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The Formation Mechanism and Structure of Organic Liquids in the DFT Challenges

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Abstract

In the paper the experimental and theoretical approaches to problem of organic liquids formation mechanism and its structure are reviewed. It was shown that all presented models have the advantages and disadvantages at interpretation of molecular interaction and arrangement in liquid phase. The DFT calculation in different variant of models including paired interaction hydrogen atom transfer, model of transformation and the general conclusion following from this consideration are presented.

Keywords: DFT calculation, organic liquids, model of formation

1. Introduction

Chemistry have stepped in the last 40–50 years to the incredible mountain. Nowadays the scientists can synthesize large composite organic molecules including important biological active species and apply physicochemical instruments with digital operating and rapid registration to the insight of pure and technological processes.

However, the current formation mechanism theory and organic liquid structure models can be questioned. Even in the late 50s–early 60s, attempts were made, basically by spectral methods, to study the nature of interactions in liquid phase of organics that lead to its high resistance to external actions and at the same time preserve its mobile properties. After numerous studies on this topic, at one point there was a pause. However, no intermolecular forces, except for classical hydrogen bonds, have been discovered.

The hope arose that with the discovery of new diffraction wave scattering methods with Fourier transformation for studying liquid substances, this problem would be clarified. Nevertheless, back in 2005, S. Ballint, studying liquid dichloromethane, concluded that the internal parameters of individual molecules that form a liquid-phase system are well defined, but their intermolecular arrangement is ambiguous.

This is strange, but we have not found a single comprehensive review that would include a comparative analysis of different approaches, including *ab initio* calculations, in a unified vision. The theory of dipole–dipole coupling, in other words Coulomb interactions, is generally accepted, although in this theory there are many contradictions with the modern theoretical and experimental findings. At the same

time, the concept of specific intermolecular interactions existence in organic liquids is verified by structural, thermodynamic and spectroscopic studies. These studies are presented and discussed in Section 2.

Ten years ago, when conducting the IR investigation of simplest organic solvents to account their role in the reactivity of some organic substrates, we have paid attention to the IR bands, which could not be assigned to any known internal mode of substance. In terms of classical vibrational spectra theory these bands can be interpreted as overtones or combination bands, if any, or Fermi resonance. However, we have suggested another assignment that was combined with DFT calculations and allowed us to make the assumption that these bands are a manifestation of specific interactions in organic liquids. In first regard, our arguments were based on the principle that mutually exclusive approaches of classical and quantum mechanics cannot be mixed in the same approach. The results of our investigations are presented and discussed in detail across Sections 2–3.

The analysis of current theoretical and experimental methods exhibits the value of DFT in the knowledge progress in the field of organic liquid phase molecular arrangements. We have presented the traditional DFT calculations and our approach to this problem as well in Section 3. Unlike quoted literature that use the paired interactions model for description of condensed phase, which arises, as a rule, under hydrogen bond, in our approach, the mechanism of liquid phase formation is considered in terms of molecular transformations. This insight applies not only to the substances with hydrogen bond, but also to the systems of identical molecules without hydrogen bonds. The conclusions of our research are formulated in Section 4.

2. Theoretical and experimental approach to the molecular arrangement in organic liquids

In this section the fundamentals of molecular structure and its formation mechanism in liquid organic phase are presented, including the experimental data and theoretical study (dynamic simulation theory) in combination with the authors analysis of this approach.

Although there are numerous papers and books devoted to this problem, none of them fully resolved the problem of organic liquids molecular arrangement, and the character of long-range molecular interaction in liquid bulk is still ambiguous. Therefore, in the first part of this chapter we tried to present the current state of considered problem in terms of theoretical and experimental approach to evaluate the role of DFT calculation in the solution of the presented problem.

However, at the beginning of this consideration we would like to review the dipole–dipole interaction concept briefly because it is the oldest and most common theory of liquid formation. In fact, this theory is based on the model of Coulomb interactions between polar systems or temporary dipoles caused by fluctuation in electronic distribution.

2.1 Classical dipoles interaction model

Cooled and pressed real gases become liquid due to the intermolecular interactions called van der Waals. This intermolecular interaction energy can be defined as the heat of a liquid evaporation or rather the difference between the vaporization temperature and the work of expanding one mole of gas at the atmospheric pressure. Value of this interaction at the boiling point of gases is 1–3 kJ/mol. As it was shown by the quantum mechanical calculations, the energy of the van der Waals interactions consists of electrostatic, inductive, and dispersive components [1].

The so-called orientational interaction of polar molecules is the most important part of the electrostatic interaction. Its essence, known as the Keesome effect, consists in the orientation of two interacting polar molecules with identical dipole moments that leads to the minimization of the system energy. In this case, the head-to-tail orientation becomes the most advantageous configuration. The energy of the orientational binding can be calculated as the sum of the Coulomb attractions and repulsion of the pole charges in the dipoles, expressed in terms of the dipoles [2].

Inductive interaction, or the Debye effect [3], is the interaction of the constant dipole moment and the induced dipole moment, arising due to an additional charge separation. Inductive interactions occur with the formation of noble gases hydrates with the dissolution of polar substances in the non-polar liquids and they are valuable only for the molecules with significant polarizability (ex. molecules with conjugated bonds) [3].

The dispersion interaction, or the London effect [4], arises between the electrons in the interacting molecules. There are molecules that have no dipole moment – for example, homoatomic molecules of noble gases. The additivity of dispersion forces is manifested in adsorption, in the processes involving gas condensation, etc. Dispersion forces play the important role not only in the individual molecules, but also in the macroscopic particles (ex. colloids). However, these forces are relatively weak.

The intermolecular interaction is the summarizing action of attraction and repulsion forces. At large distances, the attraction prevails, and at very short distances the repulsion is the main contributor. The attractive forces of Van der Waals are long ranged [5, 6], and the attraction energy rather decreases with distance. Van der Waals interaction forces at the equilibrium distance is small: $\sim 1\text{--}5$ kJ/mol, which is considerably less than the chemical bond energy.

The main conclusion is that Coulomb and Van der Waals interactions can relate to the formation of liquid from the gaseous substances at the cooling or pressing. However, this theory is very limited for organic liquids. There are at least three fundamental reasons for that: i) the intermolecular forces in organic liquids are sufficiently stronger, accounting their vaporization enthalpy [7]; ii) there is no direct dependence of liquid stability on dipole and molecular volume of consisting molecules in many cases [7]; iii) the interaction of dipoles in organic fluids should have a certain orientation, while the molecules in liquid do not have any anisotropy [5, 6]; iv) this conception ignores the specific non-valence interaction in liquid systems [7].

2.2 Thermodynamic data source

The concept of the specific interaction in liquid systems based on the thermodynamic data is developed in [7]. The regularities in the homologal series exhibit no correlation between the molecular mass and the vaporization enthalpy in many cases. The numerous thermodynamic data indicate the existence of specific non-valence interaction in organic liquids. In case of substances with the different variant of hydrogen bond (ex. with OH-, NH_i-, C=O- or COOH-group) the specific interaction providing molecular structure can be explained by classical H-donor–H-acceptor interaction [7].

