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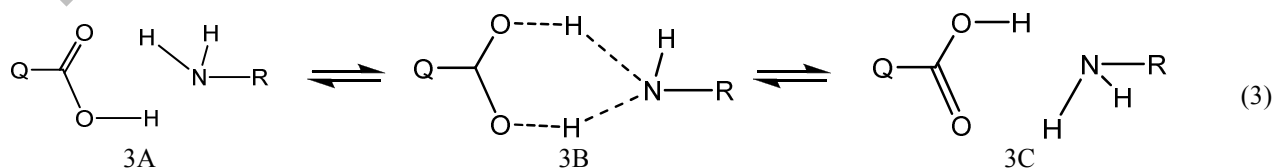
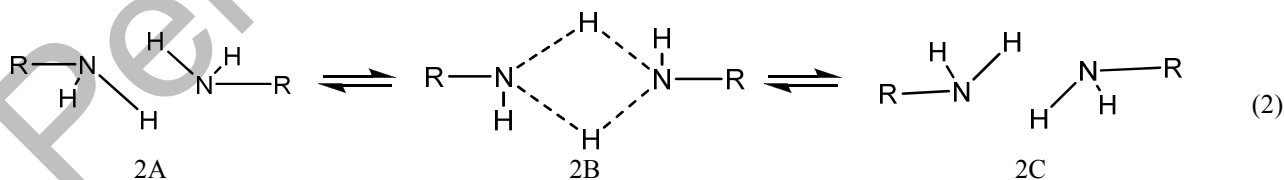
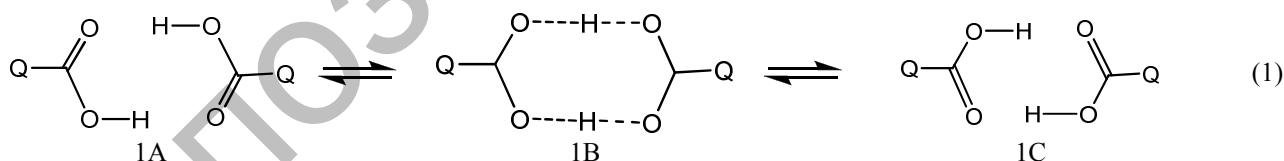
Ye.A. Buketov Karaganda State University, Kazakhstan
(E-mail: kutzhanovak@mail.ru)**Nonempirical modeling of protolytic processes in dimeric molecules of amino acids**

Quantum-chemical modeling of intermolecular proton exchange in dimers of aminoacetic acid was carried out using an unempirical unrestricted Hartree-Fock method using the 3-21G basis set. Three main structural isomers of dimeric molecules of aminoacetic acid have been quantum-chemically identified. For these isomers, the search for the structure of the transition state of the proton exchange reaction was carried out using the quadratic synchronous transit QST2 (Quadratic Synchronous Transit Approach) procedure. The symmetrical structure of the transition state for the dimer of aminoacetic acid is noted, in the formation of hydrogen bonds of which two carboxyl functional groups are involved. The kinetics and mechanism of intermolecular migration of a proton in the dimer of aminoacetic acid have been studied using the internal IRC (Intrinsic Reaction Coordinate method) method. Curves are obtained for the dependence of the total energy of the reaction system under consideration on the internal coordinate of the reaction. The activation energy of proton exchange in dimers of aminoacetic acid is estimated as the difference in the total energies of the transition and initial states of the reaction system. The minimum value of the activation energy (26 kJ/mol in the forward direction and 34 kJ/mol in the reverse direction) was obtained for the intermolecular proton exchange reaction in the dimer of aminoacetic acid, in the formation of the hydrogen bonds of which two carboxyl functional groups are involved. The maximum value of the activation energy (244 kJ/mol in the forward direction and 236 kJ/mol in the reverse direction) was obtained for the intermolecular proton exchange reaction in the dimer of aminoacetic acid, in the formation of hydrogen bonds of which two amino groups are involved.

