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DFT Study of Complexation Reactions Involving Dicarboxylic Acids: Hydrogen Bonds, Influence of Solvent Nature

Quantum chemical studies of the protolytic ability of some dicarboxylic acids are carried out. The geometric and kinetic parameters of the dimeric molecules of maleic, succinic, tartaric, oxalic, and adipic acids are investigated. The dimerization energies of these substances are determined by considering the basis set superposition error (BSSE). The effect of the presence of a carbon skeleton, unsaturated bonds, and hydroxy substituents on the dicarboxylic acids kinetic parameters is confirmed. The frontier molecular orbitals of the studied dimeric acids molecules are considered and the HOMO-LUMO energy gap is determined. The obtained values of the energy gaps show an increase in the stability of a number of cyclic compounds formed by the participation of two hydrogen bonds. The ability of the acids to form complexes with the 3,6-di-tert-butyl-2-hydroxyphenoxyl semiquinone radical is studied. The effect of the nature of the solvent on the activation barrier of the complexation reaction of the semiquinone radical — dicarboxylic acid system is analyzed using the CPCM and IEFPCM models. The dependence of the energy parameter on the solvent polarity is established using the examples of toluene, tetrahydrofuran, and nitrobenzene. The DFT method at the B3LYP level, together with the 6-31+G (d, p) basis set, is used to optimize molecular structures. The calculations are carried out using the Gaussian 16 Revision A.03 WIN64.

Keywords: quantum chemical calculations, density functional theory, hydrogen bond, intermolecular hydrogen bonds, transient formation; complex compounds, frontier molecular orbitals, dimerization energy, complexation energy, effect of the nature of the solvent.

Introduction

Hydrogen bonds and proton transfer reactions are of great importance and the subject of discussion, both in chemistry and other sciences such as biology, physics, and material science. At the same time, the mechanism of such interactions is complex and not fully understood. Experimental methods, such as NMR, IR, and ESR spectroscopy, are widely used to study hydrogen bonds. These methods make it possible to determine the initial and final structures of hydrogen-bonded complexes. The same methods are used in dynamic mode to determine the kinetic characteristics of these processes. However, the detailed mechanism of the proton transfer and exchange processes remains not fully elucidated. Today, it would be interesting to use computational modeling in the study, and in particular DFT calculations, since they are relevant for comparing experimental results with theory [1, 2].

Previously obtained ESR spectroscopy data suggest the ability of carboxylic acids to form dimer associates in nonpolar solvents. The authors of [3–7] showed that the proton exchange between the semiquinone radical and formic acid in toluene occurs predominantly with the dimeric form of the acid. Dicarboxylic acids containing two carboxyl groups are of greater interest compared to monosubstituted analogues since they have more pronounced electron acceptor properties [8]. An analysis of the obtained rate constants of the proton exchange reaction between molecules in combination with an ortho-substituted semiquinone radical in the dioxane showed that an increase in the degrees of freedom in acids leads to the raise of their reactivity. In addition, it is assumed that intermolecular proton exchange is facilitated by the formation of a complex transition intermediate of the reaction due to the coordination of both carbonyl groups. Furthermore, the presence of different functional groups affects the coordination of the four-center cyclic complex due to steric hindrances when approaching the reaction centers [3–8]. However, modern physical methods that make it possible to determine the kinetic parameters of reactions, such as the rate constant or the activation energy of the process, are not suitable for detecting the formation of intermediate particles in the composition of hydrogen-bonded complexes. The structure of the transition state itself remains unstudied since the lifetime of such complexes is much shorter than the characteristic frequencies of physical methods.

In this regard, there is the task of determining the structure of the intermediate complex by the density functional theory method, in which the corresponding processes with the participation of hydrogen bonds take place. Also, the purpose of this study is to establish the dependence of the stability of molecular complexes with the participation of dicarboxylic acids on the length of their structural skeleton and the nature of the solvent.

Experimental

Modern instrumental methods enable the researchers to study the kinetics of elementary chemical processes occurring in nano- or femtosecond modes. However, it is not always possible to register each individual stage of fast reactions by experimental methods. This also applies to proton transfer and exchange processes. Therefore, computer technologies and computational modelling are widely used to predict the electronic structure and physicochemical properties of various molecules.

