Fig. 1.6). In the solid state, it has the structure of a distorted trigonal bipyramid with interatomic distances of $\text{Tl}-\text{Tl}$ equal to 5.46 ± 0.01 and $5.63 \pm 0.01 \text{ \AA}$ and interatomic distances between carbon atoms of 3.76, 3.91, 4.25, and $4.43 \text{ \AA}$. The distances $\text{Tl}-\text{C}$ of the alkyl groups are equal to 2.22–2.30 and $2.34 \text{ \AA}$ [33]. Methyl groups of the coordinated molecules are located almost perpendicular to the distorted planar structure of $\text{Tl}(\text{CH}_3)_3$, with distances of 3.16 and $3.31 \text{ \AA}$, with the formation of the intermolecular bond $(\text{H}_3\text{C})_3\text{Tl}-\text{CH}_3\text{Tl}$. The

Table 1.5 Energies (kJ mol^{-1}) of specific interactions of liquid trialkylaluminums

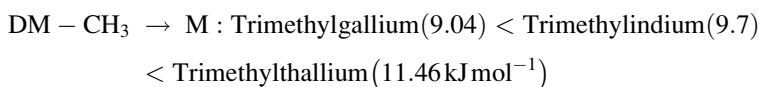
Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K)	References	T (K)	$\text{DM}-(\text{CH}_2)_n-\text{CH}_3 \rightarrow \text{M}$	$\text{DH}_3\text{C} \rightarrow \text{H}-\text{CH}_2$
Tripropylaluminium	AlC_3H_9	$\text{C}_3\text{H}_7-\text{Al}-\text{C}_3\text{H}_7$	42.5 ± 1.2	[7]	—	$n = 2, 8.5$	—
		C_3H_7	43.0 ± 2.0	[34]		8.6	
Trimethylgallium	GaC_3H_9	$\text{H}_3\text{C}-\text{Ga}-\text{CH}_3$	33.1 ± 0.8	[35]	266–305	$n = 0,$	—
		H_3C	32.6 ± 0.1			6.52	
Triethylgallium	$\text{GaC}_6\text{H}_{15}$	$\text{C}_2\text{H}_5-\text{Ga}-\text{C}_2\text{H}_5$	43.1 ± 1.6	[35]	299–387	$n = 1,$	—
		C_2H_5				8.62	
Tripropylgallium	$\text{GaC}_9\text{H}_{21}$	$\text{C}_3\text{H}_7-\text{Ga}-\text{C}_3\text{H}_7$	46.6 ± 0.5	[35]	316–385	$n = 2,$	—
		C_3H_7				9.32	
Triisopropylgallium	$\text{GaC}_9\text{H}_{21}$	$\text{H}_3\text{C}-\text{CH}(\text{CH}_3)-\text{Ga}-\text{CH}(\text{CH}_3)-\text{CH}_3$	46	[35]	—	$n = 1,$	0.5
						8.62	
Tributylgallium	$\text{GaC}_{12}\text{H}_{27}$	$\text{C}_4\text{H}_9-\text{Ga}-\text{C}_4\text{H}_9$	51.6 ± 1.3	[35]	330–378	$n = 3,$	—
		C_4H_9				10.32	
Trimethylindium	InC_3H_9	$\text{H}_3\text{C}-\text{In}-\text{CH}_3$	42.1 ± 4.1	[36]	361–408	$n = 0,$	—
		H_3C				8.42	
Trimethylindium	InC_3H_9 mp	$\text{H}_3\text{C}-\text{In}-\text{CH}_3$	15.8	[37]	361	—	—
Triethylindium	$\text{InC}_6\text{H}_{15}$	$\text{C}_2\text{H}_5-\text{In}-\text{C}_2\text{H}_5$	44.95 ± 0.7	[38]	326–376	$n = 1,$	—
		C_2H_5				8.99	
Triisopropylindium	$\text{InC}_9\text{H}_{21}$	$\text{H}_3\text{C}-\text{CH}(\text{CH}_3)-\text{In}-\text{CH}(\text{CH}_3)-\text{CH}_3$	52.3 ± 0.7	[18]	318–366	$n = 1,$	1.23
						8.99	
Triethylthallium	$\text{TlC}_6\text{H}_{15}$	$\text{C}_2\text{H}_5-\text{Tl}-\text{C}_2\text{H}_5$	52.3 ± 0.7	[7]	297	$n = 1,$	—
						10.46	

Table 1.6 Energies (kJ mol^{-1}) of specific interactions of crystalline trimethylgallium, trimethylindium, and trimethylthallium

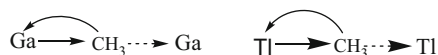
Compounds	Formula	Structure	$\Delta_{\text{sub}}H^0$ (298 K)	References	T (K)	DM- $\text{CH}_3 \rightarrow \text{M}$
Trimethylgallium	GaC_3H_9 sub		45.2	[35]	252	9.04
Trimethylindium	InC_3H_9 sub		48.5 ± 2.5	[38]	298	9.7
Trimethylthallium	$\text{C}_3\text{H}_9\text{Tl}$ sub		57.3	[39]	285	11.46



A similar pattern in the stabilization of specific interactions takes place in the crystal methyl compounds of the elements of the gallium subgroup:



This indicates the increased stabilization of the specific interaction due to the shifted electron density from the carbon atom to the fifth energy level of the indium atom, and an even more advantageous location at the thallium atom in comparison with the location at the fourth gallium atom or at the third aluminum atom. This is possible if: first, by shifting from the carbon atom of the terminal methyl group there is ever increasing electron density at the more distant energy level of the metal atom of the third group; and second, the metal atom transfers more electron density from the more distant energy level to the carbon atom of the alkyl ligand.



Therefore, the third energy level of the aluminum atom is less able to shift the electron density to the carbon atom and has an even lower ability to take it from the same carbon atom in the shape of the reverse dative bond. As a result, the increase in negative charge remains significantly reduced at the carbon atom, with the formation of the specific interaction of the methyl compound or AlR_3 with the aluminum atom: $\text{Al} \longrightarrow \text{CH}_3 \cdots \longrightarrow \text{Al}$ $\text{Al} \longrightarrow \text{CH}_2 \longrightarrow \text{CH}_3 \cdots \longrightarrow \text{Al}$.

As a consequence, the trialkylaluminums form dimeric molecules (Fig. 1.7), and the dissociation energies are described by the natural sequence of their reduction (Table 1.7):

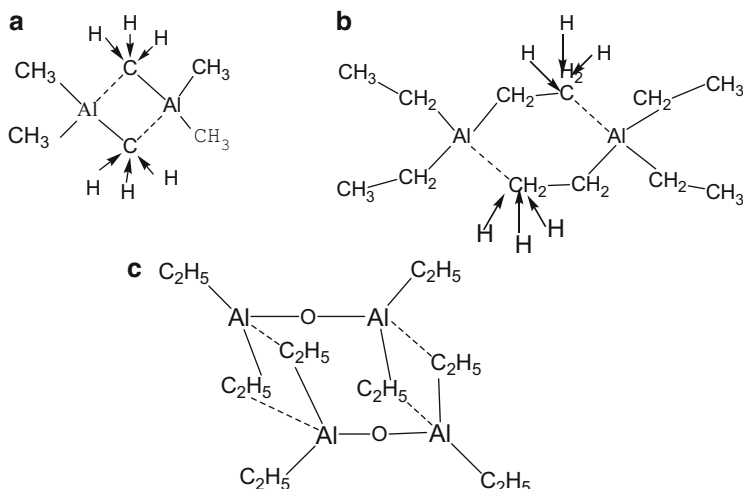
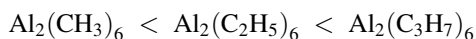


Fig. 1.7 Dimer molecule of trimethylaluminum (a), triethylaluminum (b), and tetraethylalumoxan (c)

Table 1.7 Dissociation energies (kJ mol^{-1}) of dimer molecules of alkylaluminum and its derivatives

Compounds	Formula	Structure	T (K)	$\Delta_{\text{vap}}H^0$ (TK)	$\Delta_{\text{dis,dim}}H^0$ (TK)	DAI– (CH_2) $_n$ – $\text{CH}_3 \rightarrow \text{Al}$
Trimethylaluminum	AlC_3H_9		297– 367	63.2 ± 1.7	88.4 ± 0.9	$n = 0$ 44.2
Triethylaluminum	$\text{AlC}_6\text{H}_{15}$		323– 423	63.7 ± 37	66.2 ± 1.1	$n = 1$ 33.1
Tetraethylalumoxan	$(\text{C}_2\text{H}_5)_2\text{Al}–\text{O}–\text{Al}–(\text{C}_2\text{H}_5)_2$		410– 432	69.0 ± 3.3	89.3 ± 5.8	$n = 1$ 22.4



The substantiation of dimerization in the couples trimethylaluminum and triethylaluminum [26, 27] and the obtained energy values of their dissociation became the key for new ideas and concepts. These include: the idea of the pentacoordinated condition of the carbon atom, the existence of a new type of interaction – the intermolecular reverse dative bond and its influence on the energies of the specific intermolecular interactions formed by the carbon atoms, substantiation of the changes in the enthalpy characteristics of the vaporization of alkyls of main group elements, and the failure of the model of sp^3 -hybridization of the carbon atom [9].