Keywords: quantum chemical calculation, *ab initio* UHF 3-21G, hydrogen bond, aminoacetic acid, dimer, cyclic complexes by hydrogen bonding, geometric and energy parameters, complexation energy, hydrogen bond energy.

Most of the applied quantum chemical work is connected with the calculation of the geometry of organic compounds. Such researches are carried out for both stable molecules and short-lived intermediates and transition states. Analysis of the calculated data allows to obtain reliable information on their structure and therefore to be of independent interest from the point of view of organic chemists. In addition, knowledge of geometry is necessary for calculating the thermal formation, thermal effects and activation energies of the reactions [1].

In this paper, the process of proton exchange between molecules in dimers of aminoacetic acid by quantum chemical methods was considered. If the studied molecules contain two reaction centers [2, 3], it is possible to consider three main possible complexes formed by the hydrogen bond:



where Q — is $-\text{CH}_2\text{-NH}_2$; R — is $-\text{CH}_2\text{-COOH}$.

(1) is a complex due to the hydrogen bond in which carboxyl functional groups of an amino acid are involved in the formation of hydrogen bonds;

(2) is the complex due to the hydrogen bond, in which the amino groups of the amino acid are involved in the formation of hydrogen bonds;

(3) is a complex due to the hydrogen bond in which the carboxyl functional group of one molecule and the amino group of another amino acid molecule are involved in the formation of hydrogen bonds;

On the proposed scheme of intramolecular hydrogen transition inside the cyclic dimer of aminoacetic acid: A) the initial geometry of dimer 1; B) transition state; C) finite dimer geometry.

Simulation of the process of intermolecular proton exchange was carried out by an *ab initio* method in the 3-21G basis in the unrestricted Hartree-Fock approximation of the Gaussian09 Revision-B.01-SMP software package [4].

When creating the dimer molecule, the GaussView program was used — a visualizer program designed to create input files, as well as visualization of the output files generated during the Gaussian calculation.

To study the kinetics and mechanism of intermolecular migration of a proton in the dimer of aminoacetic acid, the quantum chemical procedure IRC was used [5].

The initial (A) and final (C) structures of the dimer of aminoacetic acid with full optimization of all geometric parameters are shown in Figure 1. It should be noted that the numbering of atoms in the molecules of the intended reagents and reaction products must be strictly preserved.

