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Theoretical study of some phenomena and processes in the course of organic chemistry

Introduction

In the context of increasing the pace of development of science, which contributes to the rapid accumulation of new knowledge and the development of materials and technologies of another generation, it is necessary to connect the processes in the educational system to the society evolution in order to prepare people adapted to the labour market conditions which are in a permanent change. These processes call for qualitative changes in the field of education whose primary objective is to synchronize research and technology transfer. Based on this, it is necessary to integrate the information and communication technologies in the training-educational process. The new demands of the school curriculum on Chemistry and the desire of pupils as well as teachers to use modern information tools in teaching-learning-assessment in Chemistry require a new configuration of the modern didactic design [1]. There appears a need to develop a new concept that would ensure the development of formative training with the use of modern technologies to help young people (pupils/students) discover the mysteries of the exact and natural sciences also with the help of information technologies - a motivating contemporary trend in education. Achieving a successful integration of training with research involves deep inter- and trans-disciplinary connections [2].

Today, modern chemistry is an area whose specific results contribute substantially to the development of human society. An important role belongs to organic chemistry, which develops in a stormy way, holds the largest share of compounds and deals with the establishment of the structure of the compounds it studies. Respectively, the composition-structure-property relationships, as well as the energy state of the molecules, require a profound and multilateral study. In order to propose specific examples of the study of the energy of organic molecules, there have been made theoretical researches of the isomeric phenomenon of some representatives of the hydrocarbon series and the condensation process of some aldehyde amines. The methodology can be used in the pre-university Chemistry course. For the specialties in the field of Chemistry at university level the methodology is mandatory, as well as in the context of scientific research on molecules and chemical phenomena.

Theoretical research methods

The results obtained in the modeling of the geometric structures of the studied isomers are based on the Density Functional Theory (DFT) with the exchange-correlation hybrid function B3LYP (Becke with the functional correlation of three parameters, Lee, Yang and Parr) [3, 4].

The calculations were made using the modern set of software GAUSSIAN 09. For all calculations the space symmetry C1 was used. Upon optimizing the structures of the five isomers of the hexane, the exchange-correlation hybrid function B3LYP was used and the standard basic sets 6-311G for carbon and hydrogen atoms.

Results and discussions

Theoretical study of the phenomenon of isomerism

Within the discipline of Chemistry, both the gymnasium cycle (form IX) and the lyceum (form XI, XII) [5, 6] it is studied Organic Chemistry where the students acknowledge with some physical and chemical properties, different methods of production and fields of use of organic compounds. The large diversity of organic compounds is conditioned by the phenomenon of isomerism, which consists in the existence of several combinations with the same molecular composition, but different structure and properties [7].

When studying the classes of organic compounds, the following types of isomerism are encountered:

a) Flat isomery (flat formulas are used): *chain isomery* (of structure); *positional isomery; functional isomery; tautomerism*.
b) Space isomery (stereo-isomery): *geometric (cis-trans); conformational; optical.*

Studying the phenomenon of isomerism gives students certain skills related to:

- establishing the causes that lead to the emergence of different types of isomerism;
- acquiring information about the concept of isomerism;
- skills and competences of material and graphic modeling of different isomers and of predicting some properties;
- understanding the need to study the notion and phenomenon of isomerism which explains the diversity of organic compounds.

The phenomenon of isomerism can also be explained by the use of certain notions in Physics, Biology, mathematical relations, which will form a complex thinking in pupils and will finally introduce them into the problem of the interdisciplinary approach and will teach them the ability to selectively use information from other related domains. These aspects will form the basics that will form in the pupils:

- the ability to use some notions and knowledge from tangent domains;
- the orientation in the field of research leading to deciphering inter-dependence between composition-structure-properties;
- the spirit and ability to select and analyze;
- the ability to formulate some hypotheses, to draw conclusions and, most importantly, to form the scientific conception about the surrounding world.