The value of the enthalpy of dissociation of the dimeric molecule of tetraethylalumoxan obtained later [30] (Table 1.7) indicated the possibility of the formation of dimeric molecules with a large number of ethyl fragments by the oxygen compounds of aluminum. The location of the oxygen atom between the aluminum atoms in the molecule of tetraethylalumoxan points to the shifting of the reduced electron density to the carbon atom of the ethyl group, in comparison with the molecules of triethylaluminum. Nevertheless, the formation of dimeric molecules of tetraethylalumoxan points to the fact that the excessive electron density at the terminal methyl group of the ethyl fragment of this compound is sufficient for the formation of the stable bond in its dimeric molecule. With the dissociation energy value of the dimeric molecule of tetraethylalumoxan being $89.3 \pm 5.8 \text{ kJ mol}^{-1}$, and four bonds in the molecule, the value of a single bond is equivalent to 22.4 kJ mol^{-1} . This energy value is significantly higher than the energy value of the specific interaction $\text{DAI-CH}_2\text{-CH}_2\text{-CH}_3 \rightarrow \text{Al}$ (8.6 kJ mol^{-1}) of liquid tripropylaluminum.

1.4 Specific Intermolecular Interactions of Alkyls of the Nitrogen Subgroup Elements

1.4.1 Specific Interactions of Trialkyls and Trivinyls

The molecules of phosphine and alkyl compounds of phosphorus are characterized by a trigonal pyramidal structure with an equilateral triangle at the bottom and a phosphine atom at the top of the pyramid. Nevertheless, following the replacement of the hydrogen atom in the methyl group, one can observe the reduction in the ionization potential $I(n)$ by 1.03, 0.55, and 0.44 eV, the reduced stability in methylamines [2] being 1.26, 0.72, and 0.56 eV, respectively, and the difference in the effective charges at the phosphine atoms being -0.04 and $+0.07e$. The charges at the nitrogen atom and the methyl group in the molecule of trimethylamine are $+0.024$ and $-0.008e$ [22] as a result of the manifestation of the reverse dative bond, accompanied by the shifting of electron density from the p_z orbital of the nitrogen atom to the significantly undivided $2s^2$ electron pair of the carbon atom. Therefore, in analogy with phosphine, the energies of the formed specific interactions of trimethylphosphate and phosphorus alkyls should have relatively low stability. In this connection, we used the correlation dependency of the vaporization enthalpy of trialkylphosphines and trialkylamines and specified the value of the enthalpy characteristic of tripropylphosphine (Table 1.8).

Presented in Fig. 1.8 is the dependence of the vaporization enthalpy of the arsenic alkyls (line 1) and phosphorus alkyls (line 2) on the number of carbon atoms in the alkyl ligand and, on the other hand, on the number of methyl groups in the molecules of the methylstibine to trimethylstibine series (line 3). This illustrates the stabilization of specific interactions by the increasing number of carbon atoms in the chain and, for the example of methylstibines, dimethylstibines, and

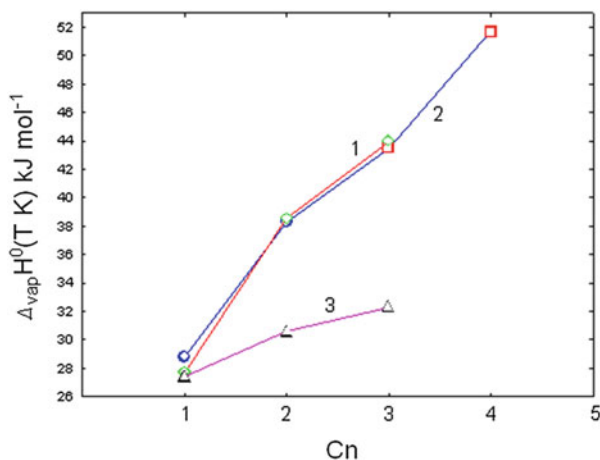
Table 1.8 Energies (kJ mol⁻¹) of specific interactions of liquid trialkyls of main group elements

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K)	T (K)	References	DE $\rightarrow$ CH ₃ -(CH ₂) _n -E	DH ₃ C $\rightarrow$ H-CH ₂
Trimethylphosphine	C ₃ H ₉ P		28.8	–	[40]	n = 0 4.8	–
Triethylphosphine	C ₆ H ₁₅ P		38.3	306	–	n = 1 6.4	–
Tripropylphosphine	C ₉ H ₂₁ P		39.4 43.5 ^a	340	[18]	n = 2 7.21	–
Tributylphosphine	C ₁₂ H ₂₇ P		51.72 $\pm$ 0.45 53.94	390	[18]	n = 3 7.21	Σ DCH ₂ = 8.2
Trivinylphosphine	PC ₆ H ₉		32.7	304	[7]	5.45	–
Trimethylarsine	AsC ₃ H ₉		27.7 $\pm$ 0.2 28.9 $\pm$ 1.3	240–280	[41]	n = 0; 4.61 4.81	–
Triethylarsine	AsC ₆ H ₁₅		38.10 $\pm$ 1.45 38.52 $\pm$ 0.74	273–339	[42]	n = 1; 6.35 6.41	–
Tripropylarsine	AsC ₉ H ₂₁		44.0 $\pm$ 0.7	314–420	[43]	n = 2; 7.3	–
Triisopropylarsine	AsC ₉ H ₂₁		45.22 $\pm$ 0.46	346–405	[18]	n = 1 6.35 6.41	1.1
Trivinylarsine	AsC ₆ H ₉		35.6	310	[7]	n = 1 5.9	–

Trimethylstibine	SbC ₃ H ₉		32.2 31.15	308	[38]	$n = 0;$ 5.38 5.2	—
Triethylstibine	SbC ₆ H ₁₅		39.9 ± 1.3 41.8	306	[44]	$n = 1; 6.65$ 7.0	—
Trivinylstibine	SbC ₆ H ₉		38.7	308	[7]	$n = 1;$ 6.45	—
Trimethylbismutine	BiC ₃ H ₉		36.0 ± 1.3 34.75	298	[7]	$n = 0;$ 6.0 5.8	—
Triethylbismutine	BiC ₆ H ₁₅		43.9	322	[7]	$n = 1;$ 7.31	—
Trivinylbismutine	BiC ₆ H ₉		48.6	306	[7]	$n = 1;$ 8.1	—
Cyano(ethyl)propylarsine	AsNC ₆ H ₁₂		38.5 ± 0.7	303–334	[7]	6.41	DC≡N → C≡N 8.1
Tricyanophosphine	PC ₃ N ₃ sol		75.3 ± 2.9 ^b	298	[7]	—	12.6 ^b

^aEstimated using the correlation of vaporization enthalpies of trialkylphosphines and trialkylamines^bSublimation

Fig. 1.8 Dependence of the vaporization enthalpy on the number of carbon atoms in alkyl chain for 1 trialkylarsines, 2 trialkylphosphines, and 3 methylstibine to trimethylstibine series. Lines 1–3 show the influence of reverse dative bonds; line 2 shows the contribution to the energy by CH_2 groups



trimethylstibines (line 3), the energy contribution to the enthalpy characteristic following the replacement of the hydrogen atom in the molecule by a methyl group. The tendency of energy reduction due to the increased contribution to the vaporization enthalpy during the transition from triethylphosphine to tripropylphosphine reflects the reduction of the reverse dative bond with the increase in the number of carbon atoms of the alkyl ligand, with completion of the influence in the compound with the propyl fragment. The further increase in the enthalpy characteristic of tributylphosphine by 8.2 kJ mol^{-1} is determined by the energy contribution of the increasing number of methylene groups. It follows that it is possible to estimate the vaporization enthalpies of tripentylphosphine and trihexylphosphine as being equal to 59.9 and 68.1 kJ mol^{-1} , respectively.

The alkyl molecules of the elements of the nitrogen subgroup with three alkyl groups at the bottom of a trigonal pyramid form liquid and crystal structures with the six-coordinated element atom, wherein the bond vacancies form six specific intermolecular interactions with the pentacoordinated carbon atom, $\text{DE} \rightarrow \text{CH}_3\text{--E}$, and the propyl ligand, $\text{DE} \rightarrow \text{CH}_3\text{--CH}_2\text{--CH}_2\text{--E}$:

$$\text{DE} \rightarrow \text{CH}_3 - (\text{H}_2)n - \text{E} = \Delta_{\text{vap}} H^0(298 \text{ K})/6 \quad (1.8)$$

The influence of the reverse dative bond ends at the third carbon atom of the chain (Fig. 1.1). As a result, the energies of the specific interactions are determined from the vaporization enthalpy or sublimation enthalpy, interconnected with the number of bursting bonds and their energies [4, 5], using Eq. (1.8). The results of the calculations are described by the natural sequence of its stabilization with an increasing number of carbon atoms in the alkyl ligand, with the maximum energy value of the specific interaction in the compound with a butyl ligand:

Trimethylphosphine (4.8) < Triethylphosphine (6.4 , 308 K) = Tripropylphosphine (17.21 , 340 K) < Tributylphosphine (7.21 kJ mol^{-1} , 360 K)

Trimethylarsine (4.81) < Triethylarsine (6.41) < Tripropylarsine (7.3 kJ mol⁻¹)
 Trimethylstibine (5.2) < Triethylstibine (7.0 kJ mol⁻¹)
 Trimethylbismutene (6.0) < Triethylbismutene (7.67 kJ mol⁻¹)