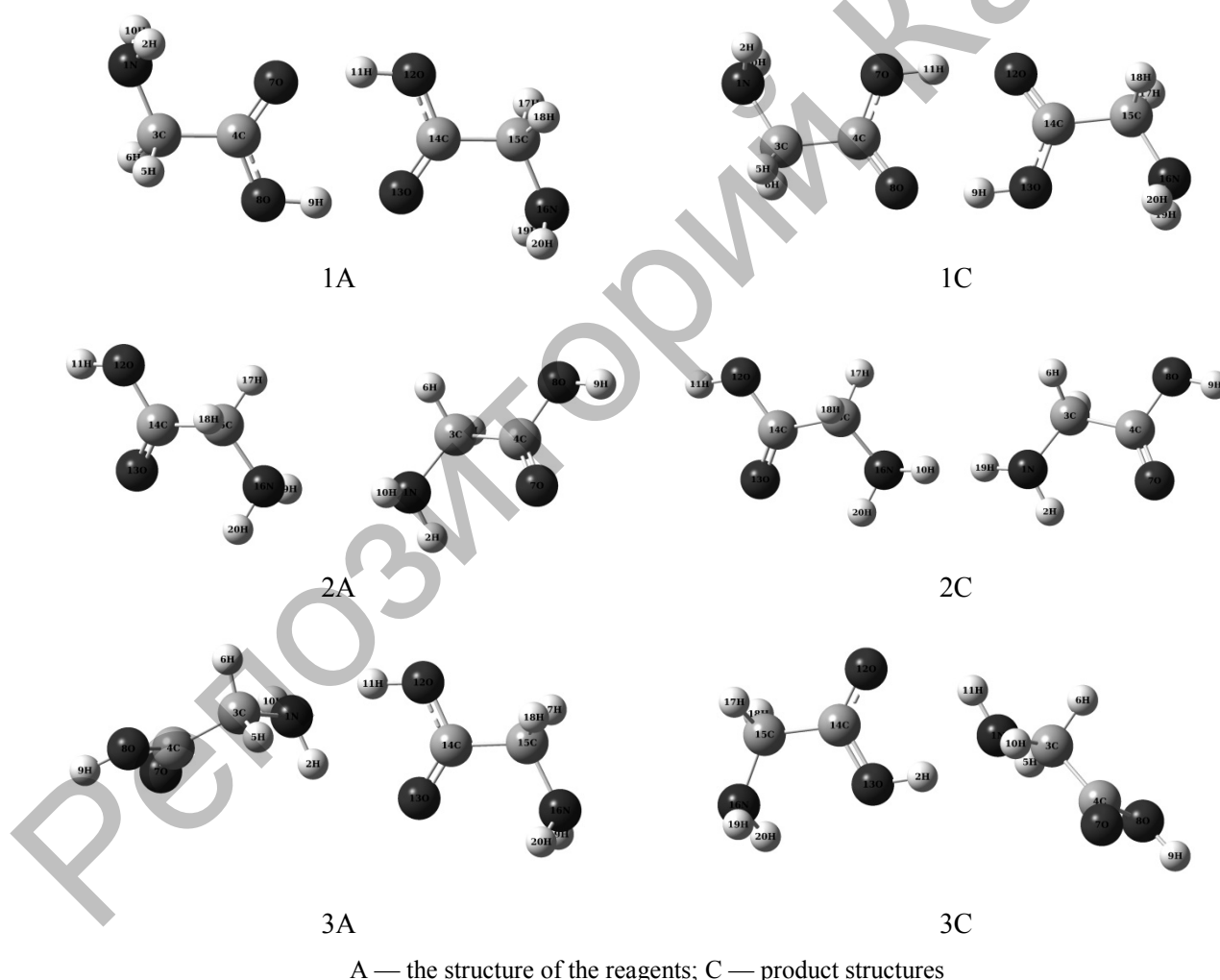


Figure 1. Structures of intermolecular complexes due to the hydrogen bond of the dimer of aminoacetic acid

Next, a transition state was calculated using the keywords Opt (QST2) UHF 3-21G. The search for a transition state of intramolecular tautomerism was carried out by the quadratic synchronous linear transit method.

Figure 2 shows the transitional structures in a complex due to hydrogen bonding of various types for dimers of aminoacetic acid.

