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STUDY OF THE REACTION AMINATION MECHANISM
OF THE DICHLORONAPHTHALENE
ON THE BASIS OF THE DENSITY FUNCTIONAL THEORY

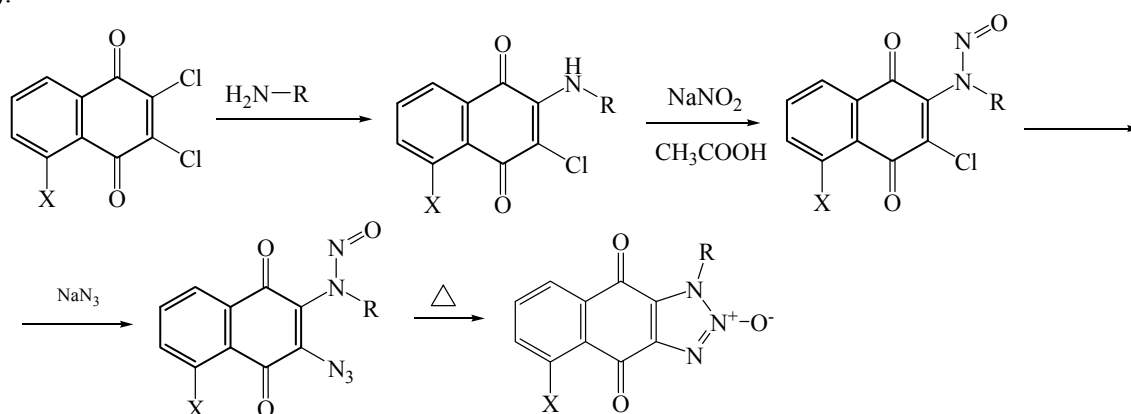
Annotation. The analysis of the thermodynamic parameters of the reaction amination in the gas phase and in solution on the basis of calculations at the density functional methods using the full-electron basis set 6-31G(d) in the GAUSSIAN'03 and TZ2P+ in the "Amsterdam density functional". It is shown that dichlorojuglone and aniline's thermodynamic and kinetic response capability. The calculated transition states, activation energies and analyzed orbital interactions were obtained.

Key words: the density functional theory; B3LYP/6-31G (d); naphthoquinones; reaction mechanism, natural bond orbital.

Introduction

In [1-2] works it was described an experimental approach to the synthesis of condensed triazole oxides. The interest in the compounds of this structure is due to the fact that some of them [3] have antitumor activity.

Given this and the need for amination reactions to obtain condensed triazole oxides, we have reviewed experimental and quantum-chemistry features of their formation, as was shown earlier [2]. Known on the basis of experimental data the simplest way to natural is the following scheme (X = H, OH):



The aim of this work was to use the density functional methods with the different functionals and basis states in the program packages GAUSSIAN and ADF for the use of the mechanism of the first stage of the condensation reaction of dichloronaphthalene with arylamine and the explanation of the observed experimental data.

Experimental part

The calculations were carried out using standard software package GAUSSIAN'03 [4]. For theoretical studies was used quantum-chemical method functional density (DFT, Density Functional Theory).

The calculations were carried out hybrid density functional method B3LYP, the exchange Beke's functional (B3) [5] and the correlation functional of Lee, Yang and the Pair (LYP) [6]. For all atoms was used fully electronic basis set 6-31G (d). The geometries of all calculated molecules was fully optimized, the lack of imaginary frequencies confirmed their stationary nature. In the study of some molecules was observed up to three imaginary frequencies, but the use in this method is IRC still pointed to the transitional state (Fig. 1).