Chemistry as one of natural sciences with an experimental character has also accumulated quite a large theoretical background. Respectively, the correct and profound understanding of this background of theoretical knowledge can only be done with some specific means which in correlation with a minimal intellectual effort can lead quickly and efficiently to the goal achievement. One of these successfully applied methods in recent years at different levels of knowledge is *modeling*. Modeling as a learning method contributes to the brief acknowledging of the essential and characteristic peculiarities of objects, phenomena and processes, thus contributing to an active learning with conscious participation of the pupils by engaging them in logical and creative thinking and developing intelligence, thus becoming an agreeable and effective learning method. The use of computer quantum calculations allows pupils/students to determine the energy of chemical systems to conclude which theoretically possible isomers are stable and represent the real spatial structural configuration of the chemical compound.

Pupils' learning based on modeling develops creativity. When pupils are in new situations, the intellect begins to investigate and the investigation is a complex mental process characterized by the manifestation of seeking, analyzing and acquiring new information. The contemporary training-educational process must be focused on a heuristic spirit that enables pupils to discover unknown relationships and characteristics, to be active and accept algorithms and concepts dictated by the teacher to obtain new information and knowledge [8].

Future society needs personalities capable of adapting to new changes, self-taught, creative, initiative and investigative because science and technology will gradually reduce the difference between physical and intellectual work giving it the possibility of permanent and continuous training.

This study is based on the theoretical aspects of the phenomenon of isomery, which also describes some exact ways of organizing modelling learning by using the programs of calculating the energy state of the isomers and determining their stability. In both school and university, most of the time only the possible isomers of an organic compound are examined, but not the geometric structure and their energy state. From the multitude of theoretically analyzed isomers only the one with the most energy-efficient molecular configuration exists, but in most cases the teachers do not have the possibility to calculate the energetic state of the molecular system and to predict their existence. The proposed method may enable Chemistry teachers to bring compelling arguments by suggesting pupils/students practical activities to calculate the energy state of the molecular configuration.

As an object of study it has been proposed the theoretical study of the geometric structure and total energy of an organic combination with C_6H_{14} molecular structure (hexane) which possesses 5 chain isomers.

Optimization takes place in several stages, where for each coordinate change, it is calculated the electron energy in the given nucleus configuration (Table 1).

Table 1. Total energy (e.a.u.) and gap energy ΔE (kJ/mol) of the studied hexane isomers.

Nr.	Isomer	E_{tot} (e.a.u.)	$\Delta E=E_{LUMO}-E_{HOMO}$
1	n-hexane	-237.0794	9.71
2	2-methylpentane	-237.0790	9.62
3	3-methylpentane	-237.0775	9.56
4	2,2-dimethylbutane	-237.0770	9.39
5	2,3-dimethylbutane	-237.0787	9.49

According to the obtained results (Table 1), the relative energy curve of the studied isomers was elaborated starting from the structure of hexane by diminishing the main chain to four carbon atoms (Figure 1).

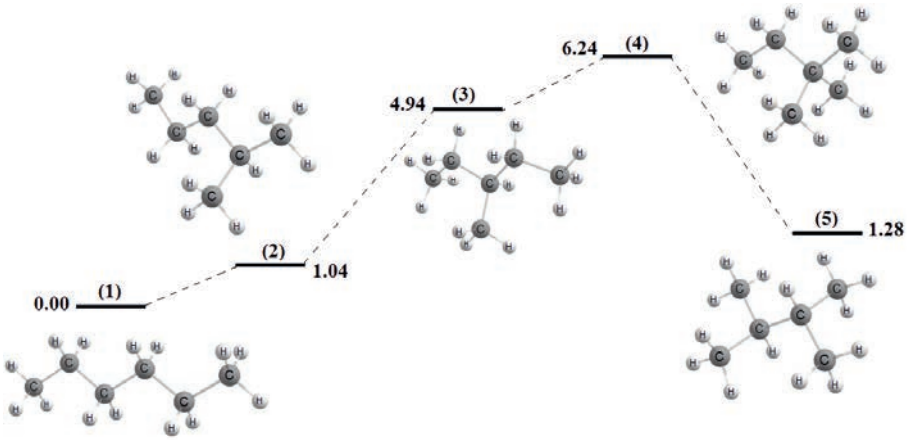


Fig. 1. The stabilizing energy of the hexane isomers (kJ/mol).

