THE QUANTUM-CHEMICAL MODELLING OF STRUCTURE AND SPECTRAL CHARACTERISTICS FOR MOLECULAR COMPLEXES IN PENTAPLAST-TERLON SYSTEM

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Abstract. Using *ab initio* methods of quantum chemistry, structure and spectral properties of the molecular complexes which were formed by monomer of pentaplast chain and *N*-phenylbenzamide, that recreate features of intermolecular interaction in the penton-terlon system were researched. Offered theoretical models reflect proper spectral and energetic characteristics of investigated system.

Keywords: *ab initio* calculation, conformational analysis, intermolecular interaction, stabilization energy, base sets of superposition error, vibrational spectrum.

1. Introduction

Pentaplast (PP), often called penton [1], belongs to a rank of peomising bonding materials that are widely used for getting composites with valuable physical and chemical properties and technical characteristics. PP is characterized by its low melt viscosity, stability of shape and geometrical dimensions of products. Its obvious advantages are high strength and chemical endurance, which outreaches famous polyvinylchloride's resistance to concentrated mineral acid up to 393 K. Only a few polar solvents dissolve it at elevated temperatures [2].

The main way for getting this thermoplastic is the 3,3-*bis*(chloromethyl)oxetane (BCMO) ring-opening polymerization process, which can be initiated by means of protonic acids, oxonium salts, hexafluoro-phosphates and Lewis acids in the presence of coinitiators (Fig. 1). Side reactions such as ring formation and backbiting can be reduced by lowering the reaction temperature. These reactions can be more or less ignored in the case of composites, if bi- and higher functional monomers are applied [3].
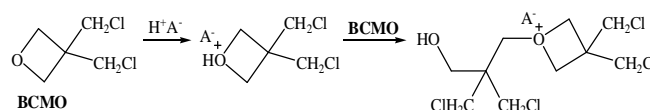
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Fig. 1. Reaction pathway for BCMO polymerization process, which occurs under the action of acidic catalysts

Recently, the importance of the research of numerous polymer systems, based on pentaplast, reinforced with different fiber materials, such as poly-*p*-phenyl-eneterephtalamide (terlon) has grown [4]. Therefore, the main goal of this research is the detailed theoretical study for some features of structural equilibrium and vibrational spectra for molecular complexes that are carried out in the pentaplast-terlon (PPT) system using *ab initio* methods of quantum chemistry.

2. Experimental

Calculations using the density functional theory (DFT) were made with the help of the Gaussian 03, Revision E.01 package of programs [5] at the B3LYP/6-311++G(d,p) level of theory [6]. The IR spectra were recorded with a SPECTRUM ONE (PerkinElmer) instrument. The samples for recording were prepared using the standard procedure with KBr [7].

3. Results and Discussion

When considering the building of a penton macromolecule in general, it should be mentioned that this thermoplastic is a polymer form of BCMO and due to that fact it is characterized by the following structure of monomer chain:

$$[-OCH_2C(CH_2Cl)_2CH_2-]_n \qquad (1)$$

which has crucially important value during the consideration of the possible conformational transformations that are carried out in this macromolecule. In addition, the zigzag structure of the main chain of the polymer that has a predictable valence angle COC, which

is 12º, is undeniable whereas the consideration of end-to-end distribution chloromethylene groups (CH₂Cl) related to each other may be of significant interest from the perspective of theoretical grounding of the typical crystalline modification of penton.