This is caused by the completion of the influence of the reverse dative bond at the fourth carbon atom of the chain. Attention needs to be paid to the fact that the changes in the stability of specific interactions were obtained using the vaporization enthalpies measured at temperatures that were higher than the standard condition. Therefore, the actual energy values of the specific interactions for, for example, tripropylphosphine, tributylphosphine, triethylstibine, and triethylbismutene, should have increased values in comparison with those given in Table 1.8:

Trimethylphosphine (4.8) ≈ Trimethylarsine (4.81) < Trimethylstibine (5.2) < Trimethylbismutene (6.0 kJ mol⁻¹)
 Triethylphosphine (6.4, 306 K) ≈ Triethylarsine (6.41, 306 K) < Triethylstibine (7.0, 306 K) < Triethylbismutene (7.67 kJ mol⁻¹)

Tripropylphosphine (7.21, 306K) < Tripropylarsine (7.3 kJ mol⁻¹, 322K)

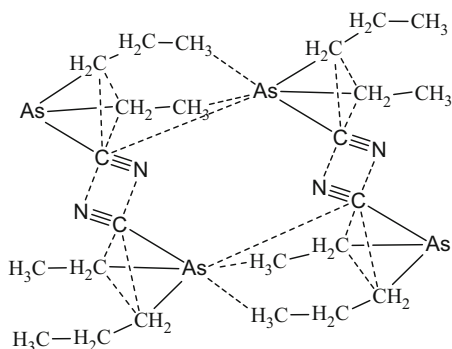
According to the specific interaction energy of compounds with a similar alkyl ligand, from the increasing sequence number of the methyl and ethyl compounds of the group element atom, the location of the shifting electron density from the carbon atom to the third and fourth energy level of the phosphorus atom and the arsine atom is not practically expressed by the energy of the specific intermolecular interaction. The influence of the shifting electron density is expressed at its location on the fourth and fifth energy level in trimethylstibine, triethylstibine, trimethylbismutene, and triethylbismutene. The increase in the number of carbon atoms in the ligand chain causes the shifting electron density, with its location at the third and fourth energy level in tripropylarsine and trimethylbismutene.

The energy of the specific interaction of low stability, formed by the isostructural methyl group of triisopropylarsine, can be determined from the difference between the vaporization enthalpies of the compounds with a similar ethyl fragment of triethylarsine, obtained using Eq. (1.8a) and given in Table 1.8:

$$\text{DH}_3\text{C} \rightarrow \text{H} - \text{CH}_2 = \Delta_{\text{vap}}H^0(\text{TK})_{\text{ip}} - \Delta_{\text{vap}}H^0(\text{TK})_{\text{et}}/2 \quad (1.8a)$$

A clearly defined pattern of the stabilization of the specific interaction formed by the unsaturated vinyl fragment $\text{DE} \rightarrow \text{CH}_2=\text{CH}-\text{E}$ in a number of compounds, as presented in the literature without errors (Table 1.8), is caused by an increase in the shift of electron density towards the more distant energy level of atoms of the elements P (third) < As (fourth) < Sb (fifth) < Bi (sixth):

Fig. 1.9 Schematic of the fragment of the volume chain of the network specific interaction of liquid cyano(ethyl)propylarsine



Trivinylphosphine (5.45) < Trivinylarsine (5.9) < Trivinylstibine (6.45) < Trivinylbismutene (8.1 kJ mol⁻¹),

The increased energy values of the specific interactions formed by the ethyl ligand DE → CH₃-CH₂-E in comparison with the formed vinyl fragment DE → CH₂=CH-E in liquid compounds is natural because the reduced number of hydrogen atoms of the vinyl ligand provides the reduced electron density at the carbon atoms and, relatively, at the atoms of arsine and stibine:

$$\begin{aligned} \text{Triethylarsine (6.35)} &> \text{Trivinylarsine (5.9 kJ mol}^{-1}\text{)}; \\ \text{Triethylstibine (7.0)} &> \text{Trivinylstibine (6.45 kJ mol}^{-1}\text{)} \end{aligned}$$

In this connection, there are doubts about the correctness of the values given in the literature for the vaporization enthalpies of triethylbismutene and trivinylstibine, without any indication of the error:

$$\text{Triethylbismutene (7.67)} < \text{Trivinylbismutene (8.1 kJ mol}^{-1}\text{)}$$

The carbon atom of the cyanide group of molecules of cyano(ethyl)propylarsine, with the cyano, ethyl, and propyl fragments, participates in the formation of the specific interaction with the arsenic atom and the nitrogen atom, and is in a pentacoordinated condition (Fig. 1.9). An energy contribution to the vaporization enthalpy of cyano(ethyl)propylarsine is given by the two formed propyl fragments, two ethyl fragments, and two specific interactions of the nitrile group. Taking the energies of the specific interactions $\text{DAs} \rightarrow \text{CH}_3\text{-CH}_2\text{-As}$ and $\text{DAs} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-As}$ equal to 6.4 and 7.3 kJ mol⁻¹, respectively, which are the energies of the same interactions in liquid triethylarsine and tripropylarsine, we determined the energy of the specific interaction of $\text{DC}\equiv\text{N} \rightarrow \text{C}\equiv\text{N}$ of liquid cyano(ethyl)propylarsine, with the help of Eq. (1.9):



$$= (\Delta_{\text{vap}}H^0(T\text{K}) - 2\text{DAs} \rightarrow \text{CH}_3 - \text{CH}_3 - \text{As} - \text{DAs} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{As})/2 \quad (1.9)$$

The energy of the specific interaction $\text{DC}\equiv\text{N}\rightarrow\text{C}\equiv\text{N}$ of crystal tricyanophosphine, formed by the three cyanide groups, is determined by dividing the sublimation enthalpy by the six bond vacancies. The obtained energy values of the interaction of the two compounds are presented in Table 1.8 and illustrate its high stability for the compounds.

1.4.2 Alkyl Hydrogens and Alkene Hydrogens of the Phosphorus Subgroup Elements

Shown in Table 1.9 are the vaporization enthalpies of trialkyl hydrogens of the phosphorus subgroup elements, which point to an increase of 3.2 and 1.6 kJ mol^{-1} in the vaporization enthalpy following replacement of a hydrogen atom by a methyl group.

Methylstibine (27.4, 248 K) < Dimethylstibine (30.6, 254 K) < Trimethylstibine (32.2 kJ mol^{-1} , 308 K)

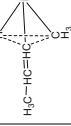
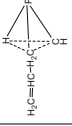
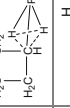
Similar changes take place in the compounds of the bismuth derivatives. Based on these data, it can be concluded that the formed specific interactions are more stable than the formed hydrogen bonds. The low energy values of the specific interactions of liquid methyl, ethyl, and butyl compounds of the phosphorus subgroup elements (Table 1.9) with one to four carbon atoms of the alkyl chain are little susceptible to the change in energy of the formed specific intermolecular interactions following replacement of the alkyl ligand by the hydrogen atom. This allows estimation of the energy value of the hydrogen bond, formed by the hydrogen atom in liquid methylstibine, dimethylstibine, and in the corresponding compounds of arsenic and bismuth. The energies of the formed hydrogen bonds of the compounds are obtained from Eqs. (1.10) and (1.11):

$$\text{DSb} \bullet \bullet \bullet \text{H} - \text{Sb} = (\Delta_{\text{vap}}H^0(T\text{K}) - 2\text{DSb} \rightarrow \text{CH}_3 - \text{Sb})/4 \quad (1.10)$$

$$\text{DSb} \bullet \bullet \bullet \text{H} - \text{Sb} = (\Delta_{\text{vap}}H^0(T\text{K}) - 4\text{DSb} \rightarrow \text{CH}_3 - \text{Sb})/2 \quad (1.11)$$

The calculation results for the hydrogen bonds (Table 1.9) indicate the stabilization of the hydrogen bonds $\text{DSb} \bullet \bullet \bullet \text{H} - \text{Sb}$ following the replacement of the hydrogen atom in stibine by the methyl group, showing the influence of the increasing shift of electron density from the hydrogen atom to the Sb atom:

Table 1.9 Energies (kJ mol^{-1}) of specific interactions of liquid methyl- and dimethylphosphine, arsine, stibine, and bismutine

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K) [7]	T (K)	DE $\rightarrow$ $\text{CH}_3-(\text{CH}_2)_n-\text{E}$	DE $\cdots$ H-E
Methylstibine	SbCH ₅		27.4	248	5.38	4.16
Dimethylstibine	SbC ₂ H ₇		30.6	254	5.38	4.55
Methylbismutine	BiCH ₅		29.9	224	6.0 5.8	4.42
Dimethylbismutine	BiC ₂ H ₇		32.7	228	6.0	4.47
Diethylarsin	AsC ₄ H ₁₁		34.2	298	6.41	4.3
Allylmethylphosphine	C ₄ H ₉ P		34.4	276	4.8 DP $\rightarrow$ $\text{CH}_3-\text{CH}=\text{CH}-\text{P} = 8.3$	4.0
2-Propylphosphine	C ₃ H ₇ P		32.7	241	4.8 DP $\rightarrow$ $\text{CH}_2=\text{CH}-\text{CH}_2-\text{P} = 8.3$	4.0
3-Butenylphosphine	C ₄ H ₉ P		34.5	273	DPCH ₂ =CH-CH ₂ -P = 8.3 DCH ₂ = 1.8	4.0
Phospholane	C ₄ H ₉ P		37.4	272	10.7	4.0
Propynylphosphine	C ₃ H ₅ P		36.8	298	4.8 D-C≡C- = 5.5	4.0