Many methods have been developed to describe accurately weak interactions, including dispersion interactions. Thus, many authors prove by comparison that the B3LYP method generally gives good results in calculation of the length of hydrogen bonds and the binding energy of dimers [9]. To optimize the geometric structures of a number of dicarboxylic acids and to establish the activation characteristics of protolytic processes, the DFT B3LYP method with the 6-31+G(d, p) basis set was used. This method was chosen because it contains both polarization and diffusion functions, which are important in the study of systems containing intramolecular hydrogen bonds and radical particles. The 6-31+G(d, p) basis includes one set of d-functions for non-hydrogen atoms (such as C, O and N), one set of p-functions for the hydrogen atom, and diffuse functions for heavy atoms.

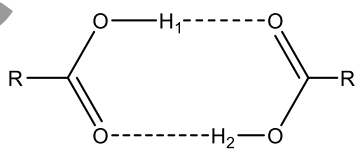
All calculations were carried out using Gaussian 16.

Results and Discussion

The objects of study were the most abundant dicarboxylic aliphatic acids, such as oxalic, succinic, adipic, as well as maleic and tartaric unsaturated acids. It was interesting how the structural features of molecules affect their protolytic ability.

Different conformers of carboxylic acids are described in the literature [9–15]. We chose the most kinetically stable conformations for study. Carboxylic acids form strong dimeric hydrogen-bonded complexes, which are stable even in the gas phase. Bonds between atoms in the reaction center can form linear (LHBC) or cyclic (CHBC) hydrogen-bonded complexes. These are especially interesting for the study by the methods of quantum mechanics since they allow us to consider them as a model in the study of protolytic processes involving semiquinone radicals.

The structure of a cyclic complex of two molecules of dicarboxylic acids in a dimer can be represented by the scheme:



where R — the radical of a dicarboxylic acid.

It can be assumed that a hydrogen bond is formed between the acidic hydrogen of one carboxylic acid molecule and the carbonyl oxygen of the second molecule. Thus, two pairs of intermolecular hydrogen bonds between the carboxyl groups of two distinct molecules can be observed in a cyclic complex. Wang Xu and co-authors [16] determine the strength of the intermolecular hydrogen bond by the O-H elongation in O–H....O fragment and the reduction in the H…O distance. A shorter H…O distance corresponds to a stronger hydrogen bond.

In our studies, theoretical calculations were carried out in the gas phase without taking into account the influence of the medium. An analysis of bond lengths showed that O–H bond elongation is observed in a number of dimers: oxalic acid (1.0055 Å) < adipic acid (1.0057 Å) < maleic acid (1.0069 Å) < tartaric acid (1.0094Å) < succinic acid (1.012Å). At the same time, the strength of the hydrogen bond decreases from succinic acid to oxalic acid, respectively. The geometric parameters of the cyclic complex, such as the bond length R(H..O), R(OO), R(CO) and the valence angles formed by the H–O–C and O–C–O atoms, can also be used to describe the hydrogen bond (Table 1). Isomers molecules with the lowest energy were selected for the study of monomers and dimers.

Table 1

Geometric parameters of dicarboxylic acid dimers obtained using DFT B3LYP/6-31G+(d, p) calculations

No.	Compound	$R_{(OH)}$, Å	$R_{(OO)}$, Å	$R_{(O\_\_H)}$, Å	∠HOC, deg	∠OCO, deg
1	Oxalic HOOC-COOH	1.0055	2.6500	1.6448	110.1	126.8
2	Maleic HOOCCH=CHCOOH	1.0069	2.6362	1.6293	110.3	124.6
3	Succinic HOOC-$(CH_2)_2$-COOH	1.0120	2.6171	1.6051	110.6	124.3
4	Tartaric HOOC-(CH-OH)$_2$-COOH	1.0094	2.6580	1.6159	110.9	125.6
5	Adipic HOOC-$(CH_2)_4$-COOH	1.0057	2.6456	1.6401	110.4	124.1

As can be seen from Table 1, there is no explicit dependence on the hydrogen bond strength in the dimers of the considered dicarboxylic acids. Perhaps this is due to the fact that the number of possible conformers increases significantly with the carbon skeleton growth, and we were not able to identify more stable possible structures. Also, it can be seen that DFT methods are sensitive to changes in the geometric structure of molecules, the presence of multiple bonds, and the presence of substituents.