For this reason at the primary stage of our research, we studied the properties of a pentaplast monomer chain of conformational transformation using the 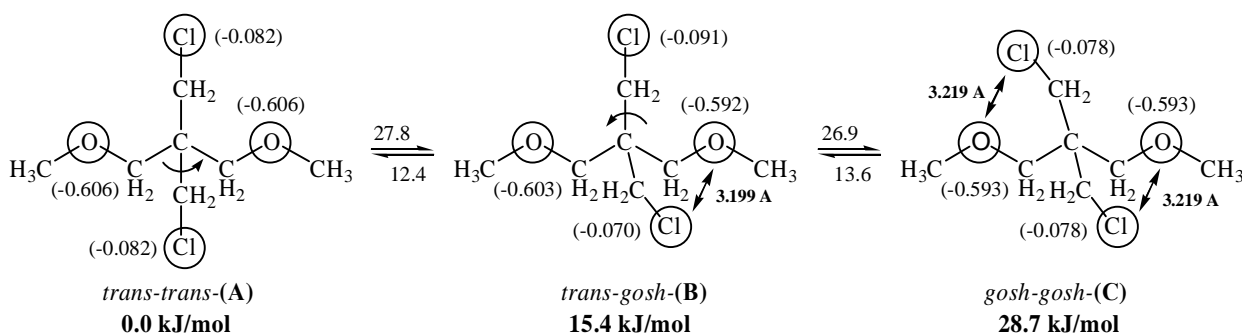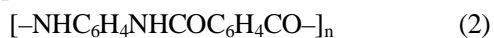density functional method in approximation B3LYP/6-311++G(d,p). The theoretical model along with the structure (1) also included an extra oxygen atom that was related to the nearest chain element and also terminal methyl groups to record the most significant intramolecular interactions. Corresponding sets of vibrational frequencies were calculated for all critical points. We took into account special corrections at zero-point vibration during the calculation of the activation barriers [8, 9]. The calculation results are shown below (Fig. 2).
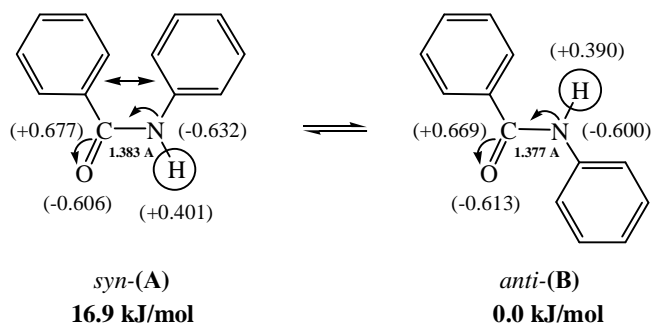

Fig. 2. Stabilized conformer structures **(A–C)** of penton monomer chain element and activation barriers of their reciprocal switchovers (kJ/mol), relative energies and NBO-charges on atoms [10, 11], are calculated in *DFT*-B3LYP/6-311++G(d,p) approximation

Comparative analysis of the obtained values of relative energies of the localized structures showed that the most stable is conformer *trans-trans-***(A)**, which is characterized by the maximum possible space remoteness of oxygen and chlorine atoms that are carrying a huge negative charge. Rotation of CH₂Cl groups around carbon-carbon bonds, in contrast, leads to the pairwise convergence of these atoms, that destabilize *trans-gosh-***(B)** and especially *gosh-gosh-***(C)** conformer forms, which are confirmed with calculated values of activation barriers and their relative transitions. Taking into account the great contribution of the electrostatic repulsion energy in the structure formation of the pentaplast monomer chain element, we can certainly claim that these polymer macromolecules will have a helix form and a helix pitch distance mostly depends on the existence of structural branching, indicating the type of crystalline modification.

In addition to penton molecular structure research, there is a significant interest in the establishment of the most likely monomer chain configuration of terlon, which is *p*-substituted benzene rings, separated by bridged type of amide groups:

$$[-NHC_6H_4NHCOC_6H_4CO-]_n \qquad (2)$$

The *N*-phenylbenzamide molecule can be used as a theoretical model that reflects the structural properties of such systems properly. Its typical property is creating two isomeric forms that differ by the disposition of benzene rings relative to each other. Meanwhile, the earlier described method of calculation was completely saved, and it allowed for comparison of the acquired results (Fig. 3).