In this study the structure and energy stability of hexane molecule isomers have been analyzed. The most energetically stable isomer is hexane, while the least stable is 2.2-dimethylbutane with a stabilizing energy of 6.24 kJ/mol.

The described method can be applied to determine the energy status of organic molecules at both university and pre-university level.

Theoretical study of the condensation process

Several models that would allow the completion of some complex studies of molecular features [9] and some chemical processes can be proposed for the discipline of Chemistry.

One of the chemical processes encountered in the course of Organic Chemistry is the condensation process. For the purpose of organizing profound studies it is proposed to analyze an integrated training-research application model in which the condensation reaction of organic molecules to be studied by means of quantum-chemical calculations based on specialized software which allows the determination of the energy of the studied processes and the probability of chemical reaction. It has been studied the condensation process of 3-pyridinaldehyde with hydrazine under the ratio 2:1, resulting in a new organic product – 3-pyridinealdehyde azine.

The set of applied methods allows a detailed analysis of certain features related to the structure and properties of the new chemical compounds and is recommended for application at university level and for students interested in at the pre-university level.

Transition states were localized and verified by vibration analysis. For these transition states an imaginary frequency has been obtained, which demonstrates the presence of these activated states of the investigated systems. The values of the imaginary frequencies are described in the text and figures below.

The scheme of the reaction overall mechanism is shown in Figure 2.

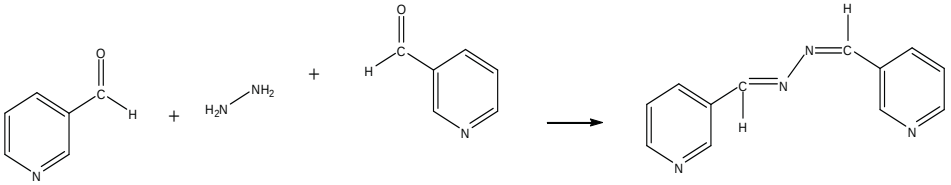


Fig. 2. The overall reaction of the examined mechanism.

Initially, the values of the total energies of the structure of reagent and reaction products are calculated (Table 2).

For each particle of the mentioned reaction the optimal geometry is determined and the total energies are calculated. In all cases it was considered that the spatial nuclear configuration of the studied molecules corresponds to the symmetry group C_1.

The values of the geometric parameters and the total energies for the studied species, obtained as a result of the optimization, correlate to a large extent with those in the literature.

On the basis of the obtained results (Table 2), the energy gain for this condensation reaction has been calculated to obtain an exothermic energy of -22.03 kcal / mol.

Table 2. Total energy of calculated systems.