DSb•••H–Sb: Stibine (3.51, 254.8 K) < Methylstibine (4.16, 248 K) < Dimethylstibine (4.55 kJ mol⁻¹, 254 K)

The obtained increased negative charge of the Sb atom transferred partly from the p_z orbital to the carbon atom, in turn, provides the carbon atom with the ability to form more stable specific interactions $DSb \rightarrow CH_3-Sb > DSb\bullet\bullet\bullet H-Sb$ by the methyl group in comparison with the hydrogen bond. At the same time, by the method of photoelectron spectroscopy [45, 46], it was shown that the replacement of the hydrogen atom by a methyl group in amines is accompanied by an insignificant reduction in the electron density at the nitrogen atom and reduced stability of the formed specific interaction $DN \rightarrow CH_3-N < DN\bullet\bullet\bullet H-N$, which is proved by the obtained energy values [9]. The same sequence in the stabilization of the hydrogen bond following replacement of the hydrogen atom in the molecule of bismutene by methyl groups is expressed in methylbismutene and dimethylbismutene, with a disparity in the energies of the hydrogen bonds and the specific interaction $DBi\bullet\bullet\bullet H-Bi < DBi \rightarrow CH_3-Bi$:

$DBi \bullet \bullet \bullet H - Bi$: Methylbismutene(4.42, 224 K) < Dimethylbismutene (4.47 kJ mol⁻¹, 228 K) < $DBi \rightarrow CH_3 - Bi$: Trimethylbismutene(6.0 kJ mol⁻¹)

The replacement of the hydrogen atom in arsine by ethyl groups is accompanied by an increased difference in the stabilization of the hydrogen bond $DAs\bullet\bullet\bullet H-As$ and with the energy of specific interactions formed by the ethyl ligand:

$DAs \bullet \bullet \bullet H - As$: Arsine(3.02, 210.68 K) < Diethylarsine(4.3 kJ mol⁻¹, 298 K) < $DAs \rightarrow CH_3 - CH_2 - As$: Triethylarsine (6.41 kJ mol⁻¹)

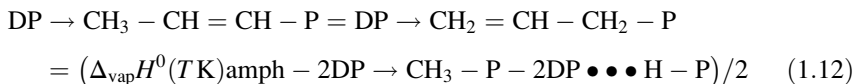
Based on the obtained data, it can be concluded that the low negative charge of the phosphorus atom in alkyl and trialkyl hydrides increases in the analogs of arsenic, antimony, and bismuth, and that reduced stability of the hydrogen bonds can be seen in comparison with the energies of specific interactions formed by the methyl and ethyl ligands.

The reduced energy value of the formed specific interaction of the vinyl ligand in comparison with the ethyl ligand is caused by the reduced shifting of the electron density, for example, at the phosphorus atom. This indicates that allyl and 2-propyl ligands with the same number of carbon atoms give the phosphorus atom practically adequate electron densities. This means that the difference in the vaporization enthalpies of allylmethylphosphine and 2-propylphosphine (1.7 kJ mol⁻¹) is equal to the difference between the energies of specific interaction formed by the methyl group and the energy of the hydrogen bonds formed by hydrogen atoms with the phosphorus of these compounds:

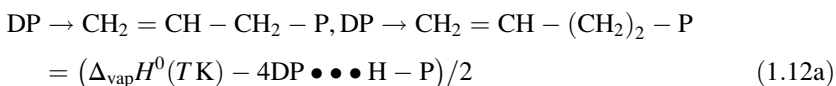
$$\Delta_{\text{vap}}H^0(TK)_{\text{amph}} - \Delta_{\text{vap}}H^0(TK)_{\text{pph}} = 2(DP \rightarrow CH_3 - P - 2DP \bullet \bullet \bullet H - P)$$

Taking into account the energy value of the specific interaction $DP \rightarrow CH_3-P$

(4.8 kJ mol⁻¹), the energy of the hydrogen bond can be obtained as being equal to 4.0 kJ mol⁻¹. This makes it possible to calculate the energy value of the specific interaction formed by the allyl ligand of allylmethylphosphine, with the help of Eq. (1.12):



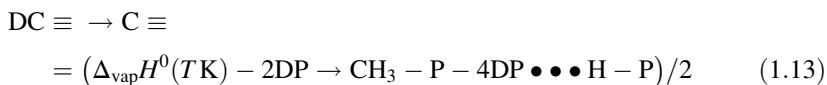
The obtained energy values of the hydrogen bonds (Table 1.9) allows the determination of the energies of the specific interactions of liquid 2-propylphosphine, 3-butenylphosphine, and phospholane from the difference in vaporization enthalpies of the compounds using Eq. (1.12a), taking into account the energy contribution of the four bonds formed by the two hydrogen atoms of the contacting molecules:



Taking into account the completion of the reverse dative bond influence at the third carbon atom of the chain, the energy contribution of the methylene group to the vaporization enthalpy is subtracted, equal to the difference with the vaporization enthalpy of 2-propylphosphine. The calculated energy values of the specific interactions of the liquid compounds of the phosphines with unsaturated ligands are described by the natural sequence of the energy stabilization with an increase in the number of carbon atoms in the chain (up to three), caused by the reduction of the influence of the reverse dative bond on the formation of intermolecular interactions:

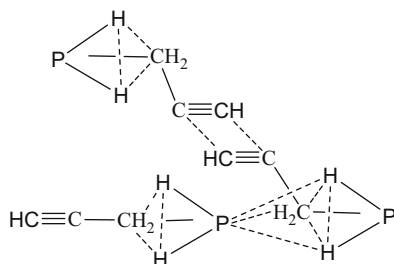
Trivinylphosphine (5.45) < Allylmethylphosphine (8.3) = 2-Propylphosphine (8.3) < 3-Butenyl-Phosphine (8.3 kJ mol⁻¹)

The molecule of propynylphosphine with the triple bond $-\text{C}\equiv\text{C}-$ gains two additional bond vacancies, expressed by the carbon atoms with the triple bond [9]. The formed specific interactions participate in the crosslinking of the volumetric chains of the liquid structure (Fig. 1.10). The methylene group of the propynyl fragment forms specific interactions with energy values close to the energy of the interaction formed by the methyl group (4.8 kJ mol⁻¹). The known energy values of hydrogen bonds, formed by the hydrogen atoms of the propynylphosphine molecule, allow the energy of the specific interaction $\text{D}-\text{C}\equiv\text{C}-$ to be calculated with the help of Eq. (1.13):



The obtained energy value of this interaction type is equal to 5.5 kJ mol⁻¹ and

Fig. 1.10 Schematic of a fragment of the volume–chain liquid structure of propynylphosphine



agrees with the result for liquid organic compounds in the literature (5.0 kJ mol^{-1}) [9].

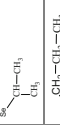
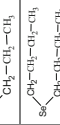
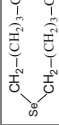
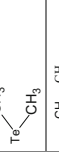
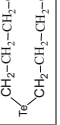
1.5 Energies of Specific Interactions of Selenium and Tellurium Alkyls and Their Unsaturated Analogs

1.5.1 *Selenium and Tellurium Alkyls*

Research into the electron structure of dimethyloxygen and dimethylsulfur point to a match in the sequence of the four upper orbitals and to the contribution increase of the *p*-orbitals in a number of elements, the increased shifting of electron density with its location at the more distant energy level [2]. This may cause the stabilization of specific interactions formed by the element atom of the sixth group, shifting the electron density from the more distant energy level. The increasing value of the vaporization enthalpies of dialkyl elements of the group (Table 1.10) is related to the number and energy of the bursting specific interactions, combined with the conclusion drawn from the results of spectral studies.

Presented in Fig. 1.11 is the dependency of the vaporization enthalpies of selenium alkyls and telluride alkyls on the number of carbon atoms in the alkyl chain. There is a distinctly inadequate energy contribution because of the reduction of the reverse dative intramolecular bond influence on the shifting of the electron density on the chain, ending at the propyl ligand. The further sharp increase in the vaporization enthalpy of the butyl compounds of selenium and telluride is caused by the contribution of the fourth carbon atom, free from the influence of the reverse dative bond. Therefore, the contribution of each following chain methylene group is additive for this group of compounds, and the value is equal to the difference in the vaporization enthalpies of neighboring compounds in the series or to the vaporization enthalpy of the group of compounds divided by the corresponding number of methylene groups [9]. The molecule of the dimethyl, diethyl, and dipropyl compound of the sixth group elements, with two bond vacancies of the two free electron pairs and two terminal methyl groups with essentially undivided $2s^2$ electron pairs of carbon atom of the terminal methyl group, form four specific interactions

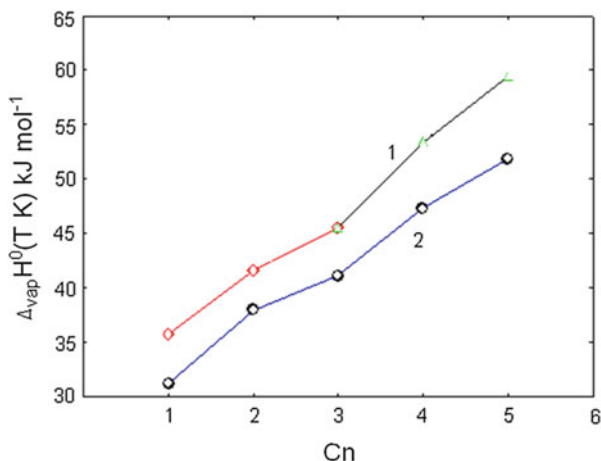
Table 1.10 Energies (kJ mol⁻¹) of specific interactions of liquid dialkyl selenides and tellurides