However, for the liquid saturated hydrocarbons, alkenes, and alkynes this approach is not applicable. The author of [7] has suggested the scheme of hydrocarbon interactions. The main idea is that the carbon atoms in chains have a different negative charge owing the shift of 2 *s*-electronic pair between the carbon atoms. The electron density of carbon with a larger negative charge transfers partially to the carbon atom with the reduced negative charge.

In other words, the alkane molecules can be bound in the liquid state so that the carbon atoms with an enhanced negative charge would be closer to the carbon atom with a reduced charge. The carbon atoms of the methyl groups in hydrocarbons that have the enhanced negative charge can participate in the specific interaction between molecules under the donor–acceptor mechanism resembling the hydrogen bond.

In author's opinion, the non-equivalence charges distribution in hydrocarbon chains leads to the appearance of charge shift not only for the carbon atom, but for the hydrogen atom as well. It means that the hydrogen atom of the neighboring molecules can form the donor–acceptor $C \cdots H$ bond and even the dihydrogen bond. The comparison of thermodynamic data indicates the relatively high contribution of similar pair interactions in vaporization energy of organic liquids. These specific interactions are the nature of liquid saturated hydrocarbons formation mechanism and their stability without involving of the specific hydrogen bond. The evaluation of specific interaction energy is given in [7] and relates to the range 3–10 kJ/mol. These values correspond to the weak hydrogen bond [1, 2, 6].

The thermodynamic analysis of the vaporization enthalpy of unsaturated hydrocarbons leads to the conclusion that the presence of a double or a triple bond in the molecule results in a stronger electron density shift from one or two hydrogen atoms to the carbon atoms of neighboring molecule [7]. For example, the hydrogen atoms of the CH_2 -group in propene and CH -group in propyne possess enhanced positive charges, and the carbon atoms acquire higher negative charges. Therefore, the acceptor and donor properties of these substances are more pronounced than in the propane molecule (this statement are cited fully in accordance with [7]).

2.3 Molecular light scattering (MLS) and X-ray data source

In the 70s – 80s the professor at Moscow University M.I. Shachparonov has published a work, which was, unfortunately, limitedly known in the scholar community [8, 9]. In this paper he has predicted the existence of the specific interaction in the non-polar liquids, in which the hydrogen bond lacks. For benzene, the existence

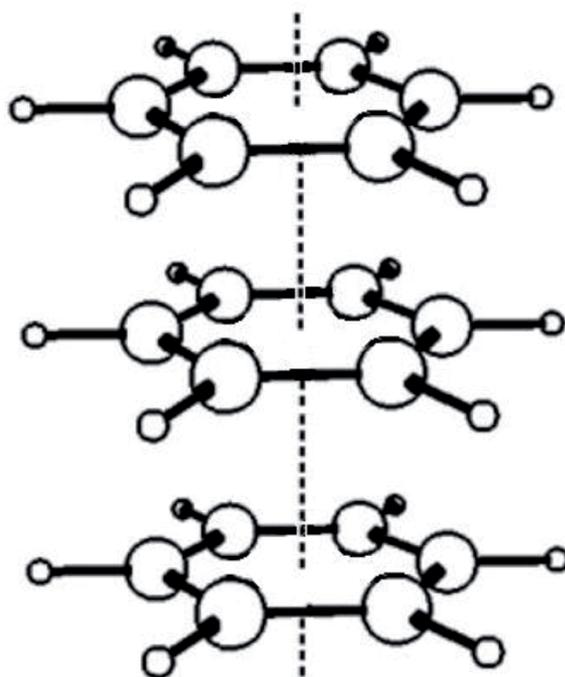


Figure 1.
The stack of aromatic rings in liquid benzene.

of a new specific interaction in liquids – the formation of molecular π -complexes (molecules stacks) between aromatic rings – was suggested (**Figure 1**).

At present, this concept was confirmed and developed in the works of I. A. Abramovich and the coauthors [10–17], devoted to the structure of the liquid system in benzene and its substituted species. The specific interaction with different spatial geometry can form in a liquid bulk of molecules without hydrogen bonds. For example, in solution of *di*-chlorobenzene, there are strong interactions in neighboring molecules between chlorine atom and carbon in aromatic ring and between carbon atoms.

Since the arrangements of molecules in a crystal always correspond to the potential energy minima of the system, it can be used for the verification of the obtained data in LS experiments combined with the modeling procedure. This approach allowed to reveal the structure and characteristics of the mutual arrangement in molecules as well as the types of intermolecular contacts in the liquid phase [18, 19].

For the determination of intermolecular arrangement in liquid *di*-chlorobenzene and other compounds with chlorine atoms, the Cambridge crystallographic database for these organics in solid state were used. The intermolecular distances between molecules, obtained by MLS study, are 4–5 Å, which is considerably longer than the internal distances in molecules. However, the liquid system has a quite certain spatial geometry realized by this long-ranged molecular binding.

X-ray studies allow to define the internal parameters of molecules, but the intermolecular structure of organic liquids stays in an ambiguous conclusion: on one hand, in the liquid phase the distances between nearest molecules are longer than 4 Å, and on the other hand, the peak of distribution function was observed in dichloromethane at distance about 2 Å. However, in these experiments it was confirmed that the organic liquids have certain intermolecular composition and labile binding between identical molecules. However, this does not exclude the spatial transformation in liquid bulk [20–22].

2.4 IR-data source

The IR spectra of organic liquids in the middle- and high-frequency regions have “additional” bands [23] that cannot be expected by the normal coordinates’ analysis [24–26]. The observed spectral phenomenon was interpreted in literature as a manifestation of the vibration anharmonicity or Fermi resonance (ex. [27, 28]). Such a version has a few contradictories; firstly, it is non-logic to mix the approach using the vibrational theory based on the classical mechanics of vibration (normal coordinates’ analysis) and the quantum mechanical interpretation; secondly, many systems that are considered in this conception include heavy molecular weight atoms and their vibration anharmonicity is negligible; thirdly, the overtones and combination bands should have considerably lower intensities than the basic bands. At last, these bands remain in the solid state (in a low-temperature spectra), and they are observed for homological analogs [20]. We have suggested another variant of assignment based on the conception observing spectral features relating to the manifestation of specific interaction in liquids.

In the spectra of liquid CCl_4 , in accordance with the selection rules for the T_d symmetry in IR spectra, only one stretching band should be active, but for the C_{3V} symmetry, two bands of E - and A_1 -symmetry species are permitted. In the IR spectrum of liquid carbon tetrachloride two overlapping bands at 786 and 761 cm^{-1} having an approximately equal intensity were observed. These bands are well-resolved in IR spectrum of the low-temperature film recorded at 20 K [29].

In the gas phase two bands were also observed (at 795 and 776 cm^{-1}), but they have a different counter structure: the first of them consists of overlapped components and another one is a single band. Therefore, we can conclude that carbon tetrachloride exists in gas phase not only in the single molecular shape that has T_d symmetry, but also in the transformed shape having C_{3v} symmetry. The first one is manifested by the band at 776 cm^{-1} and another one – by the band at 795 cm^{-1} . The spectra recorded for different temperatures of gaseous CCl_4 confirm this assumption [29].