Fig. 3. *Syn-***(A)** and *anti-***(B)** structures of *N*-phenylbenzamide forms as a prototype of terlon monomer chain, relative energies and NBO-charges on atoms [10, 11], are counted in *DFT*-B3LYP/6-311++G(d,p) approximation

As expected, the most stabile is the structure of *anti-***(B)** form. The advantageous spatial location of aryl fragments in this case contribute to the effective linking of its own, not shared electronic nitrogen pair with *p*-orbitals, that are near the carbonyl group. In favour of this, we can see the calculations made according to the NBO-theory on appropriate atoms and also of C–N bonds of Wiberg's indexes, which are 1.135 and 1.137 for *syn-***(A)** and *anti-***(B)** forms, indicating their partially unsaturated nature.

Based on these results which describe the structural characteristics of monomer chain elements of each polymer, we suggested the theoretical model which recreates their direct interaction. Data of the experimental study of PPT infrared spectra can be used as a basis for

such systems. According to them, the authors [4] can make a conclusion about the CH_2Cl chemical interaction group with an amido group of fiber. In fact, such an intermolecular complex is based on the slight power of electrostatic interaction with general stabilization energy that is less than ~10 kJ/mol according to the base sets of superposition error corrections (Fig. 4) [12, 13].

According to the results of the study of particularities of the electronic density distribution in the researched system in Bader's AIM-theory [14, 15], we made some extra estimations of the discovered molecular interactions. According to the obtained information (Fig. 4), the dispersive interactions of the chlorine atom with the benzene ring`s hydrogen atoms makes the biggest contribution in the general stabilization of energy, and the dispersive interactions of the chlorine atom with the amido group`s hydrogen makes the least one. The calculated results are in correspondence with the generally accepted notion about potential inability of a chlorine atom to create typical hydrogen bindings, which can be

easily explained by the charge density reduction on its surface [16, 17]. In view of the earlier discussion, the theoretical study of the vibrational spectra of the previously considered structures of isolated polymers and molecular complex *trans-trans*-(**A**)+*anti*-(**B**), which was obtained on their basis, is of considerable interest. It is known that the overwhelming majority of quantum chemistry approaches give an overvaluation of the normal vibrational frequency [18]. To take into account the systematic error of calculation, the obtained frequencies are multiplied by scale factors in accordance with the used calculation approximation. The latter are obtained by the comparison of calculated harmonic frequencies with their experimental values for significant numbers of molecules. In the case of using the calculation in *DFT*-approximation B3LYP/6-311++G(d,p), the scale factor makes the closest to the unity and it is 0.9986 [9]. This means that a good repeatability with the provided experimental data is expected from the obtained values of vibrational frequencies (Table 1, Fig. 5).

Table 1

Harmonic vibrational frequencies (cm^{-1}), obtained experimentally and calculated in approximation *DFT*-B3LYP/6-311++G(d,p)

Intensity, band shape	Experiment			Calculation	Allocation
	PP	PPT15	PPT25	Complex	
v. w., wd.	3542	3418	3417	–	capacity of moisture [4]
	–	3313	3323	3608	$\nu_{(NH)}$ amido group of terlon
w.	2958	2948	2958	3024	$\nu_{(CH2)}$ the main chain of pentaplast
	2906	2885	2896	2996	
	2875	2865	2862	2975	
v. w.	2115	2104	2104	–	capacity of monomer traces [4]
s.	–	1646	1625	1724	$\nu_{(CO)}$ amido group of terlon
v. s.	–	1542	1531	1638	$\delta_{(NH)}$ amido group of terlon with $\nu_{(CC)}$ benzene rings
		1521	1500	1632	
		1500	1469	1559	
s.	1375	1375	1375	1525	$\delta_{(CH2)}$ the main chain of pentaplast
	1313	1313	1302		
	1260	1260	1260		
w.	–	–	–	1463	$\delta_{(CH)}$ with $\nu_{(CC)}$ benzene rings, and $\delta_{(NH)}$ amido group of terlon
				1338	
				1259	
v. s.	1104	1094	1115	1132	$\nu_{(CO)}$ the main chain of pentaplast
	1064	1052	1063	999	
av.	885	896	885	884	$\nu_{(CC)}$ with $\delta_{(CH2)}$ the main chain of pentaplast
	854	854	854		
w.	–	813	813	768	$\delta_{(CH)}$ benzene rings of terlon
		771	771	715	
av.	740	729	688	680	$\nu_{(CCl)}$ chloromethylene group of pentaplast
	688	698	677		
v. w.	–	625	594	592	$\delta_{(NH)}$ amido group of terlon
		604	563	573	
av.	500	531	500	524	$\delta_{(CC)}$ the main chain of pentaplast