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K)	T (K)	References	DE $\rightarrow$ CH ₃ -(CH ₂) ₂ -E	DH ₃ C $\rightarrow$ H-CH ₂
Dimethyl selenide	C ₂ H ₆ Se		31.2 $\pm$ 0.1	273–333	[18, 47, 48]	7.8	—
Diethyl selenide	C ₄ H ₁₀ Se		38.9 37.95 $\pm$ 0.1	298	[39] [48, 49]	9.49	—
Diisopropyl selenide	C ₆ H ₁₄ Se		43.1 $\pm$ 1.0	298	[7]	9.49	5.2:4 = 1.3
Dipropyl selenide	C ₆ H ₁₄ Se		41.1 ^a	298	—	10.3	—
Dibutyl selenide	C ₈ H ₁₈ Se		47.3	298	[7]	10.3 Σ DCH ₂ = 6.2	—
Dipentyl selenide	C ₁₀ H ₂₂ Se		51.9 $\pm$ 1.0	298	[7]	10.3 Σ DCH ₂ = 10.8	—
Dimethyl telluride	C ₂ H ₆ Te		37.4 $\pm$ 0.7 35.7 $\pm$ 0.1	298 273–372	[47, 48]	8.93	—
Diethyl telluride	C ₄ H ₁₀ Te		41.6 $\pm$ 1.0 41.6 $\pm$ 0.2B	298 273–341	[48, 49]	10.4	—
Diethyl telluride	C ₄ H ₁₀ Te sub		53.4 $\pm$ 2.3		[49, 50]	13.35 ^a	—
Dipropyl telluride	C ₆ H ₁₄ Te		46.5 $\pm$ 0.7 45.5 $\pm$ 0.3B	298 298–434	[51]	11.4	—
Diisopropyl telluride	C ₆ H ₁₄ Te		47.6 $\pm$ 0.1 40.4 $\pm$ 0.1B	358 298–399	[48, 51]	10.4	—
Dibutyl telluride	C ₈ H ₁₈ Te		53.4 $\pm$ 0.1	298	[48, 51]	11.4 DCH ₂ = 7.9	—

Diisobutyl telluride	$\text{C}_8\text{H}_{18}\text{Te}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Te} - \text{CH}_2 - \text{CH} - \text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	$47.6 \pm 0.1\text{B}$	303–409	[48, 51]	11.4	$2.1:4 = 0.5$
Di- <i>sec</i> -butyl telluride	$\text{C}_8\text{H}_{18}\text{Te}$	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Te} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	49.6 ± 0.9 $303\text{--}372$	338	[51, 52]	11.4	$2.0:4 = 0.5$
Dipentyl telluride	$\text{C}_{10}\text{H}_{22}\text{Te}$	$\begin{array}{c} \text{CH}_2 - (\text{CH}_2)_3 - \text{CH}_3 \\ \\ \text{Te} - \text{CH}_2 - (\text{CH}_2)_3 - \text{CH}_3 \end{array}$	59.5 ± 0.8	343–403	[52]	11.4 $\Sigma \text{DCH}_2 = 7.9$	–
Diisopentyl telluride	$\text{C}_{10}\text{H}_{22}\text{Te}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{Te} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3 \\ \quad \\ \text{CH}_3 \end{array}$	51.9 ± 0.7	343–403	[52]	11.4 $\text{DCH}_2 = 6.4$	$0.9:4 = 0.2$

^aEstimated on the basis of the correlation $\Delta_{\text{vap}}H^0(T\text{K})\text{SeR}_2 = f(\Delta_{\text{vap}}H^0(T\text{K})\text{TeR}_2)$

Fig. 1.11 Dependence of vaporization enthalpy on the number of carbon atoms in the alkyl chain of dialkyl tellurides (1) and dialkyl selenides (2)



DSe $\rightarrow$ CH₃–Se with the molecules of the near environment. The angled molecule of the alkyl of the sulfur subgroup, with the ligand at an angle of 90° or more, causes the formation of the volumetric chain structure of the liquid condition, for which the energies can be derived by the division of the vaporization enthalpy by the number of bond vacancies. The number of formed bonds can be found using Eq. (1.14):

$$\text{DE} \rightarrow \text{CH}_3 - (\text{CH}_2)_n - \text{E} = \Delta_{\text{vap}} H^0(TK)/4 \quad (1.14)$$

For calculation of the energy of the hydrogen bonds formed in liquid hydrogen sulfide, taking into account that the reverse dative bond completes its influence at the third carbon atom of the chain in the molecule with the propyl ligand, there is reason to assume that the energy value is constant in the compound with the butyl ligand and the ligand with a large number of carbon atoms in the alkyl chain. The energies of the specific interactions formed by the butyl fragments are determined using Eq. (1.15):

$$\text{DE} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{E} = (\Delta_{\text{vap}} H^0(TK) - Dq\text{CH}_2)/4 \quad (1.15)$$

where q is the number of methylene groups of the compound with butyl or bigger ligands.

Taking into account that the energy contribution of the propyl fragment of diisobutyl selenide and diethyl selenide to the vaporization enthalpy of these compounds is similar, the value of the energy contribution of isostructural methyl groups can be obtained from the difference in the enthalpy characteristics of these compounds by division by the number (n) of methyl groups:

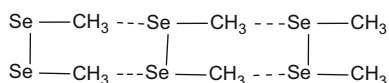
$$\begin{aligned} \text{DisoCH}_3 = 2\text{DH}_3\text{C} &\rightarrow \text{H} - \text{CH}_2 \\ &= (\Delta_{\text{vap}}H^0(\text{TK})_{\text{ip}}) - (\Delta_{\text{vap}}H^0(\text{TK})_{\text{et}})/n \end{aligned} \quad (1.16)$$

The calculated energy results of the formed liquid specific interactions of the considered compounds (Table 1.10) are described by the natural sequence of stabilization of tellurides, with increased stability of the specific interactions for the liquid dialkyl tellurides:

Dimethyl selenide (7.8) < Diethyl selenide (9.45) < Dipropyl selenide (10.) < Dibutyl selenide (10.3 kJ mol⁻¹).

Dimethyl telluride (8.93) < Diethyl telluride (10.4) < Dipropyl telluride (11.40 = Dibutyl

It follows that the electron pair at the more distant energy level of the tellurium atom provides the increased shifting of the electron density from the alkyl chains in comparison with selenium and especially the sulfur atoms. This observation is confirmed by the research results on the electron structures using photoelectron spectroscopy of the methyl compounds of the basic group VI elements [53, 54] and the calculation of the electron structure by an ab initio method [54]. This work shows that the sequence of the four upper orbitals of O(CH₃)₂ and S(CH₃)₂ coincide: $1b_1 < 4a_1 < 3b_2 < 1a_2$. Following the replacement of sulfur by selenium and tellurium, the contribution of the *p*-orbitals of the sixth group to the three upper MOs increases. According to the literature [55], using the example of compounds of E(CH₂)₄ of the oxygen group elements, it is shown that, following the increase in the size of the heteroatom, the oscillation circuit of the first band significantly narrows and, therefore, the level of localization of the *n*-electrons at atom E^{VI} of the group significantly increases. The obtained energy values of the specific interaction DTe → CH₃–CH₂–Te in liquid (10.4 kJ mol⁻¹) and crystal (13.35 kJ mol⁻¹) diethyl telluride allows a conclusion to be made regarding the significant influence of the crystalline field on the stabilization of the bonds of tellurium alkyls, caused by the participation of the electrons located at the sixth energy level in the formation of the bonds. As shown in Table 1.10, the energies of the specific interactions (except for diisopropyl selenide) of isostructural compounds of tellurium indicate their low stability, which lies within the rather high error values of the experimentally measured vaporization enthalpies.



The selenium and tellurium atoms of the molecules of dialkyldiselenide and dibutyl ditelluride with six bond vacancies retain one free electron pair at the selenium and tellurium atoms not engaged during formation of the specific interactions between the selenium atom or the tellurium atom by crosslinking chains or during shifting of the electron density to the carbon atom of the methyl group of

Table 1.11 Energies (kJ mol^{-1}) of specific interactions of liquid dialkyl diselenides and dibutyl ditelluride at 298 K

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0$ (298 K) [7]	$\text{DE} \rightarrow \text{CH}_3-(\text{CH}_2)_n$
Dimethyl diselenide	$\text{C}_2\text{H}_6\text{Se}_2$	$\begin{array}{c} \text{Se}-\text{CH}_3 \\ \\ \text{Se}-\text{CH}_3 \end{array}$	42.0 ± 1.0	$n = 0,$ 10.5
Diethyl diselenide	$\text{C}_4\text{H}_{10}\text{Se}_2$	$\begin{array}{c} \text{Se}-\text{CH}_2-\text{CH}_3 \\ \\ \text{Se}-\text{CH}_2-\text{CH}_3 \end{array}$	47.1 ± 0.9	$n = 1,$ 11.8
Dibutyl ditelluride	$\text{C}_8\text{H}_{18}\text{Te}_2$	$\begin{array}{c} \text{Te}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3 \\ \\ \text{Te}-\text{CH}_2-(\text{CH}_2)_2-\text{CH}_3 \end{array}$	57.3 ± 1.0	$n = 3,$ 14.32

dimethyl diselenide, the end methyl group of diethyl diselenide, or dibutyl ditelluride. The shifting of the electron density should be expressed by the stabilization of the specific interaction of $\text{DE} \rightarrow \text{CH}_3-(\text{CH}_2)_n$, where n is the number of methylene groups in the chain. As a result, the selenium and tellurium atoms of the molecules of dialkyl diselenide and ditelluride in their liquid condition are in the three-coordinated condition and the molecule forms four specific interactions, whose energies can be calculated using Eq. (1.14).