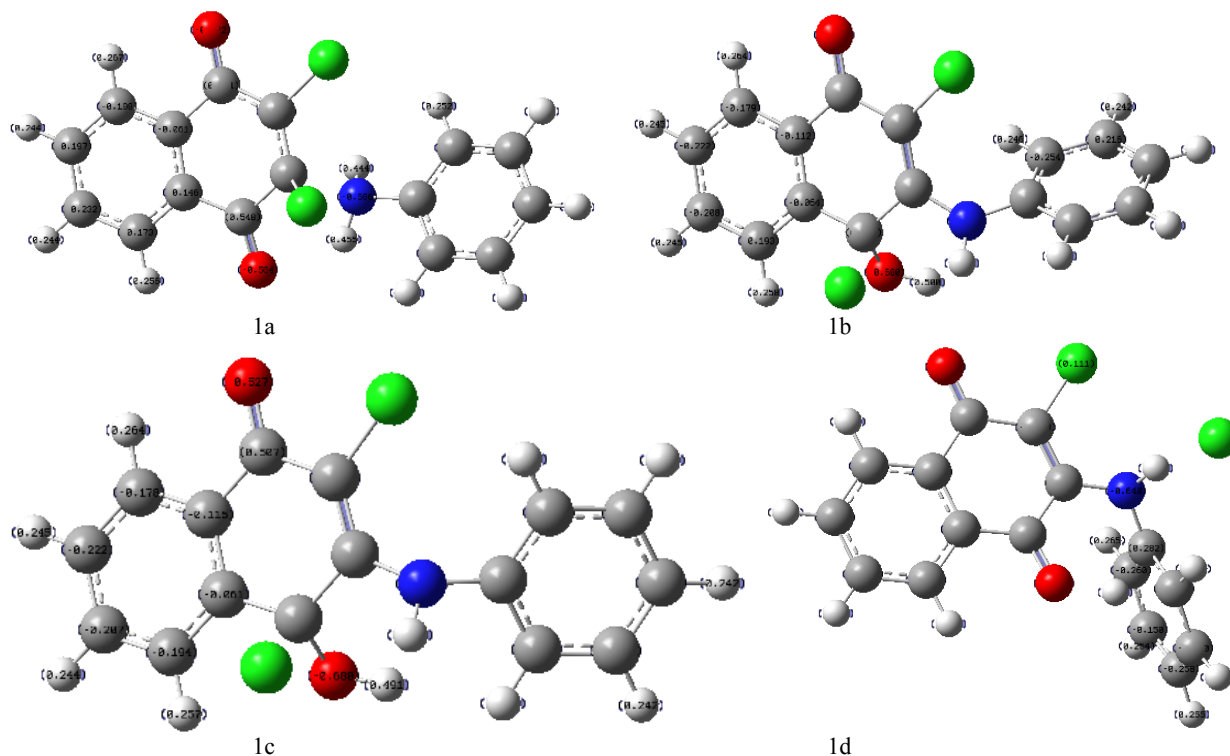


Figure 1 - Optimized at the B3LYP/6-31G(d) structure of the first transition state (a), intermediate (b), second transition state (c), the third transition state (d) with indicating of the natural charges on the atoms

The optimization of the transition states carried out using the STQN method [7], the transition states in most cases had only one imaginary frequency. The calculations in the solution of the ethanol carried out with the same methods using the polarized continuum model (PCM) optimization [8]. Energy of the calculated compounds adjusted to the zero vibration energy (ZPVE) and reduced to standard conditions (298.15 K, 1 ATM.) with the use of the thermal corrections to enthalpy and free energy.

Optimized geometry was used for calculating the total energy of the molecules within the software package ADF'2004 (Amsterdam density functional) in the gas phase and solution at the COSMO-optimized [9]. We have used the OPTX exchange functional [10] combined with the PBE correlation functional [11], and fully electronic triple- ζ with the given polarization Slater basis set orbitals.

Results and discussion

It is well known that all quantum chemical calculations are determined by the correspondence between the experimental and calculated geometric parameters of the molecules. Comparison of the calculated geometrical parameters with the experimental shows that the calculated lengths of the bonds mostly underestimated, the valence angles are too high. However, the statistical analysis leads to good quality of the correlation ratios between the calculated and experimental bond lengths and valence angles

[12-15] for a number molecules:

$$R^{\text{exp.}} = -0.04 + 1.03 R^{\text{calc.}} \quad (r = 0.996; s = 0.02; n = 22) \quad (1)$$

$$\omega^{\text{exp.}} = -17.9 + 1.14 \omega^{\text{calc.}} \quad (r = 0.982; s = 1.5; n = 32) \quad (2)$$

In these and the following correlation equations, r is the correlation coefficient, s is the standard deviation, and n is the number of compounds included in the correlation.

The calculated and experimental [16-18] values of the wavelengths of the UV spectra (λ), IR spectra (ω) spectra and the ^1H and ^{13}C NMR (δ) of some well-known quinones compounds allowed us to obtain the correlation ratios between the experimental and the calculated values. These equations (3-6) show that our calculations allow collected to evaluate the spectral parameters with a sufficient degree of accuracy

$$\lambda^{\text{exp.}} = -16 + 1.06 \lambda^{\text{calc.}} \quad (r = 0.998; s = 7; n = 22) \quad (3)$$

$$\delta^{\text{exp. } ^1\text{H}} = 0.16 + 1.01 \delta^{\text{calc. } ^1\text{H}} \quad \text{H} \quad (r = 0.983; s = 0,5; n = 50) \quad (4)$$

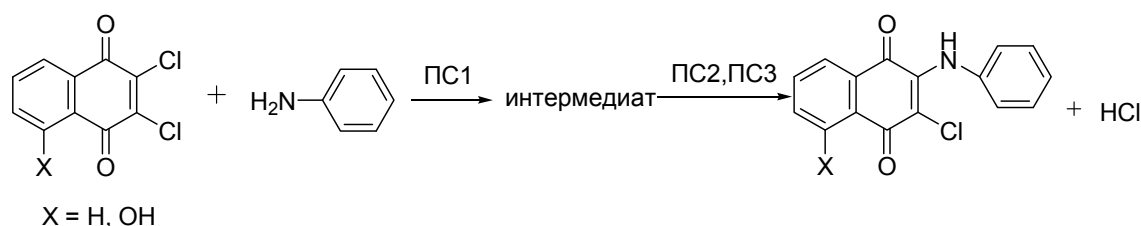
$$\delta^{\text{exp. } ^{13}\text{C}} = -1.8 + 1.05 \delta^{\text{calc. } ^{13}\text{C}} \quad \text{C} \quad (r = 0.985; s = 4; n = 50) \quad (5)$$

$$\omega^{\text{exp.}} = 32 + 0.99 \omega^{\text{calc.}} \quad (r = 0.995; s = 30; n = 18) \quad (6)$$

The obtained correlation ratios of the geometric and the spectral parameters suggest us that the calculated structure of our molecules, apparently, is close enough to real. In addition, in [19] it was shown that among the methods of the density functional (BLYP, B3LYP, PB86, B3P86, BPW91, B3PW91 and SVWN) B3LYP method most accurately predicts the thermodynamic parameters with an error of 13 kJ/mol, suggesting that the calculated thermodynamic parameters are quite close to experimental values.