It is reasonable to resume that the pyramidal structure relates to the cluster shape, in which the chlorine atom provides the binding between molecules. The shift of the chlorine atom in the cluster can occur in the condensed phase owing to the association of the molecules [29]. It leads to transformation of the molecular geometry to the almost planar D_{3h} symmetry, in which A_1 stretching band is forbidden in IR spectra.

In the high-frequency region of chloroform in the liquid phase, the bands at 3020 cm^{-1} (stretching vibration of the CH bond) and at 2401 cm^{-1} with a shoulder at 2435 cm^{-1} are detected (**Figure 2**, left side, spectrum 2) [30]. A similar spectrum is observed for bromoform: the bands at 3021 и 2256 cm^{-1} are shown (**Figure 2**, left side, spectrum 1). The bands in 2400–2200 cm^{-1} range cannot be assigned to overtones 2δ (bending of angle CHalH , where Hal-halogen), because the band have the isotopic D/H shift (**Figure 2**, right side), corresponding to the theoretical values (1.32–1.34) and their intensities relative to CH stretching band at 3020–3021 cm^{-1} are considerably stronger than it could be expected for anharmonic components. Besides, in bromoform molecule, the contribution of anharmonic components should decrease due to a significant increase of molecule mass. However, the opposite picture is observed in the spectra: the relative intensity of the band at 2256 cm^{-1} for bromoform is stronger than the band at 2401 cm^{-1} of chloroform [30].

The similar spectral picture is detected for water associates in liquid phase: the band of OH stretching vibration in 3400–3600 cm^{-1} region is combined with the band in 2200–2400 cm^{-1} range, assigned to stretching vibration of hydronium ion. This band manifests the hydrogen atom transfer in hydrogen bonded structures [31, 32].

The presented results indicate that the specific interaction between molecules exists in liquid haloforms due to the proton binding and its intermolecular shift, leading to the transformation of initial geometry.

The geometry of single benzene molecule is taken as a planar ring due to the conjugation of p_z -orbitals and π -aromatic configuration appearance. This state corresponds to D_{6h} symmetry point group. According to selection rules, only one stretching CH band (E-specie) should be active in IR spectra. However, in the real spectra of liquid benzene there are three bands (3092, 3071, 3036 cm^{-1}) and in the

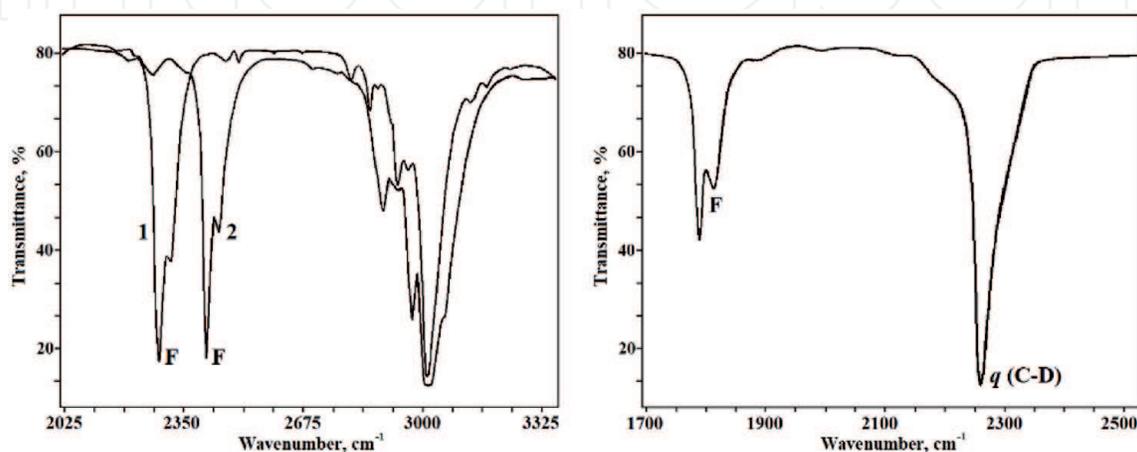


Figure 2. Fragments of FTIR spectra of chloroform and bromoform (left side) and chloroform-d in liquid phase (right side).

solid benzene (spectra were recorded at 20 K) there are four bands (3090, 3071, 3034, 3005 cm^{-1}) (**Figure 3**, right side) in CH stretching region [33].

Three bands that have isotopic H/D shift (**Figure 3**, left side) close to the theoretical prediction also were detected in benzene- d_6 spectrum. This spectral picture can be assigned to the existence of two molecular shapes existing in the liquid phase: planar, in which one IR band is active (D_{6h} symmetry), and shape with two IR bands (A_{1g} - and E-species), corresponding to the C_{3v} symmetry.

For the interpretation of the observed effect, we can assume that the benzene molecule exists in the liquid state as a cluster system. In this shape CH bonds deviate from the ring plane to the neighboring molecule (**Figure 4**). This leads to a distortion of the symmetry of the stretching vibrations of the CH bond.

In the middle IR range two bands at 1952, 1814 cm^{-1} were revealed (**Figure 5**, bands A), which cannot be assigned to the internal vibration modes. They also cannot be assigned to combination modes, because these bands have an isotopic shift close to the CH bond vibrations of aromatic ring, and the same bands are observed in substituted homologs of benzene as well (**Figure 5**). Besides, their amount in $\text{C}_6\text{H}_5\text{X}$ spectra corresponds to the non-equivalent *o*-, *m*- and *p*-position in molecules [23]. These data confirm the idea that the benzene can form the π -stacks structure in the liquid phase (see section 2.3). The hydrogen atom in this system, as it was mentioned above, can interact with the carbon atom of the neighboring molecule in the stacks. Therefore, CH stretching band can shift to the middle IR interval due to the mixing of $\nu(\text{C}-\text{C})$ and $\nu(\text{C}-\text{H})$ stretching vibrations in the intermolecular bond ($\text{C}-\text{C}-\text{H}\cdots\text{C}-\text{C}$).

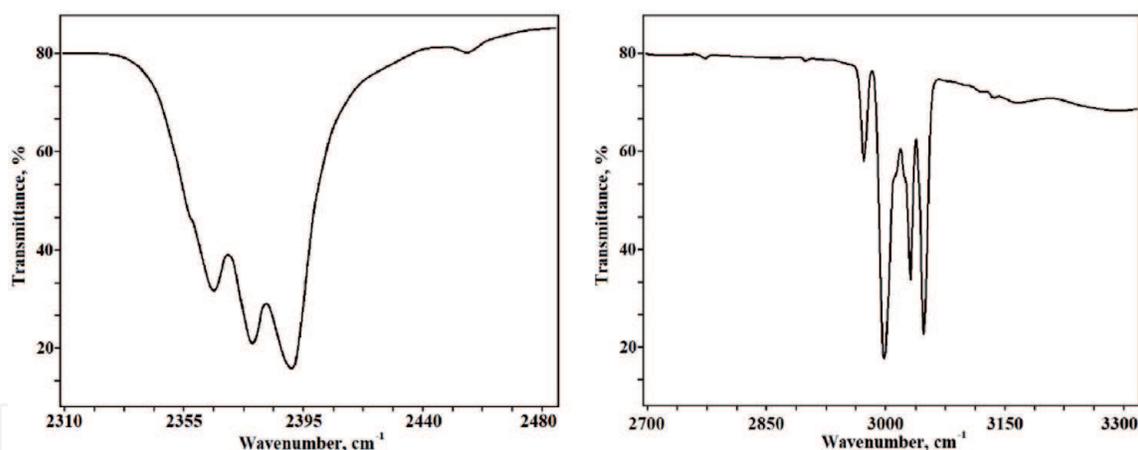


Figure 3. Fragment of liquid benzene- d_6 FTIR spectrum at 295 K (left side) and solid benzene film at 20 K (right side) in CH/CD stretching region.