The obtained energy values of the bonds (Table 1.11) point to its stabilization, completing at the three carbon atoms of the alkyl chain. Consequently, the real value of the specific interaction energy of dibutyl ditelluride is overstated by approximately 1.2 kJ mol^{-1} , which is equal to the energy contribution of the methylene group.

1.5.2 Dialkenes of Selenium and Tellurium

The vaporization enthalpies of alkyls of selenium and tellurium have been determined for a limited number of compounds. The value of the vaporization enthalpy of divinyl selenide (Table 1.12) raises doubts about its correctness because it is greater than the enthalpy characteristic of diethyl selenide and dipropyl selenide (Table 1.10). The similarity in the molecular structures with the saturated and unsaturated ligands determines the analogous structure of the liquid and crystal conditions and the formed network of specific interactions. Thus, the energy values of the formed specific interactions are calculated using Eq. (1.15). Cyclic molecule of selenophene with the planar structure has four bond vacancies two of which display the end of the CH group and the two free electron pairs of tellurium atom.

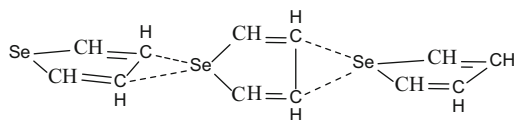
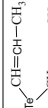


Table 1.12 Energies (kJ mol^{-1}) of specific interactions of liquid dialkene tellurides and selenophenes

Compounds	Formula	Structure	$\Delta_{\text{vap}}H^0(298\text{ K})$ [7]	T (K)	$\text{DE} \rightarrow \text{CH}_2=\text{CH}-$
Divinyl selenide	$\text{C}_4\text{H}_6\text{Se}$		42.0 ± 1.0	298	13.0
Divinyl telluride	$\text{C}_4\text{H}_6\text{Te}$		38.1 ± 2.1	–	9.52
Diallyl telluride	TeAl_2		44.3 ± 0.5 [18]	314–397	$\text{DTe} \rightarrow \text{CH}_3-\text{CH}=\text{CH}- = 11.1$
Selenophene	$\text{C}_4\text{H}_4\text{Se}$		38.1 ± 1.0	298	$\text{DSe} \rightarrow \text{CH}=\text{CH}- = 9.52$
Selenophene	$\text{C}_4\text{H}_4\text{Se}$		$\Delta_{\text{sub}}H^0(225)$ [39] 47.1	225	$\text{DSe} \rightarrow \text{CH}=\text{CH}- = 11.8$

The two free electron pairs of the tellurium atom in the network of the liquid and crystal conditions participate in four specific interactions $\text{DTe} \rightarrow \text{CH}=\text{CH}-\text{Te}$, whose energies are determined from Eq. (1.15). Comparison of the data (Table 1.12) indicates invariance in the energy of the formed $\text{DTe} \rightarrow \text{CH}_2=\text{CH}-\text{Te}$ (9.52 kJ mol^{-1}) in the liquid divinyl telluride and $\text{DSe} \rightarrow \text{CH}=\text{CH}-\text{Se}$ (9.52 kJ mol^{-1}) in the liquid selenophene with the cyclic ligand and, on the other hand, in the liquid diethyl telluride (10.4 kJ mol^{-1}) with the saturated ethyl ligand. A similar tendency in the energies of the specific interactions takes place at the replacement of the unsaturated allyl ligand of liquid diallyl telluride by the saturated propyl ligand of dipropyl telluride: $\text{DTe} \rightarrow \text{CH}_2=\text{CH}-\text{CH}_2-\text{Te}$ (11.1 kJ mol^{-1}) and $\text{DTe} \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{Te}$ (11.4 kJ mol^{-1}). Note that the energy values of the specific interactions with allyl and propyl ligand are the highest and remain practically unchanged in the corresponding series of compounds. The obtained energy values of the specific interactions of selenophene illustrate the stabilization of $\text{DSe} \rightarrow \text{CH}=\text{CH}-\text{Se}$ (9.52 kJ mol^{-1}) by 2.3 kJ mol^{-1} during interaction by the crystal field (11.8 kJ mol^{-1}). In accordance with the given data, the energies of the formed specific intermolecular interactions of the unsaturated ligand have a reduced value and its stabilization of the crystal field in diethyl telluride is lower by 2.0 kJ mol^{-1} .

1.5.3 Energies of Specific Interactions of Phenyl Selenides and Diphenylmercury

In the literature [9, 56], a detailed analysis is presented of the specificity of the interactions of the benzene molecule, caused by the alternating charge difference of the carbon atom of the CH groups and the energy contribution of the saturated hydrogen atom to the vaporization enthalpy and sublimation enthalpy, equal to 0.60 and 1.00 kJ mol^{-1} , respectively. This provides the energies of the three types of specific interactions formed in liquid and crystal benzene in dependence on the number of saturated ring hydrogen atoms: $\text{DHC} \rightarrow \text{CH}$ (5.63), $\text{DHC} \rightarrow \text{C}$ (5.35), and $\text{DC} \rightarrow \text{C}$ (5.05 kJ mol^{-1}) in liquid conditions and $\text{DHC} \rightarrow \text{CH}$ (7.43), $\text{DHC} \rightarrow \text{C}$ (6.90), and $\text{DC} \rightarrow \text{C}$ (6.40 kJ mol^{-1}) in crystals.

Molecules of methylphenyl selenide with five bond vacancies of the CH group, one of the carbon atom with a saturated hydrogen atom of the benzene ring, the carbon atom of the methyl group (expressed by the essentially undivided $2s^2$ electron pair), and two free electron pairs of the selenium atoms is able to form nine specific interactions. There are five interactions $4\text{DHC} \rightarrow \text{CH}$ and $\text{DHC} \rightarrow \text{C}$ (Fig. 1.12a) with known energy values, $\text{DSe} \rightarrow \text{CH}$ and $\text{DSe} \rightarrow \text{C}$ interactions of similar energies, and two $\text{DSe} \rightarrow \text{CH}_3-\text{Se}$ interactions. Taking the energy value of the specific interaction of $\text{DSe} \rightarrow \text{CH}_3-\text{Se}$ to be equal to the value of the same type of interaction of the liquid dimethyl selenide (7.8 kJ mol^{-1}) and using the known energy values of the formed specific interactions of the benzene ring, the total

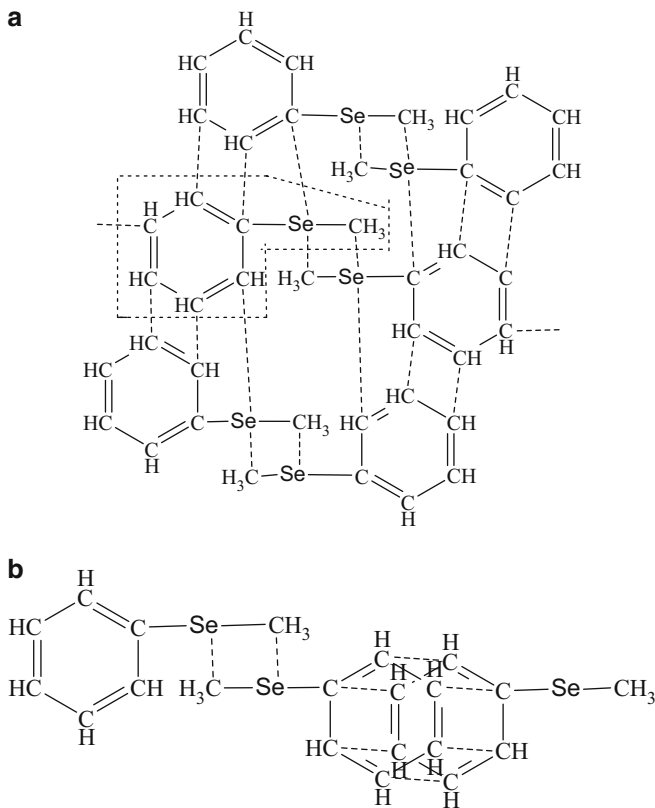


Fig. 1.12 (a,b) Schematics of the liquid methylphenyl selenide with the chain network of specific intermolecular interactions

energy value of the two interactions $\text{DSe} \rightarrow \text{CH}$ and $\text{DSe} \rightarrow \text{C}$ can be obtained using Eq. (1.17):

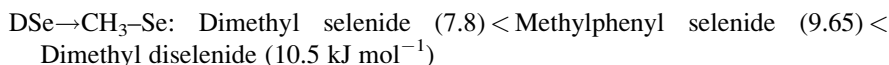
$$\begin{aligned}
 &\text{DSe} \rightarrow \text{CH} + \text{DSe} \rightarrow \text{C} \\
 &= (\Delta_{\text{vap}} H^0(T\text{K})_{\text{mps}} - 4\text{DHC} \rightarrow \text{CH} - \text{DHC} \rightarrow \text{C} - \text{DSe} \rightarrow \text{CH}_3 - \text{Se}) \\
 &\hspace{15em} (1.17)
 \end{aligned}$$

The obtained value of 8.75 kJ mol^{-1} for $\text{DSe} \rightarrow \text{CH} > \text{DSe} \rightarrow \text{C}$ plus the value of the energy contribution of the saturated hydrogen atom (0.60 kJ mol^{-1}) allows the estimation of their values as 4.70 and 4.10 kJ mol^{-1} , respectively. Taking into account the reduced energy values of the two types of interactions in comparison with those of the formed benzene ring, $\text{DHC} \rightarrow \text{CH}$ (5.63) and $\text{DHC} \rightarrow \text{C}$ (5.35 kJ mol^{-1}), it can be concluded that the specific interactions $\text{DSe} \rightarrow \text{CH}$ and $\text{DSe} \rightarrow \text{C}$ are realized in the liquid and crystal methylphenyl selenide.