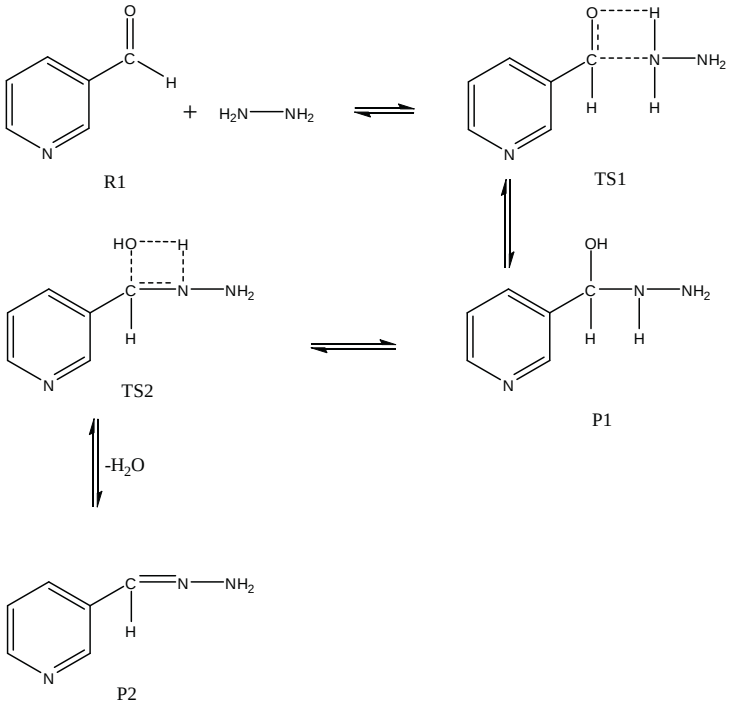
Species	Energy calculation	Total energy
Reactants (R)	2 • (-361.4999)+(-111.7853)	-834.7851
Produts (P)	-682.0479+2 • (-76.3861)	-834.8202
ΔE(e.a.u)		-0.0351

Based on this, we intend to calculate all the species involved in the reaction (reagents, reaction products, intermediates and transition states) and on the basis of these calculations to obtain the energetic profile of the studied reactions.

Later on it has been carried out the optimization of the geometric configuration of the pairs of molecules involved in the reaction that were initially in the immediate vicinity. The general aspect of this reaction, the way the particles interact and the reaction mechanisms act are described and discussed below.

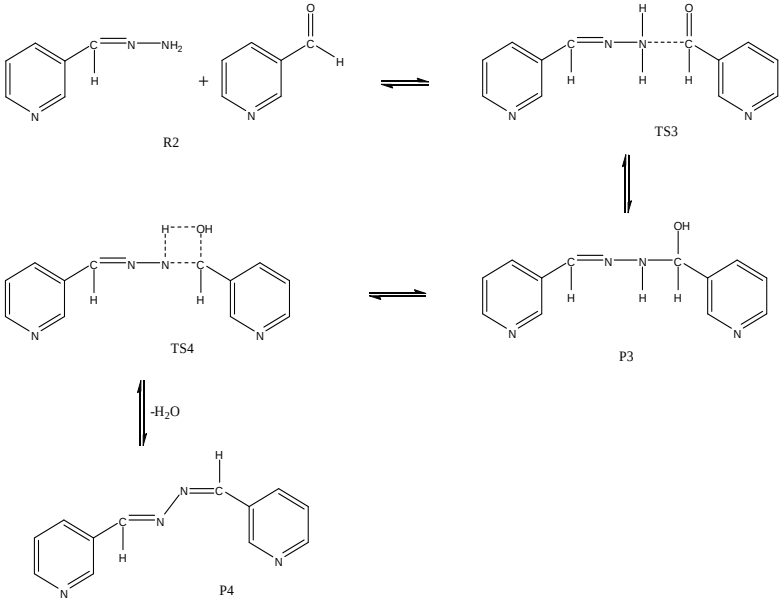
As mentioned above, the object of the study was the mechanism of condensation of 3-pyridinaldehyde with hydrazine according to the following two schemes.

I-st stage of condensation reaction:



Scheme 1. The first stage of condensation reaction.

II-nd stage of condensation reaction:



Scheme 2. The second stage of condensation reaction.

Optimization takes place in several stages where for each coordinate change the electron energy is calculated in the given nuclei configuration (Table 3).

Table 3. Total energies of reactants, products, transition states and imaginary frequencies of studied intermediates.