The dimerization energy can be another parameter that makes it possible to judge the stability of hydrogen-bonded complexes [17–19]. Table 2 illustrates the energies of individual molecules (E_{acid}) and the energies of dimers (E_{dimer}), which were calculated considering the BSSE (Basis Set Superposition Error) correction for the imperfection of the basis set. To calculate the dimerization energy ($\Delta E(d)$), the following formula was used:

$$\Delta E(d) = 2E_{acid} - E_d \quad (1)$$

where E_{acid} — the calculated energy values of the acid molecule; E_d — the calculated energy values of the dimer molecule.

Table 2

Dimerization energies of a number of dicarboxylic acids obtained by the DFT B3LYP/6-31G+(d, p) calculations

No.	Acid	E_{acid}, a.u.*	E_{dimer}, a.u.*	ΔE_d, kJ/mol
1	Oxalic	–378.324383	–756.67244	62.15
2	Maleic	–455.740552	–911.493814	33.37
3	Succinic	–456.974237	–913.975589	71.19
4	Tartaric	–607.403223	–1214.82758	55.48
5	Adipic	–535.610467	–1071. 249247	74.34
Note: *1 a.u. = 2625.5 kJ·mol^{-1}				

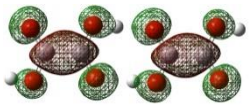
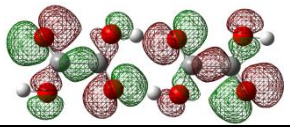
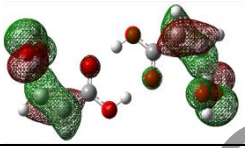
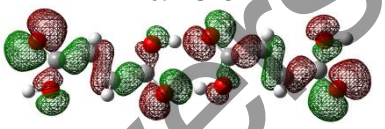
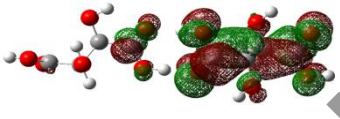
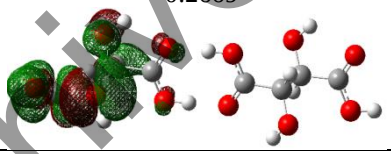
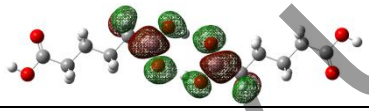
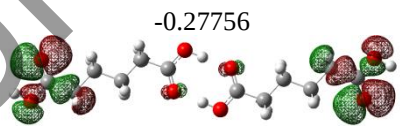
As can be seen from Table 2, the dimerization energies depend on the length of the carbon skeleton of dicarboxylic acid molecules. The values of ΔE_d in the considered series from oxalic (62.1 kJ/mol) to succinic (71.2 kJ/mol) and adipic (74.3 kJ/mol) acids increase, which can be interpreted in favor of the strength of the resulting intermolecular hydrogen-bonded complexes. The presence of an unsaturated bond destabilizes the dimer molecule in the case of maleic acid (ΔE_d = 33.4 kJ/mol). A similar effect is produced by the influence of steric factors, particularly in hydroxy-substituted tartaric acid. Theoretical calculations show lower dimerization energy for tartaric acid (ΔE_d = 55.5 kJ/mol) compared to the unsubstituted analogue (ΔE_d = 71.19 kJ/mol, succinic acid).

The analysis of frontier molecular orbitals allows us to study such an important parameter of quantum chemistry as a population. The highest occupied molecular orbitals (HOMO) are outer orbitals that tend to donate the electrons they contain, thereby being electron donors. The next orbital is the lowest unoccupied molecular orbital (LUMO) capable of receiving electrons. The energy difference between the described levels allows for measuring the HOMO-LUMO gap and can be used to characterize the stability of the molecule under study: If the energy gap is smaller, then the chemical reactivity is higher and the kinetic stability of the molecule is lower.

Table 3 demonstrates the HOMO and LUMO energies of dicarboxylic acid dimers. These data ensure the determination of the values of the HOMO-LUMO gap.