The rigidity of the benzene ring and the increased ability of the carbon atom of the methyl group to shift the electron density to the remote energy level of the selenium atom provide the increased difference in charge of the carbon atom and the increased stability of the formed specific interaction $\text{DSe} \rightarrow \text{CH}_3\text{-Se}$. Therefore, the selenium atom of the methylphenyl selenide molecule participates in the formation of the specific interaction by one free electron pair, and the second pair provides it with the increased stabilization. Given in Fig. 1.12b is a schematic of the structure of liquid methylphenyl selenide with the network of eight specific interactions: six interactions of two types, $4\text{DHC} \rightarrow \text{CH}$ and $2\text{DHC} \rightarrow \text{C}$ formed by the benzene ring, and two interactions of $\text{DSe} \rightarrow \text{CH}_3\text{-Se}$ with unknown energy calculated using Eq. (1.18), summarizing the energy contributions of all types of interactions to the vaporization enthalpy [9]:

$$\begin{aligned} \text{DSe} \rightarrow \text{CH}_3 - \text{Se} \\ = (\Delta_{\text{vap}}H^0(T\text{K})_{\text{mps}} - 4\text{DHC} \rightarrow \text{CH} - 2\text{DHC} \rightarrow \text{C})/2 \end{aligned} \quad (1.18)$$

Note that the CH groups of benzene rings are able to form specific interactions with the neighboring chains, matching them with stable interactions. The calculated energy value of the interaction $\text{DSe} \rightarrow \text{CH}_3\text{-Se}$ (Table 1.13) is described by the natural sequence:



This reflects the correct position of the high electron density shift from the carbon atom of the CH_3 group to the selenium atom of methylphenyl selenide in comparison with dimethyl selenide, providing an increased difference in the charges of the selenium and carbon atoms and the stability of the formed specific interaction. It follows that the rigid benzene ring should be quite clearly expressed by the stability reduction of the formed specific interaction of the selenium atom of diphenyl selenide with the carbon atom of two rings.

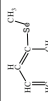
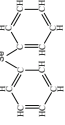
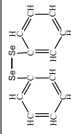
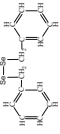
Presented in Fig. 1.13a is a schematic of liquid diphenyl selenide with the network of 14 formed specific interactions of two types, $10\text{DHC} \rightarrow \text{CH}$ and $4\text{DSe} \rightarrow \text{CH}_3\text{-Se}$, which allows the unknown energy value of the second type to be obtained with the help of Eq. (1.19):

$$\text{DSe} \rightarrow \text{CH}_3 - \text{Se} = (\Delta_{\text{vap}}H^0(T\text{K})_{\text{dps}} - 10\text{DHC} \rightarrow \text{CH})/4 \quad (1.19)$$

The calculated energy value of the specific interaction $\text{DSe} \rightarrow \text{CH}_3\text{-Se}$ is 2.5 kJ mol^{-1} . Table 1.13 illustrates its low stability, which is significantly reduced in comparison with the energy of the same type of interaction of liquid diphenyl selenide < dimethyl selenide (7.8 kJ mol^{-1}).

The low ability of CH groups of the benzene ring to shift the electron density is also expressed by diphenyl diselenide, whose selenium atoms participate in the formation of specific interactions by one free electron pair. Figure 1.13b presents a

Table 1.13 Energies (kJ mol⁻¹) of specific interactions of diphenyl diselenide and diphenyl mercury

Compounds	Formula	Structure	$\Delta_{\text{evap}}H^0$ (298 K) [7]	T (K)	DHC $\rightarrow$ CH	DHC $\rightarrow$ C=	DSe $\rightarrow$ CH ₃ -Se
Liquid							
Methylphenylselenide	C ₇ H ₈ Se		52.5	282	5.63 $\times$ 4	5.33 $\times$ 2	DSe $\rightarrow$ C-Se 9.4
Diphenyl selenide	C ₁₂ H ₁₀ Se		63.6 $\pm$ 2.5	294	5.63 $\times$ 10	—	2.5
			63.4	395			
Crystalline [39]							
Diphenyl diselenide	C ₁₂ H ₁₀ Se ₂		116.7 $\pm$ 2.5	313	7.43 $\times$ 10	—	10.6
Diphenylmercury	C ₁₂ H ₁₀ Hg		112.8 $\pm$ 0.8	—	7.43 $\times$ 10	—	9.6
Dibenzyl diselenide	C ₁₄ H ₁₄ Se ₂		130.5	—	7.43 $\times$ 8	6.93 $\times$ 4	DSe $\rightarrow$ CH ₂ -Se = 10.8

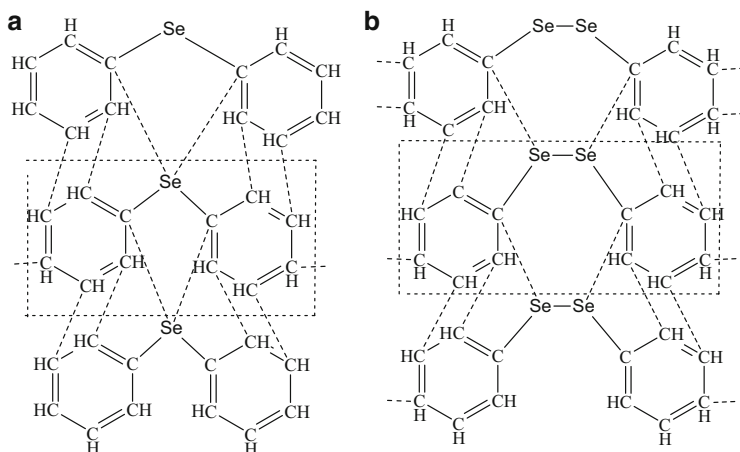


Fig. 1.13 Schematic of the liquid diphenyl selenide (a) and crystal diphenyl diselenide (b) with the chain network of specific intermolecular interactions

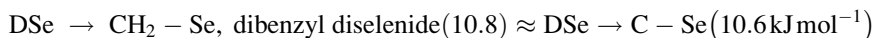
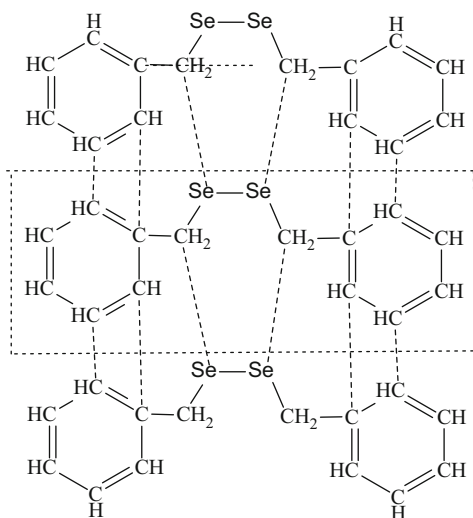
schematic of the crystal diphenyl diselenide structure, which reflects the specificity of the interaction and points to the formation, by CH groups, of ten specific interactions $10\text{DHC} \rightarrow \text{CH}$ and the specific interactions of $\text{DSe} \rightarrow \text{C}-\text{Se}$ by the two selenium atoms and the two carbon atoms of the two benzene rings, whose energies are derived from Eq. (1.19). The obtained energy value of the specific interaction (10.6 kJ mol^{-1}) of the crystal diphenyl diselenide is unusually low, despite the stabilizing effect of the crystal field. Thus, the Se-Se bond in the molecule of diphenyl diselenide does not significantly influence the stabilization of the specific interaction $\text{DSe} \rightarrow \text{C}-\text{Se}$.