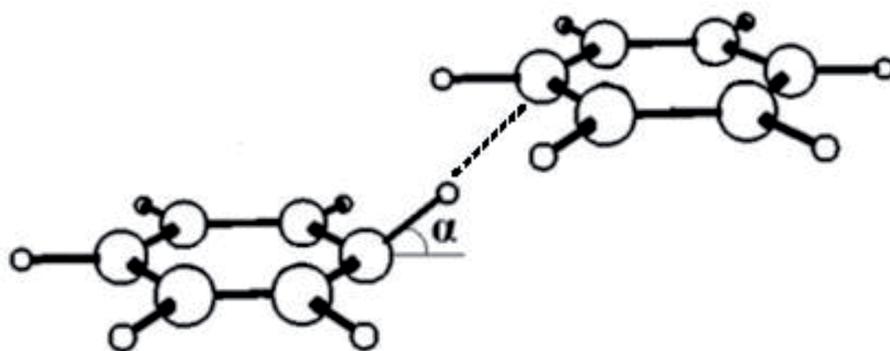


Figure 4. Hydrogen atom shift in molecular stacks of liquid benzene.

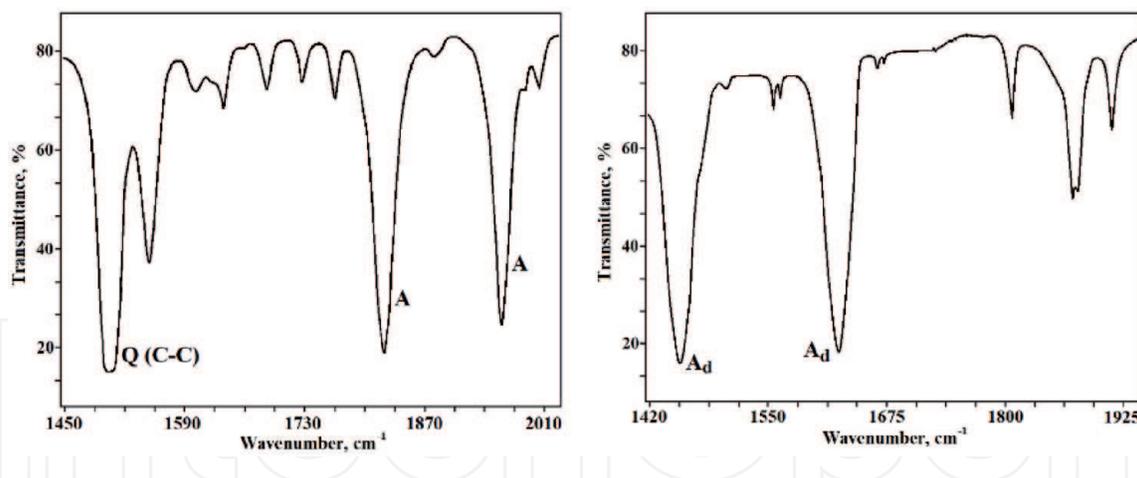


Figure 5. Fragment of liquid benzene (left side) and benzene- d_6 (right side) FTIR spectrum in middle IR region.

2.5 Dynamic simulation data source

This approach was developed in numerous works and their complete citation was beyond the scope of this study. Therefore, we would like to highlight the studies that present the molecular arrangement of organic systems as a supramolecular structure, forming not only under hydrogen bond, but also existing in the shape of identical molecular associates [34–37].

The obtained data allow to discuss the thermodynamic and kinetic aspects of the processes in liquid phase, in terms of the supramolecular organization. These investigations give the knowledge about the composition of the aggregates as well as the general approach to their transformation due to the intermolecular binding. In author's opinion, the dynamic simulation model combined with the experimental findings allows to explain the supramolecular formation mechanism under the long-ranged interactions. The model of the homogeneous molecules' association is a key to manifold conclusions of the liquid properties' nature [37].

This approach gives the complementary information about the structure of aggregates, which is not possible by other methods, especially when long-ranged molecular binding is present. The application of this method is useful to interpret some regularities of organic liquids, although it does not detail the specific interactions' appearance [34, 37].

2.6 Section conclusion

As we have shown in the short review of the modern approaches to the problem of molecular arrangement in organic liquids, all data sources agree that the structure of liquid phase can be described as a supramolecular system with non-polar or weak polar long-ranged interactions. This binding arises at the distances close to 4–5 Å, but its energy contribution is comparable with vaporization enthalpy of liquids [7, 17, 18, 20]. The thermochemical, wave scattering, X-Ray and dynamic simulation data interpret well the lability of the system, but do not explain its high stability.

Unlike the mentioned methods, IR data predict that the initial molecular geometry transformation in comparison to a single molecule occurs in the liquid system. These changes are caused by the intermolecular forces between neighbors in bulk, even if they do not correspond to the hydrogen bond [23, 29, 30].

Applied to this problem, the DFT calculation could be useful for explaining the reasons of the transformation under weak interactions in terms of general electronic distribution. Therefore, in the following section we consider the essential results of the DFT study referring to the problems discussed in this paper.

3. DFT approach to the molecular binding in organic liquids

In this section, we have presented the traditional methods of DFT calculations together with our approach. In most works, the application of DFT to the problem of formation mechanism and arrangement of organic liquids is reduced to the non-covalent interactions' model of dimers with hydrogen bond. Although this approach is available for the gas phase binding only, such interactions arise quite rarely in the gaseous systems. Nevertheless, this concept is conventionally extrapolated to the condensed phase structure. However, the geometry and molecular interactions in this system sufficiently differ from the gaseous one. Therefore, we have suggested the DFT approach based on our IR spectral observations that indicates the certain changes of the molecular structure in the organic liquids in comparison to a single molecular state (see Section 3.4).

3.1 Geometry optimization (GO) procedure in DFT calculations of molecular system

The basic idea of system geometry optimization (GO) is that in *ab initio* calculations the SCF energy optimization procedure often leads not to a global minimum but to the local extremum. Therefore, besides of the SCF procedure, the additional mathematical method named GO is practically used.

For large molecules, which to a certain extent can simulate a supramolecular system, a method of delocalized internal coordinates within the framework of the DFT has been proposed. It was shown that the combination of the trust radius and line search method gives good accuracy in the geometry calculation of a single molecule. A performance analysis of the new geometry optimizer using different start Hessian matrices, basis sets and grid accuracies is given in [38]. This scheme has been successfully used for the study of enzyme reactions, treating the active site by a high-level method, particularly DFT, and the protein environment by molecular mechanics.

The minimum of energy is reached when the geometry characteristics of molecule is close to the experimental values. A few variants of the GO procedure for the DFT calculation can be found in the other papers, in which the findings are in a good agreement with experimental data [39, 40].