Table 3

Theoretical levels of the HOMO-LUMO transition calculated by the DFT B3LYP/6-31G+(d, p) method

No.	Dimeric compounds of carboxylic acids	$E_{(LUMO)}$, a.u.	$E_{(HOMO)}$, a.u.	ΔE, a.u.
1	Oxalic	-0.08232 	-0.28977 	0.20745
2	Maleic	-0.07292 	-0.28046 	0.20754
3	Succinic	-0.01101 	-0.27518 	0.26417
4	Tartaric	-0.03833 	-0.2669 	0.22857
5	Adipic	-0.00101 	-0.27756 	0.27655

The data presented in Table 3 are ordered by increasing carbon skeleton of dicarboxylic acid molecules. The value of the energy gap rises from 0.20745 a.u. for oxalic acid to 0.26417 a.u. for succinic acid, and to 0.27655 a.u. for adipic acid. Comparison of dimers of acids with the same carbon skeleton showed that stability increases in the presence of multiple bonds (ΔE for maleic acid is 0.20754 a.u.), and reactivity increases with the introduction of hydroxy substituents (ΔE for tartaric acid is 0.22857 a.u.).

Another method for studying the strength of H-bonds is the analysis of natural bond orbitals (NBO). NBO analysis shows the role of intermolecular orbital interaction in the dimer due to charge transfer. Thus, knowing the charges on the O1–H....O2 atoms of the cycles formed because of hydrogen bonds in dicarboxylic acid dimers, it is possible to estimate the electrostatic forces affecting the strength of the hydrogen bond. According to our calculated data, the charge on the O1 atom of carboxyl groups increases in the series: oxalic acid (–0.624) < succinic acid (–0.663) < adipic acid (–0.670). The charge on the H atom decreases in the same sequence of acids: oxalic acid (0.525) > succinic acid (0.523) > adipic acid (0.521). This pattern indicates an increase in the electron density and, accordingly, shows an increase in the strength of the hydrogen bond with an increase in the length of the carbon chain of the aliphatic acid.

Based on the results of numerous studies on the proton exchange between semiquinone radicals and H-acids, there were ideas about the formation of a hydrogen-bonded complex (HBC), which has a cyclic structure. Figure 1 shows the spatial structure of the intermolecular complex of the studied dicarboxylic acids with 3,6-ditert.butyl-2-oxyphenoxyl, calculated with full optimization of all geometric parameters by the DFT method.

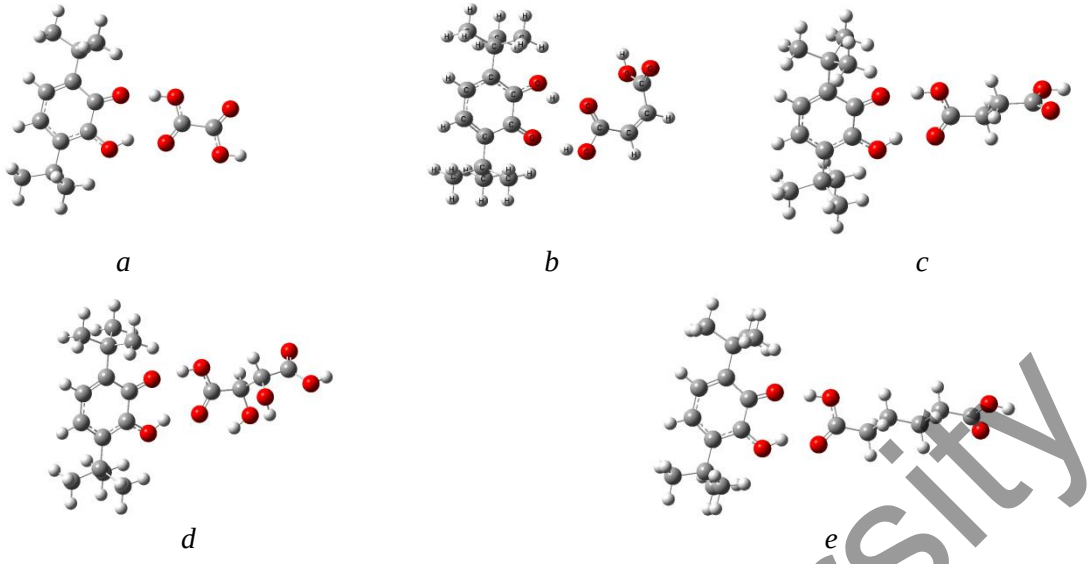


Figure 1. Spatial structures of HBC between 3,6-ditert.butyl-2-oxyphenoxyl and *a*) oxalic acid; *b*) maleic acid; *c*) succinic acid; *d*) tartaric acid; *e*) adipic acid

The strength of the hydrogen bond increases correspondingly in a number of complexes with oxalic acid (1.84 Å) < succinic acid (1.78Å) < adipic acid (1.67 Å), thereby showing the possibility of faster proton transfer or exchange over a shorter intermolecular O–H...O bridge.