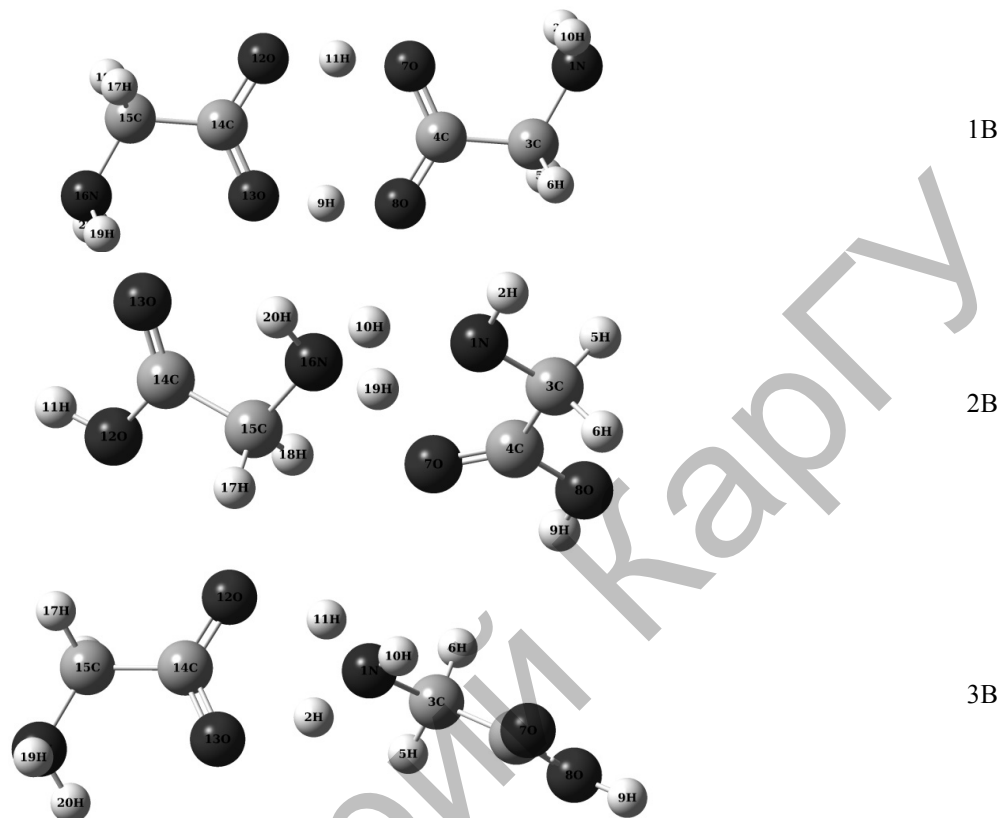


Figure 2. The transition state of the proton transfer process in dimeric aminoacetic acid complexes

Figures 3–5 depict the dependence of the total energy of the dimer systems and the RMS normal gradient on the internal coordinate of the RMS (root-mean-square) reaction.

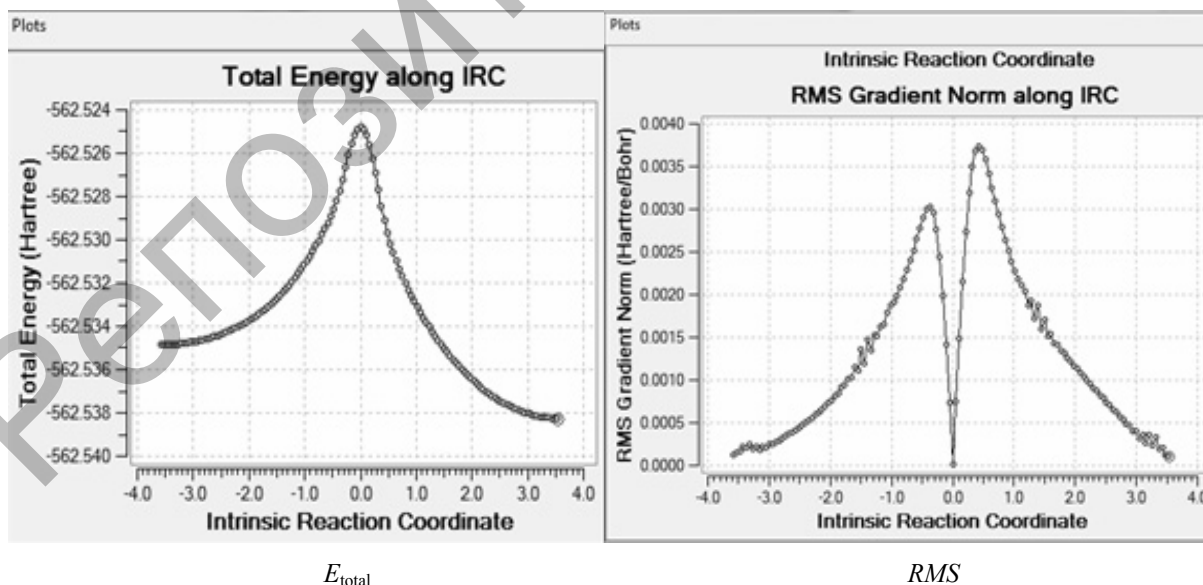


Figure 3. Kinetic curves as a function of the reaction coordinate in the complex due to the hydrogen bond (1) of aminoacetic acid