Considering these results, one can ask, firstly, why the calculation referring to single molecule can reproduce the geometry of condensed phase so well while the thermodynamic, kinetic, and spectral properties of molecular bulk differ from the individual species; secondly, the used regularity of energy change from geometric parameters, for example, from bond length, is strictly suitable only for diatomic molecules. For the polyatomic ones, this procedure can be attributed only with a sufficient approximation, because the bonds and angles in a molecule cannot vary independently. This situation is well known for the small vibrations of point masses near the interatomic equilibrium [24–26]. The solution of vibrational problem in, so called, internal natural coordinates (bonds and angles between neighboring bonds), requires involving the coefficients of the interactions between them. Besides, in organic liquids, the potential energy surface consists of the infinite closely located energy extremums of the single molecules. Therefore, in the real system the minimum of energy is broadly smoothed. Since the electron density in these systems is strongly delocalized, the geometric optimization procedure loses its real physical meaning. The arguments above show that the GO is an additional mathematical fit in the standard iterations shape, and it can be applied for the real systems only with the reasonable restriction. For this reason, the DFT calculations with the GO for the simplest organic molecules forming the stable liquid bulk (for example,

tetrachloromethane, dichloroethane and non-substituted hydrocarbons etc.), does not lead to the energy minima even for two-molecule interaction (see Section 3.4). Thus, the DFT calculation without the GO procedure seems to be applicable in this field as well.

3.2 Paired interaction model in DFT calculation for liquids

The study of the formation mechanism and structure of organic liquids needs to involve the models and approximations to simulate molecular interactions. One of them can be defined as a model of paired bonds, which is based on a few reasonable assumptions. Firstly, the specific interaction in a liquid is a non-covalent interaction between molecules [41–44]. Secondly, for the definition of the pair, we can choose the strongest molecular interaction in the system. Thirdly, the liquid structure is formed by the paired molecules. Fourth, the nature of this interaction is a set of the different hydrogen bond types.

Sometime, halogen bond [45] and dihydrogen bond [46] provide a non-covalent binding, but it appears quite seldom, basically, between oppositely charged hydrogen or halogen atoms and in a solid state.

Hydrogen bond can exist in many organic and inorganic species and plays a crucial role in fields of chemistry and biology. It has been considered in many reviews; in this section, we analyze only a few recent ones [47–51]. Since the hydrogen bond existence is considered as a main aspect of the condensed phase formation theory, we would like to make a few comments regarding our conception presented in this section. Arising of the hydrogen bond presumes the occurring of an interacted pair – a hydrogen donor and a hydrogen acceptor. This type of binding is known not only in the condensed phase, but also for gases. The energy of hydrogen bond changes in the interval of 8–60 kJ/mol and more, in some cases, while its length is 2–3,5 Å.

Many authors that studied the organic liquids with a hydrogen bond in their structure, draw the statement that this bond provides the stability of liquids and the high mobility as well. This concept is quite satisfactory, because the hydrogen bond theory can be considered as a universal approach to the structure of liquid organics: amines, acids, alcohols, and related compounds; many bioactive systems can also assign to this system. Besides, it is known that some species of organic liquids can turn into a shape with a mobile proton, ex. nitro-substituted hydrocarbons, aldehydes, and ketones – they can form the hydrogen-bonded liquid system as well.

At the same time, the hydrogen-bonded pair has a linear binding, where the mobile proton is bound simultaneously with its own molecule and with a neighboring one, although to a greater extent with its own. This feature of binding allows to imagine the system, in which the initial structure of molecules remains in the combination with a thermodynamic stable molecular bulk. Therefore, the hydrogen bond is the suitable instrument to simulate the formation mechanism in a liquid phase.

Besides, it is well known that the organic matter contains of water impurities that cannot be completely removed [23, 52]. Water forms the clusters with the organic molecules due to the strong hydrogen bonds. The presence of water molecules can be considered as a variant of the mechanism for the formation of a stable organic liquid (see Section 3.3). This mechanism is valid for bioactive systems as well.

The prediction of benzene dimer formation is essential for this work because the high stable liquid in this case exists without the intermolecular hydrogen bond. The DFT calculations of the binding mechanism in the benzene dimer predicts four most stable shapes of the self-association: two variants of π -shaped and two variants of T-shaped structures [53–55].

The pair interactions' model is the most common viewpoint on the mechanism formation of organic liquids. However, this concept has a few disadvantages. Firstly,

this model cannot explain, why there are many organics that exist without hydrogen bond while their stability (with the vaporization enthalpy as a criterium) is higher than in a system with hydrogen bond [7]. Secondly, this model cannot reproduce the formation mechanism of the spatial structure in organic liquids. Thirdly, the benzene dimer is one of the few examples where the DFT calculations can explain the formation of associates without involving a hydrogen bond, but they cannot explain the high stability of benzene, since the energy of the intermolecular interactions in it does not exceed 0,301 kJ/mol. The mechanism of water complex formation in organic liquids combined with the hydrogen atom transfer theory (HATT) is a positive step to clarify this problem, as it is presented in the next section.

3.3 Hydrogen atom transfer model for organic liquids

The hydrogen atom transfer theory (HATT) and the results of calculations obtained in terms of this model for gases and the condensed phase exhibit a wide area of investigations. The main data and the approaches referring to this theory are presented and reviewed in [56–60]. For our consideration, we have chosen the essential aspects of this concepts, applied for the formation mechanism and the structure of organic liquids.

The hydrogen atom transfer term is used to define the proton, hydrogen and hydride ion transfer which occur in many organic liquids. Two energy minima with a maximum between them arise in the system, determining the process of transfer.

The barrier of transfer changes considerably for different organics and can vary from 10 to 12 up to 100–200 kJ/mol [57]. The nature of these interactions is either activation, such as heating and irradiation of a substance, or a tunneling process. The last one is caused by the decrease of X–H bond energy under the hydrogen atom coupling with the Y-atom of the proton acceptor in the linear chain (X–H···Y) and the hydrogen atom vibrations with a large amplitude.

The main value of this theory for the considered problem is related to the description of the spatial arrangement formation. Presuming that the hydrogen atom transfer between the donor and the acceptor of the protons (in other words between the Bronsted acid A and the several molecules of basic B₁, B₂) occurs in a liquid phase like: (AH + B₁ → A⁻ + B₁H⁺ + B₂ → A⁻ + B₂H⁺ + B₁).

It means that in contrast with the dimer approach, the hydrogen atom transfer model predicts the multidirectional movement of hydrogen atom in a liquid space. These transformations can provide the spatial arrangement in the system. Besides, the HAT model gives a perspective idea that the molecular tautomerism involving different hydrogen atom transfers can be taken as a basic element of the liquid formation mechanism (see the next Section).

Another approach to hydrogen atom transfer mechanism can be formulated if organic liquid contains of the water molecules. As it was mentioned above, water often inserts in a liquid matter and then the hydrogen atom transfer can occur between the water molecules with hydronium ion formation [23, 32]. The water complexes with organics, where the interaction can be assisted with the hydrogen atom transfer, was confirmed by IR experiments [52].