The presence of multiple bonds in molecules (maleic acid, R(O–H...O) = 1.89 Å) and hydroxo substituents (tartaric acid, R(O–H...O) = 1.85 Å) reduces the stability of hydrogen bonds, compared with similar molecules.

To predict the ability to complex formation, we analyzed the energy of complex formation ($\Delta E_{c.f.}$) in the studied acids with an ortho-substituted semiquinone radical (Table 4). The parameter was calculated according to the following equation:

$$\Delta E_{c.f.} = (E_{acid} + E_{radical}) - E_{complex} \quad (2)$$

where E_{acid} — the calculated energy values of the acid molecule; $E_{radical}$ — the calculated energy values of the 3,6-ditert-butyl-2-hydroxyphenoxyl molecule; $E_{complex}$ — the calculated values of the energy of a molecule of an acid complex with a semiquinone radical.

Table 4

The energies of complex formation of some dicarboxylic acids with 3,6-di-tert-butyl-2-hydroxyphenoxyl calculated by the DFT UB3LYP/6-31G+(d, p) method

Dicarboxylic acids	E_{acid}, a.u.*	$E_{radical}$, a.u.*	$E_{complex}$, a.u.*	$\Delta E_{c.f.}$, kJ/mol
Oxalic	–378.3243833	–696.6086038	–1074.954094	55.42
Maleic	–455.7405525	–696.6086038	–1152.370308	55.53
Succinic	–456.9742366	–696.6086038	–1153.604634	57.22
Tartaric	–607.4032232	–696.6086038	–1304.033289	56.35
Adipic	–535.6104668	–696.6086038	–1232.240235	55.57
Octanedioic	–614.2422408	–696.6086038	–1310.871977	55.48
Note: *1 a.u. = 2625.5 kJ·mol^{-1}				

The results of computational modelling show that the energy of complex formation with an increase in the number of –(CH_2)– chain links in the series of succinic ($\Delta E_{c.f.}$ = 57.22 kJ/mol) > adipic ($\Delta E_{c.f.}$ = = 55.57 kJ/mol) > octanedioic ($\Delta E_{c.f.}$ = 55.48 kJ/mol) acids decreases. Oxalic acid, which does not contain a methylene group, has the lowest energy parameter value ($\Delta E_{c.f.}$ = 55.42 kJ/mol). It can be seen that the presence of a multiple bond in maleic acid ($\Delta E_{c.f.}$ = 55.53 kJ/mol) or hydroxy substituents in tartaric acid ($\Delta E_{c.f.}$ = 56.35 kJ/mol) also results in a decrease in the complex formation energy, in comparison with succinic acid.

In accordance with the experiment [8], the values of the HOMO-LUMO gap between the frontier orbitals in the molecules of the complexes were found (Table 5).

Table 5

SOMO-LUMO gap in a complex of dicarboxylic acids with 3,6-ditert.butyl-2-oxyphenoxyl calculated by the DFT UB3LYP/6-31G+(d, p) method

No.	Dicarboxylic acids	$E_{(LUMO)}$, a.u.	$E_{(SOMO)}$, a.u.	ΔE, a.u.
1	Oxalic acid	–0.13290	–0.21364	0.08074
2	Maleic acid	–0.14055	–0.22124	0.08069
3	Succinic acid	–0.12874	–0.20945	0.08071
4	Tartaric acid	–0.13542	–0.21622	0.0808
5	Adipic acid	–0.12616	–0.20686	0.0807

It can be seen from Table 5 that the SOMO-LUMO gap decreases in the range from 0.08074 to 0.0807 a.u. for a number of complexes with acids from oxalic to succinic and adipic. Thus, an increase in the carbon skeleton of dicarboxylic acid increases the ability to form a stronger hydrogen-bonded complex. It should be noted that the double bond in maleic acid contributes to a lower value of the SOMO-LUMO gap, compared with oxalic acid. The presence of hydroxy substituents in tartaric acid, on the contrary, increases the energy difference between the frontier orbitals to 0.0808 a.u.