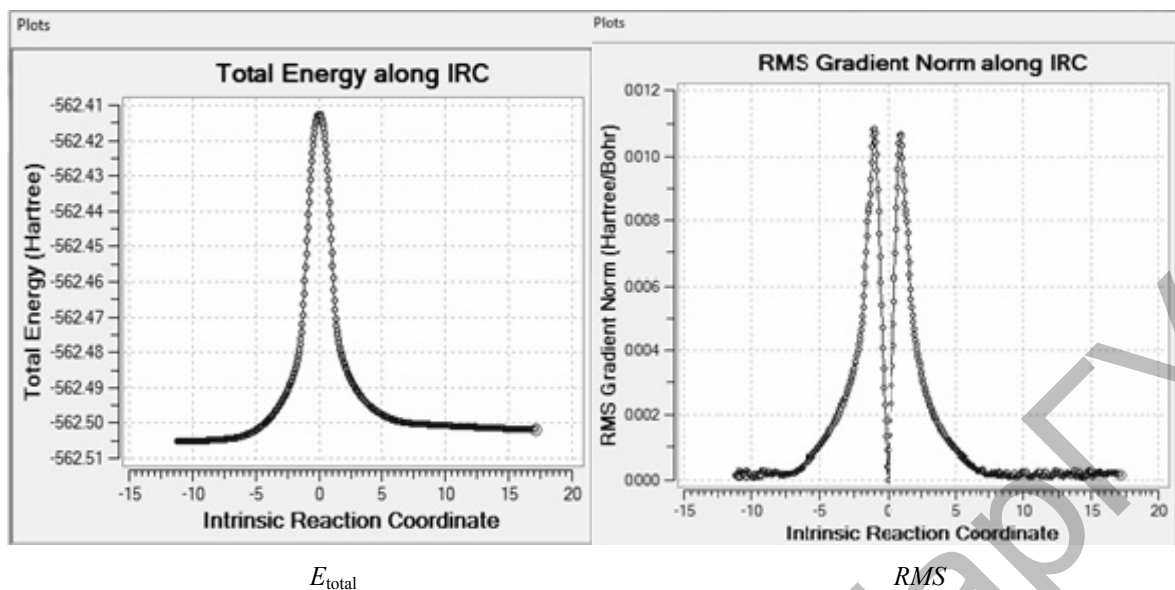


Figure 4. Kinetic curves as a function of the reaction coordinate in the complex due to the hydrogen bond (2) of aminoacetic acid