The molecule of diphenylmercury has a similar structure to the diphenyl selenide molecule, the same number of bond vacancies, and forms the same types of specific interactions (Fig. 1.13a). Therefore, the energy of the specific interaction $\text{DSe} \rightarrow \text{C}-\text{Se}$ can be obtained using Eq. (1.19). Table 1.13 shows the calculated energy value of the diphenylmercury interaction, which reflects the manifestation of the stabilizing influence of the crystal field and, on the other hand, the electron configuration of the mercury atom. The molecule of dibenzyl diselenide with CH_2 groups contains two more bond vacancies and forms 16 specific interactions (Fig. 1.14): eight $8\text{DHC} \rightarrow \text{CH}$ and four $4\text{DHC} \rightarrow \text{C}$ formed by the benzene cycle, and four interactions $\text{DSe} \rightarrow \text{CH}_2-\text{Se}$ with unknown energy, which can be obtained using Eq. (1.20):

$$\begin{aligned} \text{DSe} \rightarrow \text{CH}_2 - \text{Se} \\ = (\Delta_{\text{vap}} H^0(T\text{K})\text{dbds} - 8\text{DHC} \rightarrow \text{CH} - 4\text{DHC} \rightarrow \text{C}) / 4 \end{aligned} \quad (1.20)$$

The calculated energy value of the specific interaction is within the range of experimental error:

Fig. 1.14 Schematic of the crystalline dibenzyl diselenide with the chain network of specific intermolecular interactions



Based on the established fact that there are small differences in the energies of liquid [9] esters, ketones, alcohols, and acids formed by the methylene group at its location with the benzene ring ($5.5\text{--}5.7 \text{ kJ mol}^{-1}$), the obtained energy value should be accepted as being constant when calculating the energy properties of dibenzyl analogs of the sulfur subgroup elements.

It should be noted that the experimentally measured sublimation enthalpies of triphenylphosphine, *N*-ethyl triphenylphosphine imine, triphenylarsine, triphenylantimony, and triphenylboron with values in the range 113.2 ± 3.0 to $92.1 \pm 2.5 \text{ kJ mol}^{-1}$ are not correct because of their significant reduction compared with the total energy value contributed by the three benzene rings ($130.8 \text{ kJ mol}^{-1}$), with the saturated hydrogen atom in the case of bis(benzyl)mercury, matching the energy value (88.7 kJ mol^{-1}) of two benzene rings.

1.5.4 Energies of Specific Interactions of (Dimethyl-amino) methylarsine, Dimethylstibineborane, and Dimethyl (methylthio)borane

The molecules of $\text{EH}_3\text{--}$ for the series N--P--As--Sb are characterized by a decline in the binding character $1a_1$ MO and $2a_1$ MO. At the same time, the reduction in the destabilizing B3MO $n\text{--}\sigma$ C–H interaction in the increasing series of nitrogen subgroups elements is accompanied by an increase in the ionization potential: $\text{N}(\text{CH}_3)_3 < \text{P}(\text{CH}_3)_3 < \text{As}(\text{CH}_3)_3$ and by the stabilization of intermolecular bonds

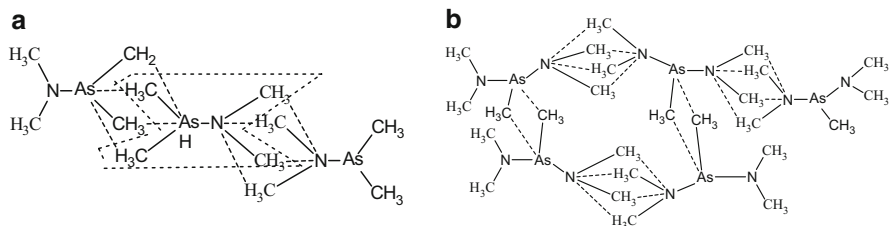


Fig. 1.15 Schematic of the network of specific interactions of crystalline (dimethylamino)dimethylarsine (a) and bis(dimethylamino)methylarsine (b)

[2]. It can be concluded that there is stabilization of the specific intermolecular interactions formed by the liquid and crystal methyl compounds of the series. This corresponds to the data in Table 1.8. Thus, it can be supposed that the shifting of the electron density in the molecule of (dimethylamino)dimethylarsine from the arsenic atom to the nitrogen atom causes the increase in the negative charge of the carbon atom of the methyl group and the difference in charge compared with the As atom. As a result, there occurs stabilization of the formed specific interaction $\text{DN} \rightarrow \text{CH}_3\text{-N} < \text{DAs} \rightarrow \text{CH}_3\text{-As}$, formed by the molecules of (dimethylamino)dimethylarsine and bis(dimethylamino)methylarsine. Since the amine and arsenide groups of (dimethylamino)dimethylarsine molecules do not form *trans* isomerism, the eight bond vacancies of the molecule form the four specific interactions $\text{DN} \rightarrow \text{CH}_3\text{-N}$ and $\text{DAs} \rightarrow \text{CH}_3\text{-As}$ (Fig. 1.15). In the literature [9], it was shown that the nitrogen atom at the maximum number of methyl groups in the molecules of $\text{N}(\text{CH}_3)_3$, $\text{NH}(\text{CH}_3)_2$, and NH_2CH_3 forms the specific interaction $\text{DN} \rightarrow \text{CH}_3\text{-N}$ with reduced stability in the liquid condition (4.25, 4.8, and 5.35 kJ mol⁻¹). Taking this value of the adequate energy of the compound in liquid (dimethylamino)dimethylarsine, we obtained the energy value of the specific interaction of the second type as being equal to 4.9 kJ mol⁻¹ using Eq. (1.21):

$$\text{DAs} \rightarrow \text{CH}_3 - \text{As} = (\Delta_{\text{vap}}H^0(TK) - 4\text{DN} \rightarrow \text{CH}_3 - \text{N})/4 \quad (1.21)$$

This value fits the calculated energy value of the same type of interaction (4.81 kJ mol⁻¹) in liquid trimethylarsine (Table 1.8).

The molecule of bis(dimethylamino)methylarsine with ten bond vacancies forms eight specific interactions of $\text{DN} \rightarrow \text{CH}_3\text{-N}$ with known energy and two interactions of the second type $\text{DAs} \rightarrow \text{CH}_3\text{-As}$, whose energy can be derived from Eq. (1.21a):

$$\text{DAs} \rightarrow \text{CH}_3 - \text{As} = (\Delta_{\text{vap}}H^0(TK) - 8\text{DN} \rightarrow \text{CH}_3 - \text{N})/2 \quad (1.21a)$$

As shown in Table 1.14, the energy value corresponds to the energy of the same type of interaction for (dimethylamino)dimethylarsine, lying within the error of the

Table 1.14 Energies (kJ mol^{-1}) of specific interactions and hydrogen bonds of (dimethylamino)methylarsine, dimethylstibineborane, and dimethyl(methylthio)borane

Compounds	Formula	Structure	$\Delta_{\text{vap}} H^0$ (298 K) [7]	T (K)	DE...H- E	DN $\rightarrow$ CH ₃ -N	DAs $\rightarrow$ CH ₃ -As
(Dimethylamino)dimethylarsine	AsNC ₄ H ₁₂		36.7	274– 342	–	4.25	4.9
bis(Dimethylamino)methylarsine	AsN ₂ C ₅ H ₁₅		39.2	–	–	3.7 (4.25)	4.8
Dimethylstibineborane	C ₂ H ₈ BSb		32.1	254	2.65	DSb $\rightarrow$ CH ₃ – Sb = 5.2	–
Dimethyl(methylthio)borane	BSC ₃ H ₉		31.6	263	–	DB-CH ₃ $\rightarrow$ B = 3.5	DS $\rightarrow$ CH ₃ -S = 8.8

experimentally measured vaporization enthalpy ($\pm 0.2 \text{ kJ mol}^{-1}$) of trimethylarsine, according to the work of Baev et al. [41].

The calculated energy values of the specific interaction for the two compounds, differing by the number of amine groups, are almost equal. This is promising as it allows the evaluation of the energies of other similar compounds. The molecule of dimethylstibineborane with the same number of bond vacancies and the formed specific interactions $\text{DSb} \rightarrow \text{CH}_3\text{-Sb}$ (with energy of 5.2 kJ mol^{-1}), and a similar network structure of specific interactions of liquid (dimethylamino)dimethylarsine (Fig. 1.15a), allows estimation of the energy value of the hydrogen bond of borane with the help of Eq. (1.22). Using the value of enthalpy sublimation of dimethylstibineborane (32.1 kJ mol^{-1} , measured at 254 K), a somewhat high value of the hydrogen bond energy $\text{DB} \cdots \text{H-B}$ (2.65 kJ mol^{-1}) is obtained in comparison with the energy of the same type of liquid diborane (1.83 kJ mol^{-1}) (Table 1.14). The molecule of dimethyl(methylthio)borane, with six bond vacancies and a vaporization enthalpy of 31.6 kJ mol^{-1} measured at 264 K, forms in the liquid condition four specific interactions $\text{DB-CH}_3 \rightarrow \text{B}$ with an energy of 3.5 kJ mol^{-1} , as calculated from the enthalpy characteristic measured at 239 K (Table 1.4). From these data the energy of the specific interaction can be calculated using Eq. (1.21b):

$$\text{DS} \rightarrow \text{CH}_3 - \text{S} = (\Delta_{\text{vap}} H^0(T\text{K}) - 4\text{DB} - \text{CH}_3 \rightarrow \text{B})/2 \quad (1.21b)$$

$$\text{DB} \cdots \text{H} - \text{B} = (\Delta_{\text{vap}} H^0(T\text{K}) - 4\text{DSb} \rightarrow \text{CH}_3 - \text{Sb})/4 \quad (1.22)$$

The energy is equal to 8.8 kJ mol^{-1} at 239 K. The energy of the same type of interaction of liquid sulfur dimethyl at 303 K has a lower value (7.8 kJ mol^{-1}). It should be noted that the vaporization enthalpies available in the literature for a great number of alkyl complexes of the third, fifth, and sixth main group elements were obtained under conditions of the joint transition to vapor of the molecules of individual compounds. This is the reason why thermodynamic analysis is not possible.

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