To establish the effect of the solvent nature on the kinetics of the proton exchange process in a cyclic type model complex between maleic acid and 3,6-di-tert-butyl-2-hydroxyphenoxyl, the activation characteristics were analyzed using a Conductor-like Polarizable Continuum Model (CPCM) and an Integral Equation Formalism Polarizable Continuum Model (IEFPCM) (Table 6). The synchronous transit method (TS) was used to find the transition states of the complexes. The values of activation barriers were determined as the difference between the energy obtained during the complete optimization of the complex (E_1) and the energy of the transition state (E_{TS}):

$$\Delta E = E_1 - E_{TS}. \quad (3)$$

Table 6

Activation characteristics of the proton exchange process in a model complex of the cyclic type of maleic acid with 3,6-di-tert-butyl-2-hydroxyphenoxyl in various solvents

Solvents	Model of a polarizable medium	E_1, a.u.*	E_{TS}, a.u.*	ΔE, a.u.*	ΔE, kJ/mol
Vacuum	–	–1152.363912	–1152.351546	0.0123653	32.465
Dioxane	CPCM	–1152.369499	–1152.357417	0.0120821	31.722
	IEFPCM	–1152.368304	–1152.356311	0.01199307	31.488
Toluene	CPCM	–1152.369878	–1152.357614	0.012264	32.199
	IEFPCM	–1152.36867	–1152.356662	0.01200827	31.528
Tetrahydrofuran	CPCM	–1152.373574	–1152.361337	0.012237	32.128
	IEFPCM	–1152.372796	–1152.360529	0.01226661	32.206
Nitrobenzene	CPCM	–1152.37506	–1152.362794	0.012266	32.204
	IEFPCM	–1152.374846	–1152.362501	0.012345	32.412
Note: *1 a.u.=2625.5 kJ·mol^{-1}					

As can be seen from Table 6, there is a decrease in the activation barrier regardless of the solvents nature and the chosen solvation model. An increase in the polarity of the solvent leads to stabilization of the complex in comparison with the data obtained for the gas phase. In the absence of a solvation medium, the calculated value of the activation barrier of the process is 32.47 kJ/mol. In the 1,4 dioxane aprotic solvent ($\varepsilon = 2.21$) the value of ΔE is lower than in vacuum. It is 31.722 kJ/mol according to CPCM and 31.49 kJ/mol according to IEFPCM model. In toluene indifferent solvent, ($\varepsilon = 2.379$) the barrier value decreases to 32.19 kJ/mol (CPCM) and 31.52 kJ/mol (IEFPCM), in the case of a tetrahydrofuran solvating solvent ($\varepsilon = 7.58$) this value is 32.13 kJ/mol (CPCM) and 32.20 kJ/mol (IEFPCM). A relatively high activation energy value of 32.2 kJ/mol (CPCM) and 32.41 kJ/mol (IEFPCM) is predicted for the nitrobenzene polar solvent ($\varepsilon = 35.72$).

Conclusions

Quantum-chemical studies using the DFT B3LYP method made it possible to establish a correlation between the activation energy obtained from the experimental kinetic parameters of protolytic processes involving dicarboxylic acids and the energies of formation of cyclic-type complexes in dimeric molecules. It was shown that an increase in the number of methylene groups in a molecule leads to a rise in dimerization energies. At the same time, the appearance of multiple bonds or substituents in acid molecules allows for detecting the opposite effect. The energy gap between the frontier molecular orbitals of the studied dimer molecules increases with the length of the carbon skeleton and decreases in unsaturated and substituted analogs. However, the observed dependencies require further confirmation.

The weakening of hydrogen bonds in the homologous series of acids, as well as in a molecule containing hydroxy substituents or multiple bonds was revealed during the study of the structure of complex formed by the semiquinone radical with dicarboxylic aliphatic acids. In addition, using the example of maleic acid and the semiquinone radical, it was found that with an increase in the polarity of the solvent, the activation characteristics of the complex formation process decrease.