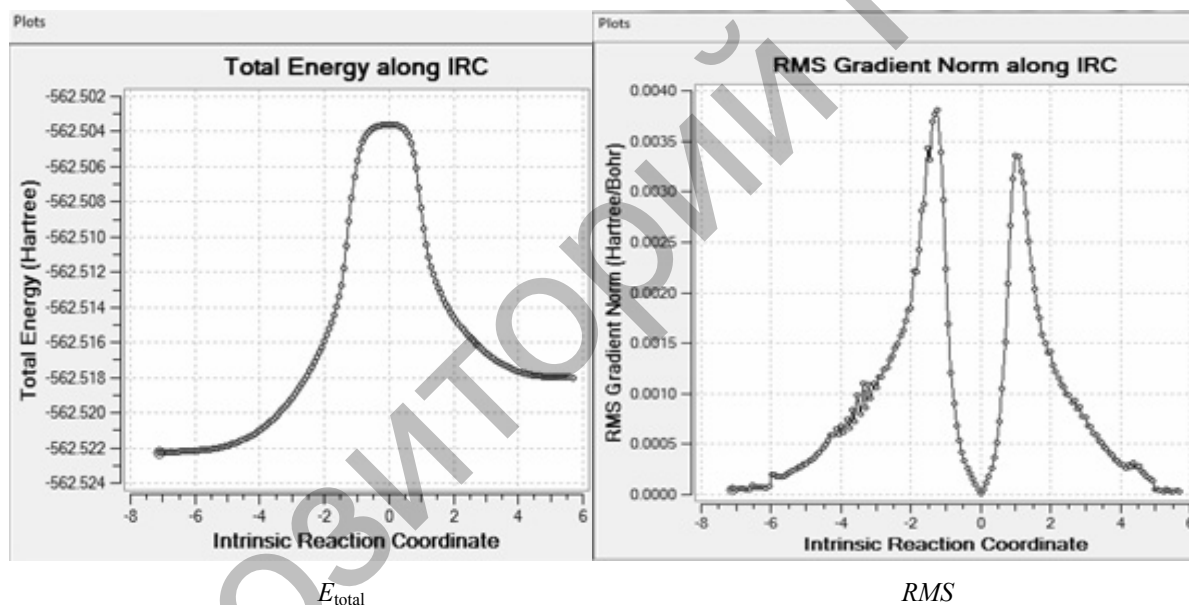


Figure 5. Kinetic curves as a function of the reaction coordinate in the complex due to the hydrogen bond (3) of aminoacetic acid

As can be seen from Figures 3–5, the extreme points of the curves of kinetic dependencies are identical to the points on the graphical dependence of the root-mean-square deviation standard along the coordinates of the reaction path.

The program GaussianView allows you to determine the structure of each studied point of the curves examined, optimizing all the geometric parameters of the molecules. It should be noted that the calculation procedure for internal coordinates is carried out automatically, which significantly reduces the time required for calculation. So in the calculation of the complex due to the hydrogen bond (1), in the automatic mode 134 optimized structures are investigated, the complex due to the hydrogen bond (2) — 563 and the complex due to the hydrogen bond (3) — 168.

Table shows the energy values for all types of particles: A, B, and C for all the complexes under study due to the hydrogen bond.

Kinetic characteristics of different types of complex due to the hydrogen bond of aminoacetic acid according to 3–21G UHF calculations

Complex due to the hydrogen bond	E_A , a.u.	E_B , a.u.	E_C , a.u.	ΔE_{AB} , a.u.	ΔE_{BC} , a.u.
(1)	-562.535	-562.525	-562.538	0.01	0.013
(2)	-562.505	-562.412	-562.502	0.093	0.09
(3)	-562.522	-562.504	-562.518	0.018	0.014

Note. E_A — is the total energy of the process reagent; E_B — is the total energy of the transition structures of the process; E_C — total energy of process products.

As shown by the analysis of the energy parameters presented in Table, the minimal activation energy accompanies the process of proton transfer in the complex due to the hydrogen bond (1) in the forward and reverse directions, respectively, 26 and 34 kJ/mol, the maximum activation energy for the process in the complex due to the hydrogen (2), where the parameter corresponds to 244 and 236 kJ/mol, the intermediate position is occupied by the activation energy in the complex due to hydrogen bonds (3): 47 and 36 kJ/mol, respectively. It should be remembered that in reactions where the activation energy is greater than 150 kJ the rate is very small or practically these reactions do not flow. In reactions where the activation energy is less than 60 kJ, the rate is very high.

Thus, by using non-empirical quantum chemical methods, kinetic curves and characteristics were obtained depending on the coordinate of the reaction of the complex due to the hydrogen bond of aminoacetic acid, their kinetic stability is shown, and the characteristic of the hydrogen bond is estimated.