Explanation of symbols: s. – strong, av. – average intensity, w. – weak, wd. – wide, v. – very; ν – stretching vibrations, δ – bending vibrations; PP – clear pentaplast, PPT15 and PPT25 – polymer composites based on pentaplast, contained 15 and 25 wt % of terlon fiber.

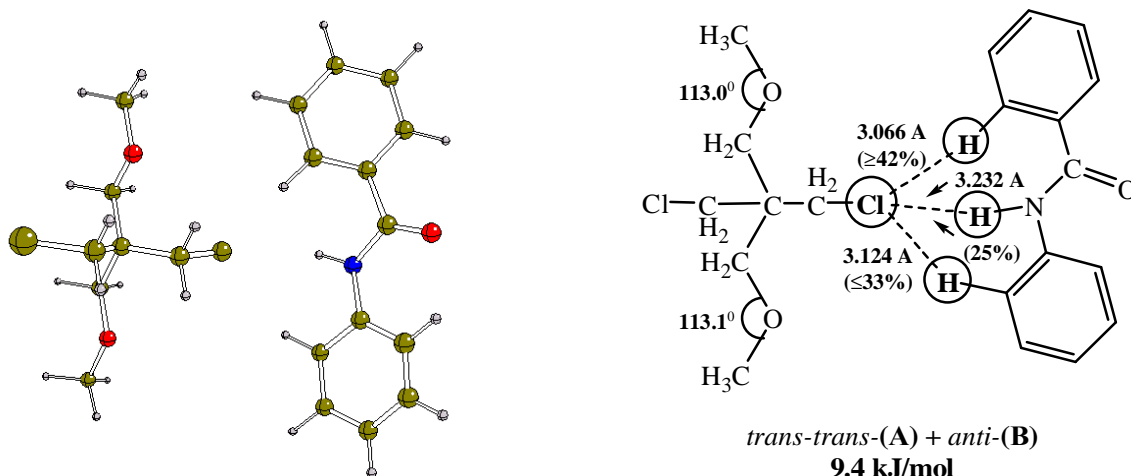**trans-trans-(A)** + *anti*-**(B)**
9.4 kJ/mol

Fig. 4. *3D*-Model with some geometrical and energetic parameters of *N*-phenylbenzamide molecular complex with the elements of penton monomer chain and general stabilization energy system, which was calculated
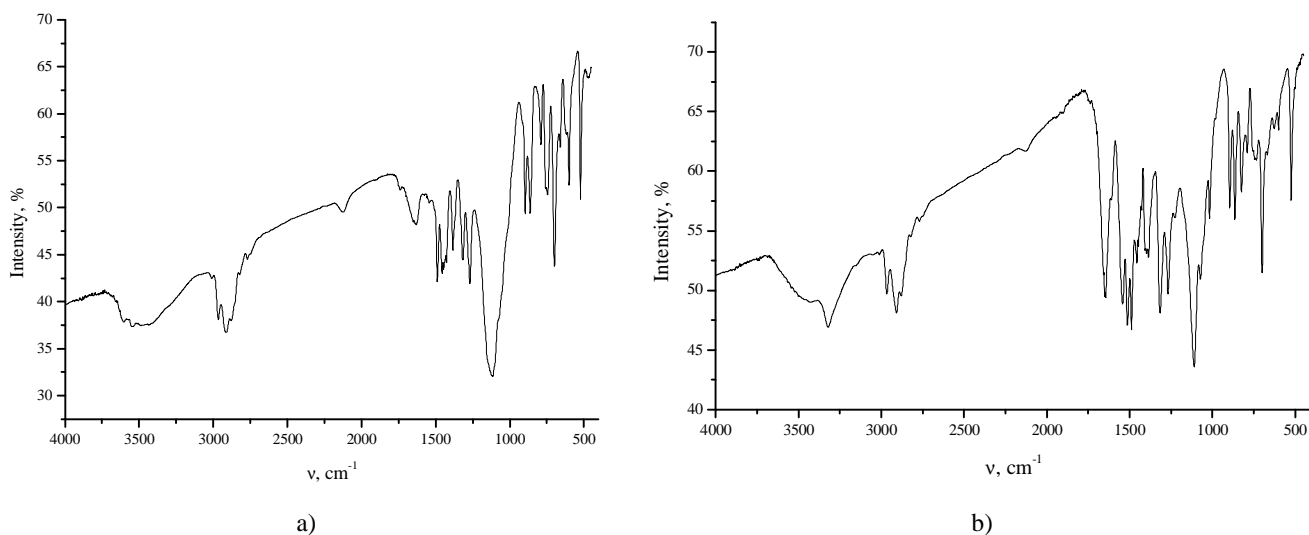in *DFT*-B3LYP/6-311++G(d,p) approximation