Based on the availability of experimental ESR spectroscopy data on the kinetics of protolytic reactions involving dicarboxylic acids, it is possible to continue theoretical studies of the mechanism of the reactions described above.

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Дикарбон қышқылдары қатысатын комплекс түзілу реакцияларын DFT зерттеу: сутектік байланыс, еріткіш табиғатының әсері

Мақалада кейбір дикарбон қышқылдарының протолиттік қабілетіне кванттық-химиялық зерттеулер жүргізілген. Малеин, янтарь, шарап, қымыздық және адипин қышқылдарының димерлі молекулаларының геометриялық және кинетикалық параметрлері зерттелді. Олардың димерлену энергиясы базалық жиынтық суперпозиция қатесін (BSSE) ескере отырып анықталды. Дикарбон қышқылдарының кинетикалық параметрлерінің көміртек қаңқасы, қанықпаған байланыстар және гидроксил алмастырғыштары болған кездегі тәуелділігі дәлелденді. Зерттелетін димер қышқылы молекулаларының шекаралық молекулалық орбитальдары қарастырылды. ЖТМО және ТБМО деңгейлері арасындағы энергия параметрлерінің айырмашылығы анықталды. Энергиялық аралықтардың алынған мәндері екі сутектік байланыстың қатысуымен түзілетін циклдік қосылыстар қатарындағы тұрақтылықтың жоғарылауын көрсетеді. Қышқылдардың 3,6-ди-трет-бутил-2-оксифеноксил семихинон радикалымен комплекс түзу қабілеті зерттелді. CPCM және IEFPCM үлгілерін пайдалана отырып, семихинон радикалы – дикарбон қышқылы жүйесінің күрделі түзілу реакциясының активтену тосқауылына еріткіш табиғатының әсерін талдау қарастырылған. Энергетикалық параметрдің еріткіштің полярлығына тәуелділігі толуол, тетрагидрофуран және нитробензол мысалында анықталды. Молекулалық құрылымдарды оңтайландыру үшін DFT әдісі 6-31+G (d, p) негізіндегі B3LYP жуықтауында қолданылды. Есептеулер Gaussian 16 Revision A.03 WIN64 бағдарламасы арқылы жүргізілді.

Кілт сөздер: кванттық химиялық есептеулер, тығыздықтың функционалдық теориясы, сутектік байланыс, молекулааралық сутектік байланыстар, өтпелі қалыптасу, комплекстер, шекаралық молекулалық орбитальдар, димерлену энергиясы, күрделі түзілу энергиясы, еріткіш табиғатының әсері.

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ДФТ изучение реакций комплексообразования с участием дикарбоновых кислот: водородные связи, влияние природы растворителя

В статье проведены квантово-химические исследования протолитической способности некоторых дикарбоновых кислот. Исследованы геометрические и кинетические параметры димерных молекул малеиновой, янтарной, винной, щавелевой и адипиновой кислот. Их энергии димеризации были определены с учетом ошибки суперпозиции базисного набора (BSSE). Подтверждена зависимость кинетических параметров дикарбоновых кислот от наличия углеродного скелета, ненасыщенных связей и гидроксильных заместителей. Были рассмотрены граничные молекулярные орбитали исследуемых молекул димерных кислот, и определена разница энергетических параметров между уровнями ВЗМО и НСМО. Полученные значения энергетических щелей свидетельствуют об увеличении устойчивости в ряду циклических соединений, образованных с участием двух водородных связей. Изучена способность кислот к комплексообразованию с радикалом семихинона 3,6-ди-трет.бутил-2-гидроксифеноксилом. Выполнен анализ влияния природы растворителя на активационный барьер реакции комплексообразования системы семихиноновый радикал–дикарбоновая кислота с использованием моделей CPCM и IEFPCM. На примерах толуола, тетрагидрофурана и нитробензола установлена зависимость энергетического параметра от полярности растворителя. Для оптимизации молекулярных

структур использовали метод DFT в приближении B3LYP с базисным набором 6-31+G (d, p). Расчеты проводились с использованием программы Gaussian 16 Revision A.03 WIN64.

Ключевые слова: квантово-химические расчеты, теория функционала плотности, водородная связь, межмолекулярные водородные связи, переходное образование, комплексы, пограничные молекулярные орбитали, энергия димеризации, энергия комплексообразования, влияние природы растворителя.

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