Species	Energy calculation	Total energy	Imaginary frequency
R1	2 • (-361.4999)+(-111.7853)	-834.7851	
TS1	-473.2707-361.4999	-834.7706	1432.10i
P1 -473.3349-361.4999		-834.8348	
TS2	-473.2618-361.4999	-834.7617	597.88i
P2=R2	-396.9430-361.4999-76.3861	-834.8290	
TS3	-758.3815-76.3861	-834.7676	1541.61i
P3	-758.4521-76.3861	-834.8382	
TS4	-758.3716-76.3861	-834.7577	1679.87i
P4	-682.0479+2 • (-76.3861)	-834.8202	

Figure 3 shows the energy profile of the entire condensation reaction cycle which includes four transition states (TS1, TS2, TS3 and TS4).

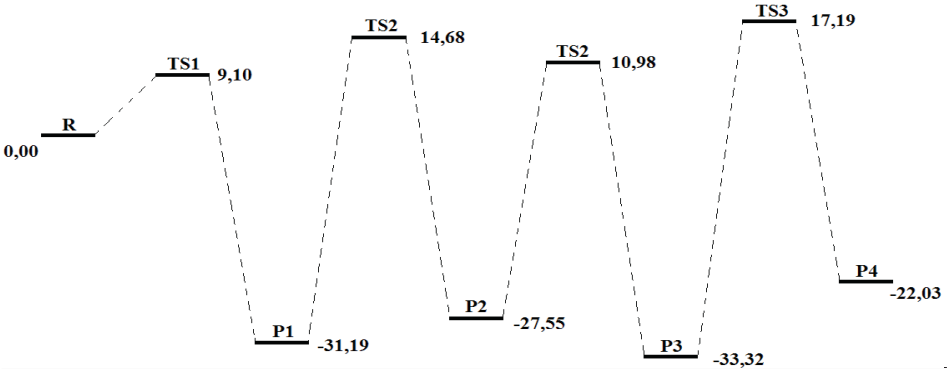


Fig. 3. Energy profile calculated for the entire reaction mechanism (all values are in kcal/mol).

For all the intermediate complexes (ST1, ST2, ST3 and ST4), more precisely for their optimized geometries, vibration frequencies has also been calculated to ensure that there is only one imaginary frequency that corresponds to a local minimum on the surface of potential energy.

The study of the energy profile of the mechanism as a whole confirmed that this is an exothermic reaction with an energy gain equal with 22.03 kcal/mol.

Conclusions: The use of calculations to determine the energy status of some molecular systems allows rational application and practice of theoretical knowledge in the field of Chemistry and the adaptation of IT skills to the needs and specifics of Organic Chemistry. On the basis of the previously done calculations, pupils/ students independently determine the energy status of each system, obtain the most advantageous spatial configuration of the studied compound and understand some structural features of organic molecules. Applying the methods of calculating the energy profile of chemical molecules based on contemporary information

technologies allows the physic-mathematical determination of the probability degree of the chemical reactions and, thus, contributes to the development of sustainable competences and the multilaterally research of some fine phenomena. These practical exercises allow the development of some individual aspects of the specialist and self-learning developmental capacity positively marking the trajectory of initial professional competence training.

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Theoretical study of some phenomena and processes in the course of organic chemistry

Abstract

The current trends of didactic methodology are oriented towards the formation of competencies applicable in the context of dynamic technology evolution. The educational system should provide pupils/students with opportunities to integrate knowledge from different fields in order to understand logically the essence of natural processes and phenomena. Integrating training with research into an interdisciplinary context presents one of the fundamental objectives of the contemporary educational system. Using computational calculations to determine the spatial configuration and energy of molecular systems allows the pupils to apply specialized programs to determine the most convenient molecular state and the direction of chemical reaction. This method allows the integrated development of chemistry skills and the use of information technologies to solve specific problems in the field, which enables the development of specialists with knowledge-applying skills in various work situations to respond to challenges of varying degrees of difficulty.

Keywords: chemistry training, energy calculation, isomerism, molecular configuration, condensation, specific skills, inter-disciplinarity, professional competence.

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