a)

b)

Fig. 5. IR absorption spectra for clear PP (a) and for composite PPT25 (b)
within the 25 wt % of terlon fiber

The most intensive in the calculated spectrum of the molecular complex is the fringe in the 1559 cm^{-1} area, which responds to the bending vibrations of an NH-group with the participation of aryl molecular fragments in close proximity. The less intensive signals of benzene rings are in the area of 715 and 768 cm^{-1}. The stretching vibrations of bindings related to the main chain of pentaplast are shown as the absorption bands with wave numbers of 1132 and 3024 cm^{-1}, responding to the vibrations of C–O bindings and acyclic elements respectively. The average intensity band for the C–Cl binding normally lays in the area of 680 cm^{-1}. We can also see that in the case of an isolated chloromethylene group of penton element monomer it moves to the area of 685 cm^{-1}. The same

dislocation of absorption bands in the case of an amido fragment of *N*-phenylbenzamide molecule: for a carbonyl group it is from 1724 to 1729 cm^{-1}, and for an NH-group it is from 3608 to 3617 cm^{-1}. The sets of wave numbers, which are shown below, correlate to each other:

$$\nu(\text{Complex}) = (1.08\pm0.02)\cdot\nu(\text{PPT15}) -$$
$$- (48.09\pm34.09),\ r=0.996,\ s_0=81.12,\ n=22 \quad (3)$$
$$\nu(\text{Complex}) = (1.07\pm0.02)\cdot\nu(\text{PPT25}) -$$
$$- (21.86\pm34.05),\ r=0.996,\ s_0=82.09,\ n=22 \quad (4)$$

This points to the strength of the reproduction of the spectrum characteristic of the researched system as a part of chosen level of theory [6].

4. Conclusions

The results of the quantum-chemical research presented in this work indicate the opportunity of using quantum chemistry methods and procedures for studying the special aspects of intermolecular interaction at the level of separate macromolecular structural fragments. The obtained data may represent a significant interest in terms of the preliminary estimation of the components compatibility in creating related composite materials on their basis.

Acknowledgments

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КВАНТОВО-ХІМІЧНЕ МОДЕЛЮВАННЯ СТРУКТУРИ ТА СПЕКТРАЛЬНИХ ХАРАКТЕРИСТИК МОЛЕКУЛЯРНИХ КОМПЛЕКСІВ У СИСТЕМІ ПЕНТАПЛАСТ-ТЕРЛОН

Анотація. *З використанням ab initio методів квантової хімії досліджено структуру та спектральні властивості молекулярних комплексів, утворених мономерною ланкою пентапласту та N-феніл-бензамідом, що відтворюють особливості міжмолекулярної взаємодії у системі пентон-терлон. Запропоновані теоретичні моделі адекватно відображають спектральні та енергетичні характеристики досліджуваної системи.*

Ключові слова: *ab initio розрахунок, конформаційний аналіз, міжмолекулярна взаємодія, енергія стабілізації, похибка суперпозиції базисних наборів, коливальний спектр.*