The DFT calculations in the different parametrizations show that in CH₃NO₂ and CH₃CN complexes with water molecules several binding variants can be realized: first of them is the interaction of the hydrogen atom of methyl group with the oxygen atom of water, and the second one is the coupling of the hydrogen atom of water with the nitrogen atom of CN group or the oxygen atom of NO₂ group (**Figure 6**, the bonds' distances are given in Å).

The calculations predict the hydrogen atom transfer between the water molecules with the barrier about 10–12 kJ/mol and stabilizing of the hydronium cluster structure

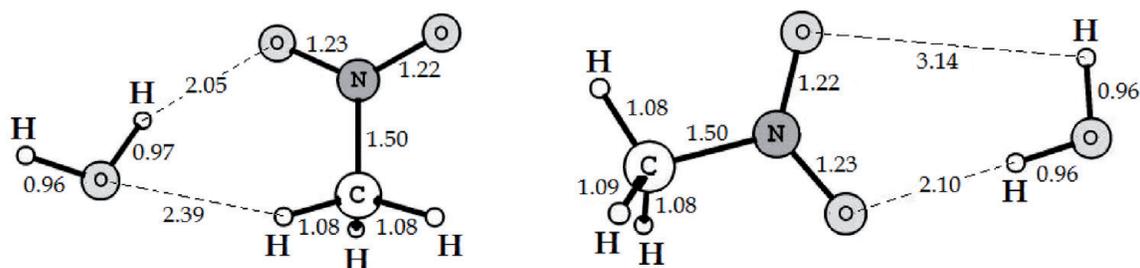


Figure 6.
The interaction model of water complex with CH_3NO_2 and CH_3CN molecules.

(**Figure 7**). In the hydronium ion, all hydrogen atoms are equal in their interaction with the organic molecules, and within the associates they can shift in all three-dimensional space, realizing the ‘relay race’ mechanism and forming the equilibrium spatial structure of the liquid. Thus, we can resume that in the liquid organics the water molecule can be a bonding agent in the formation mechanism of phase states.

The similar model was predicted by the DFT calculations for the aromatic substance – hexafluoride of benzene (**Figure 8**). In this complex, the barrier of the hydrogen atom transfer is even less than the one for CH_3X ($\text{X} = \text{CN}, \text{NO}_2$) systems (about 6 kJ/mol).

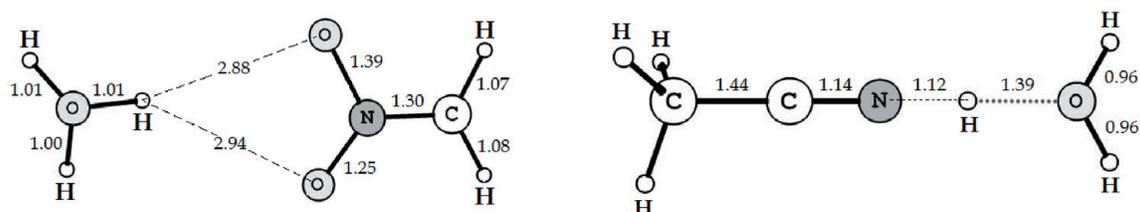


Figure 7.
The interaction model of hydronium ion interaction with CH_3NO_2 and CH_3CN molecules.

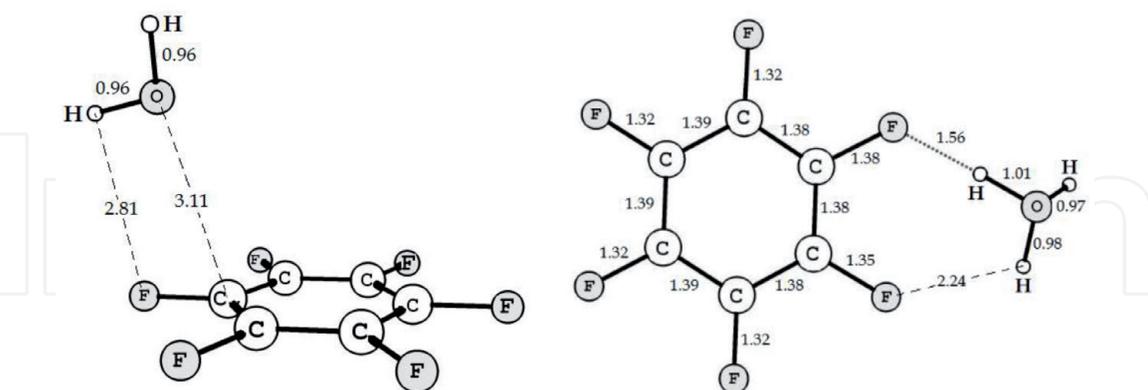


Figure 8.
The interaction model of water molecule and hydronium ion interaction with C_6F_6 molecule.

3.4 Transformations’ model in DFT calculation

None of the described experimental and theoretical models can explain the formation mechanism and the structure of organic liquids completely, although they present some useful data to insight this problem. All of them proceed from the fact that the geometry of the gas phase, or, in other words, of a single molecule, is preserved in the liquid phase as well. Although it is assumed that the values of bond lengths and angles shift to some extent under the condensation, these changes

are considered insignificant, without profound transformations of the molecular structure. At the same time, as it was shown above, the IR data source indicates the possibility of the symmetry vibrations violation caused by the structural factors. In this section we consider as an example the interpretation of IR findings for two classes of organic liquids, which are often-used solvents and initial products for many organic syntheses – methane halides and benzene – in terms of the DFT calculations in the B3LYP variant with the 6-311++G(2d, 2p) basis set.

3.4.1 Methane halides

For the interpretation of IR spectral effects, we have applied the symmetry point groups theory. In tetrachloromethane IR spectrum there should be one active C–Cl stretching band corresponding to the T_d symmetry. However, two approximately equal band intensities in 750–850 cm^{-1} region are observed (see Section 2.4). The appearance of two bands in the IR spectra can be assigned to the pyramidal C_{3V} and the biplanar D_{2h} or D_{2V} symmetry groups.

The DFT calculation predicts the transformation (**Figure 9**) of the isomer (1) into biplanar (2) and pyramidal (3) isomers. The energy barriers ΔE_1 and ΔE_2 are close to each other and relatively low: ΔE varies in 4–12 kJ/mol range. The calculated frequencies of C–Cl stretching vibrations (776, 713 cm^{-1}) are agreed with the experimental ones (786, 761 cm^{-1}) as far as it can be expected in such a calculation. Formally, the structures (1)–(3) do not differ so much, however, the distribution of charges in them changes in such a way that not only the interaction between a positively charged carbon and a negatively charged chlorine in the neighboring molecules is allowed, but also the interaction in the other direction, between two oppositely charged chlorine atoms. The calculations have shown that the atoms' charges depend on the value of (CClC) angles and not on the bond lengths. The suggested scheme sufficiently describes both spectral observation and formation mechanism of the spatial structure in liquid.

For trichloromethane, the DFT calculations were carried out for the chloroform and bromoform molecules. The obtained data predict the small barrier of transformation from a pyramidal C_{3V} isomer to a biplanar isomer not exceeding 10 kJ/mol (**Figure 10**). As is known, such energies are not sufficient obstacles for the transformation even in the gas phase and a fortiori for the liquid state.