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К.Ж. Кутжанова, А.Ф. Курманова, И.А. Пустолайкина, Б.М. Исмагулов

Аминқышқылдары димерлі молекулаларының протондану процестерін эмпирикалық емес модельдеу

Аминсірке қышқылының димерлеріндегі молекулааралық протон алмасуының квантты-химиялық модельдеуі 3–21G негізгі жиынтығын пайдалана отырып, шектеусіз Хартри-Фок әдісі арқылы жүзеге асырылды. Аминсірке қышқылы димерінің үш негізгі құрылымдық изомері квантты-химиялық түрде анықталған. Бұл изомерлер үшін протон алмасу реакциясының ауыспалы күйінің құрылымы QST2 (Quadratic Synchronous Transit Approach) квадраттық синхронды транзит процедурасы арқылы ізделінді. Аминсірке қышқылының димері үшін оның құрамында екі карбоксильді функционалды топтың сутектік байланыстары қалыптасатын өтпелі күйдің симметриялық құрылымы байқалады. Аминсірке қышқылының димеріндегі протонды молекула тасымалдануының кинетикасы мен механизмі IRC (Intrinsic Reaction Coordinate method) ішкі координат әдісімен зерттелінді. Реакцияның ішкі координатасымен қарастырылып отырған реакция жүйесінің толық энергияларының тәуелділік қисықтары алынды. Реакция жүйесінің ауыспалы және бастапқы күйлеріндегі айырмы ретінде аминсірке қышқылының димерлеріндегі протон алмасудың активтілік энергиясы бағаланды. Молекулааралық протон алмасу реакциясы үшін активтілік энергиясының минималды мәні (тура 26 кДж/моль және кері бағытта 34 кДж/моль), аминсірке қышқылының сутектік байланыстардың түзілуіне екі карбоксильді функционалды қатысатын димерінде алынды. Молекулааралық протон алмасу реакциясы үшін активтілік энергиясының максималды мәні (тура 244 кДж/моль және кері

бағытта 236 кДж/моль) аминсірке қышқылының сутектік байланыстардың түзілуіне екі амин тобы қатысатын димерінде алынды.

Кілт сөздер: квантты-химиялық есептеулер, *ab initio* UHF 3–21G, сутектік байланыс, аминсірке қышқылы, димер, сутектік байланыс арқылы түзілетін циклдік кешендер, геометриялық және энергиялық өлшемдер, кешен түзу энергиясы, сутектік байланыс энергиясы.

К.Ж. Кутжанова, А.Ф. Курманова, И.А. Пустолайкина, Б.М. Исагулов

Неэмпирическое моделирование протолитических процессов в димерных молекулах аминокислот

Выполнено квантово-химическое моделирование межмолекулярного протонного обмена в димерах аминокислотной кислоты с помощью неэмпирического неограниченного метода Хартри–Фока с использованием базисного набора 3–21G. Квантово-химически идентифицированы три основных структурных изомера димера аминокислотной кислоты. Для данных изомеров с помощью процедуры квадратичного синхронного транзита QST2 (Quadratic Synchronous Transit Approach) осуществлен поиск структуры переходного состояния реакции протонного обмена. Отмечено симметричное строение переходного состояния для димера аминокислотной кислоты, в образовании водородных связей которого задействованы две карбоксильные функциональные группы. Кинетика и механизм межмолекулярной миграции протона в димере аминокислотной кислоты изучены с использованием метода внутренней координаты реакции IRC (Intrinsic Reaction Coordinate method). Получены кривые зависимости полной энергии рассматриваемой реакционной системы от внутренней координаты реакции. Оценена энергия активации протонного обмена в димерах аминокислотной кислоты как разница в полных энергиях переходного и исходного состояний реакционной системы. Минимальное значение энергии активации (26 кДж/моль в прямом и 34 кДж/моль в обратном направлении) получено для реакции межмолекулярного протонного обмена в димере аминокислотной кислоты, в образовании водородных связей которого задействованы две карбоксильные функциональные группы. Максимальное значение энергии активации (244 кДж/моль в прямом и 236 кДж/моль в обратном направлении) получено для реакции межмолекулярного протонного обмена в димере аминокислотной кислоты, в образовании водородных связей которого задействованы две аминогруппы.

Ключевые слова: квантово-химические расчеты, *ab initio* UHF 3–21G, водородная связь, аминокислотная кислота, димер, циклические комплексы за счет водородной связи, геометрические и энергетические параметры, энергия комплексообразования, энергия водородной связи.

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