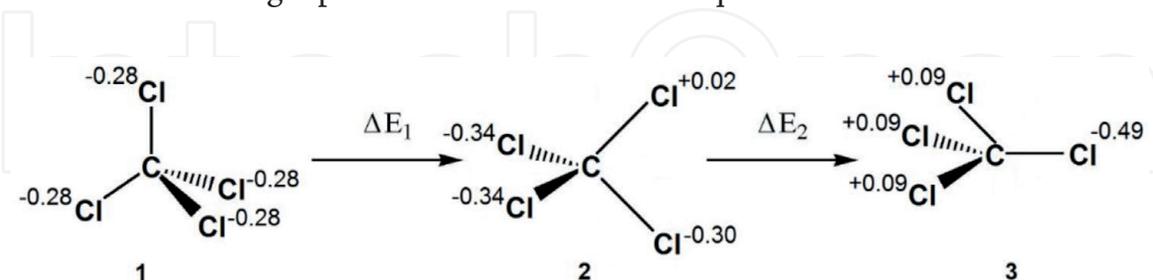


Figure 9.
The tautomeric isomers of CCl_4 , predicted in the DFT calculations.

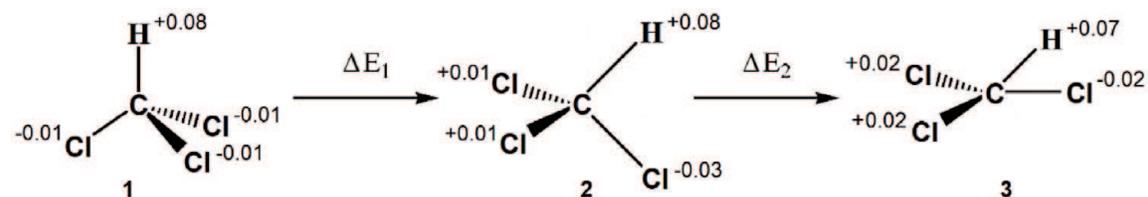


Figure 10.
The tautomeric isomers of CHCl_3 , predicted in the DFT calculations.

| Atom | Atomic charges in isomer 1 | Atomic charges in isomer 2 | Atom | Atomic charges in isomer 1 | Atomic charges in isomer 2 |
|-----------------|----------------------------|----------------------------|-----------------|----------------------------|----------------------------|
| Cl ₁ | -0,01 | +0,01 | Br ₁ | +0,26 | +0,06 |
| Cl ₂ | -0,01 | +0,01 | Br ₂ | +0,26 | +0,06 |
| Cl ₃ | -0,01 | -0,03 | Br ₃ | +0,26 | -0,02 |
| C | -0,05 | -0,08 | C | -1,03 | -0,24 |
| H | +0,08 | +0,09 | H | +0,25 | +0,14 |

Table 1.
The charge distribution in chloroform and bromoform molecules.

The calculations reveal a few directions of the intermolecular binding: one of them is the hydrogen bond between a positive charged hydrogen atom and a negative charged carbon or chlorine atom. At the same time, the obtained results allow the intermolecular binding between the oppositely charged chlorine atoms reminding the interaction in tetrachloromethane molecule. The different types of binding can provide the spatial structure of the liquid phase.

For chloroform and bromoform, the detected charge distribution is similar (**Table 1**), but the atomic charges for the bromoform molecule in the C_{3V} isomer are considerably larger than in the chloroform molecule. In the biplanar configuration of bromoform, the atomic charges are significantly less, closer to the values of chloroform. This effect means that the basic interaction in bromoform is the hydrogen bond (C–H···C) with the hydrogen atom transfer in the C_{3V} isomer, in accordance with the IR spectra interpretation (see Section 2.4). Besides, the charge growing (along with the heavier molecular mass) can lead to a stronger intermolecular binding in bromoform and, as a result, to a higher vaporization enthalpy [61].

DFT calculation predict four directions of the tautomeric transformations for dihalogenomethane. In this case, the total energies of (1)–initial biplanar isomer {(CClCl) and (CHH)}, (2)–biplanar {two CHCl planes}, (3)–non-symmetrical pyramid with (HClCl) base and (4)–non-symmetrical pyramid with (HHCl) base (**Figure 11**) are close; ΔE_1 , ΔE_2 , and ΔE_3 are about 20 kJ/mol. Therefore, we conclude that the intermolecular binding can be realized in all these directions, including the hydrogen bond (C–H···Cl) and the interaction of two chlorine atoms.

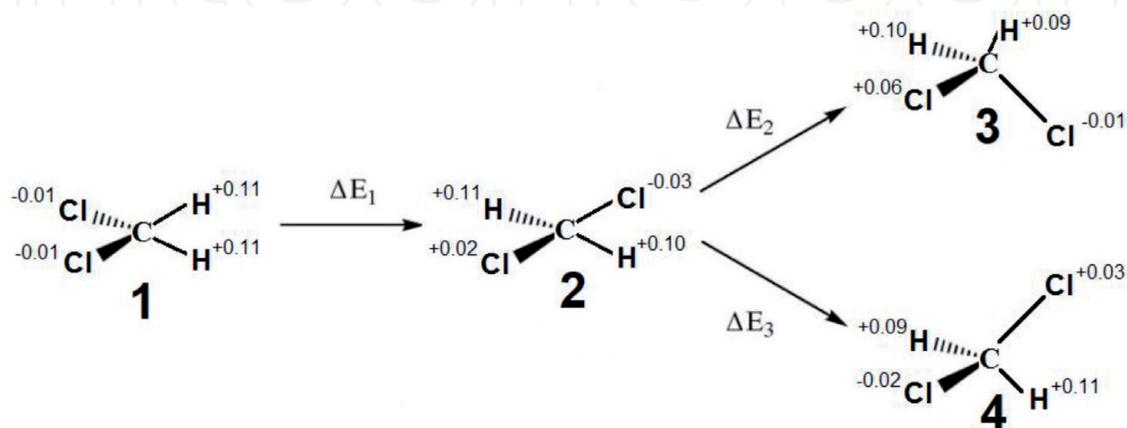


Figure 11.
The tautomeric isomers of CH₂Cl₂, predicted in the DFT calculations.

| CH ₂ Cl ₂ | | | CH ₂ Br ₂ | | | CH ₂ I ₂ | | |
|---------------------------------|----------------------------------|---------------------------------------|---------------------------------|----------------------------------|---------------------------------------|--------------------------------|----------------------------------|---------------------------------------|
| Atoms | Atomic charges in initial isomer | Atomic charges in biplanar isomer (2) | Atoms | Atomic charges in initial isomer | Atomic charges in biplanar isomer (2) | Atoms | Atomic charges in initial isomer | Atomic charges in biplanar isomer (2) |
| C | -0,20 | -0,20 | C | -0,22 | -0,21 | C | -0,26 | -0,25 |
| H ₁ | +0,11 | +0,11 | H ₁ | +0,13 | +0,10 | H ₁ | +0,09 | +0,09 |
| Cl ₁ | -0,01 | +0,02 | Br ₁ | -0,02 | -0,02 | I ₁ | +0,04 | +0,04 |
| H ₂ | +0,11 | +0,10 | H ₂ | +0,13 | +0,12 | H ₂ | +0,09 | +0,09 |
| Cl ₂ | -0,01 | -0,03 | Br ₂ | -0,02 | +0,01 | I ₂ | +0,04 | +0,03 |

Table 2.
 The charge distribution in CH₂X₂ molecules.

| Atom | Atomic charges in C _{3V} pyramidal isomer | Atomic charges in C _{3V} planar isomer |
|----------------|--|---|
| C | -0,24 | -0,19 |
| H ₁ | +0,08 | +0,11 |
| H ₂ | +0,08 | +0,11 |
| H ₃ | +0,08 | +0,11 |
| I | +0,01 | -0,14 |

Table 3.
 The charge distribution in CH₃I molecule.

For CH₂Br₂ and CH₂I₂ molecules, ΔE₂ and ΔE₃ energies are considerably higher than ΔE₁. In these molecules, the transformation into isomers (3) and (4) is less expected than the C–H···X hydrogen bond in isomer (2). Since the charge distributions for all these molecules are similar (Table 2), the direction of the transformation is determined by the energy factor.

For CH₃I molecule, the calculated charge distribution in the initial C_{3V} specie pyramidal isomer allows the interaction between the iodide atom and the carbon atom in the chains of neighboring molecules, while the charge distribution in molecule can provide the hydrogen bond between the iodide and the hydrogen atom of the methyl group in the neighboring molecules as well (Table 3). Thus, the different binding variants in liquid CH₃I can provide the formation of the stable spatial arrangement.

3.4.2 Benzene

The structural element that determinates the molecular arrangement in a benzene liquid phase, was presented in the quoted literature as a set of dimers that have several geometry configurations (see Section 3.2). Unlike this approach, we have considered the trimers as a formed element in the ‘stack model’ of the benzene liquid phase. The conducted DFT calculations with different transformations of initial molecular geometry predict that the most optimal configuration is the stack with a ‘chair’ shape of the central ring and two planar rings (Figure 12). The trimers are bonded in a spatial structure by the hydrogen bridges. This concept can explain the IR data outside the scope of traditional assignment (see Section 2.4). In the trimer spectrum, one CH stretching band assigning to both planar rings should be observed, while the CH stretching in the central ring have to exhibit two bands: the first of them assigns to a pair of equivalent (C₁–H₁) and (C₄–H₄) bonds, and the second one – to a quartet – (C_i–H_i), i = 2,3, 5,6 (Figure 12). The stretching bands of the hydrogen bridges

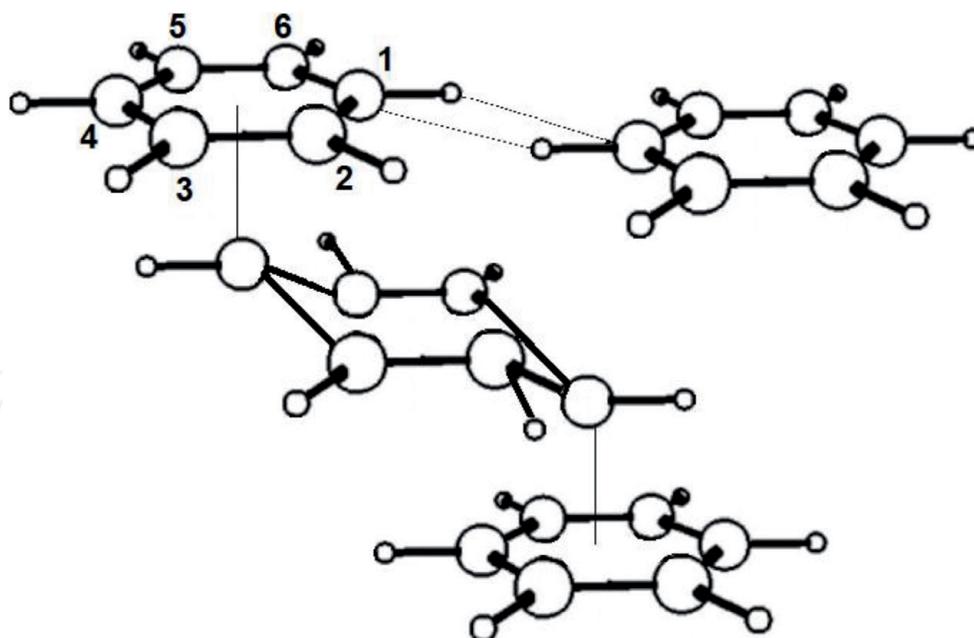


Figure 12.
The fragment of the benzene spatial arrangement in a liquid phase.

should shift in the middle IR region due to the mixing of the CH and CC stretching. Therefore, the pair of bands at $1800\text{--}2000\text{ cm}^{-1}$ corresponds to the stretching of two bridging C–H bonds in the stacks bound in two mutually perpendicular planes.

3.5 Section conclusion

The DFT calculations with the GO procedure that were used for the dimers with the hydrogen bond, had described the enthalpy of the molecular interaction and the bond lengths quite satisfactory. For most systems, the intermolecular bond energy is even overestimated. However, this model cannot explain the spatial arrangement in the condensed phase because the electronic density should be localized within a dimeric shape in this case.

Unlike the dimer model, the transformation model suggests the variants of mutual molecular disposition under the bonding between the chains or the stacks. However, it requires the use of suitable experimental data. In this case, as a criterion of the results' validation, the absence of the negative vibrational frequencies can be taken. Although these calculations are somewhat intuitive, they allow to predict the reasonable structure arrangement of the supramolecular system.

4. General conclusion

The presented experimental and theoretical findings confirm the conclusion that none of the approaches can explain completely the structure and the formation mechanism of organic liquids. However, these approaches complement each other and help to solve the problem to some extent. In **Table 4** we have listed the advantages and disadvantages of each method and model.

A promising direction in the development of the DFT approach for investigating the problem of the formation mechanism and structure of organic liquids is the elaboration of the methods for calculating molecular systems with delocalized and smoothed electron density. Studying these systems can help to clarify the nature and structure of organic liquids.

| Approach / Model | Advantages | Disadvantages |
|-------------------------------|---|---|
| Dipoles' interaction | universal; predicts the nature of formation mechanism and spatial arrangement for organic liquids | cannot explain the high stability of weak polar and non-polar liquids |
| Thermochemistry | reveals the specific long-ranged interaction in the non-polar organic liquids (with the energy values comparable to those of the vaporization enthalpy) | cannot explain the high stability of organic liquids with no hydrogen bonds; the formation mechanism interpretation is based on the intuitive model |
| MLS and X-ray study | reveal the specific long-ranged interactions and (approximately) the distances between molecules | cannot describe the formation mechanism and explain the high stability of liquid organics |
| Dynamic simulation | explains the spatial arrangement and the structural stability of the liquids | cannot describe the nature of organic liquids' phase arrangement |
| DFT paired interactions model | establishes the nature of liquid phase formation as a paired non-covalent interaction | does not predict the stable spatial arrangement in the organic liquids |
| HAT model | predicts the mechanism of stability and lability in the liquids | considers only the structure of hydrogen-bonded organic liquids |
| DFT transformations' model | predicts the mechanism of arrangement not only for hydrogen-bonded liquid organics | a set of certain experimental data and a concept for their interpretation is required |

Table 4.
Advantages and disadvantages of approaches to organic liquids structure.

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