Made earlier thermodynamic calculations of a number of organic reactions by the same method resulted in good agreement between the calculated and experimental values [20].

From general considerations of the transition state theory, we can assume a possible reaction mechanism of the naphthoquinones amination through the formation of three transition States (TS1-TS3) and intermediate:



We can see from table 1 the results of quantum-chemical calculations of enthalpies, the free Gibbs energies and activation energies of the amination reactions of various naphthoquinones by aromatic amines. The thermodynamic parameters indicate that all the studied reactions are thermodynamically favorable in the gas phase and in the solvent. However, in solvent the values of the parameters about one and a half times more, apparently due to solvation of the reagents in ethanol.

Table 1 - Calculated at the B3LYP/6-31g(d) level of the theory thermodynamic parameters of the amination reaction, kJ/mol

substrate	amin	ΔH		ΔG		E_a	
		Gas phase	EtOH	Gas phase	EtOH	Gas phase	EtOH
2,3-dichloro-1,4naphthoquinone	aniline	-47	-62	-36	-52	149	81
	p-toluidine	-46	-70	-42	-67	146	93
	m-toluidine	-45	-69	-41	-66	139	87
	p-anisidine	-60	-83	-45	-69	133	81
	p-chloroaniline	-44	-66	-34	-56	163	118
2,3- dichlorojuglone	aniline	-51	-65	-41	-55	149	80
	p-toluidine	-51	-73	-47	-71	146	91
	m-toluidine	-49	-74	-45	-65	139	91
	p-anisidine	-65	-86	-50	-72	133	79
	p-chloroaniline	-48	-43	-37	-34	163	115

To clarify the reaction mechanism it is important to know how adequately the chosen method can predict the activation energy of the amination reactions. To this end, B3LYP/6-31G (d) level of the

theory, we have calculated transition states for several reactions (table. 3). For optimization of the transition states, we used two methods: the traditional optimization of the transition state using the algorithm of Berny [21] and the method STQN (Synchronous Transit-Guided Quasi-Newton Methods) [7]. STQN method has proved to be most convenient to optimize transition structures. To check the transitional states were analyzed the vibrations corresponding to the imaginary frequency and direction of the changes in the structure along the reaction path (the IRC calculation [22, 23]).

Using both methods of the calculation, we estimated transition states for several amination reactions and the base of the obtained results was calculated the activation energy of these reactions in the gas phase and in solution, on the basis of approximate equality between the activation energy E_a and enthalpy of the activation ΔH^\ddagger , which was estimated by the enthalpy of the reactant and transition state.

However, it is known that the reaction in reality take place in the solutions [2]. The activation energy in ethanol's solution was calculated as the difference of enthalpy in solution of the reagents and of the third transition state (ΔH^\ddagger), except the reaction of condensation of dichlorophene with m-toluidine, where the activation energy was calculated as the difference between the enthalpies of the reactants and of the first transition state, since the limiting stage of the reaction in this case is the first stage of the transition state formation due to the greater activation energy compared to other transitional states.

The calculated according to transition state values of the activation energy is less in the solvent than in the gas phase and are close to known experimental values for S_NAr reactions [24].

Table 2 - The results of the analysis of natural orbital bonds

Molecule	bond (LP)	The population, e	Hybridization	The Wiberg Index	The interaction of the orbitals	$E_{ij}^{(2)}$, kcal/mol
Dichloro-naphthoquinone	C=O	1.995	$Sp^{2,24}$	1.752	LPO→BD*(C-C)	84
		1.950	P			
	C-Cl	1.987	$Sp^{3,09}$	1.100		
	LPO	1.979	$Sp^{0,72}$			
Aniline		1.882	p			
	C-N	1.992	$Sp^{1,72}$	1.119	LPN→BD*(C-C)	26
	N-H	1.983	$Sp^{2,91}$	0.828		
LPN	1.854	$Sp^{7,30}$				
TS1		1.994	$Sp^{2,27}$	1.709	LPO→BD*(C-C)	77
		1.952	P			
	C-Cl	1.984	$Sp^{3,47}$	0.967		
	N-C	1.973	$Sp^{8,3}$	0.525		
		1.876				
	LPO	1.973	$Sp^{0,75}$			
		1.876	P			
Intermediate	C-Cl	1.962	$Sp^{7,44}$	0.781	LPO _H →BD*(C-Cl)	32
	C-O	1.991	$Sp^{3,28}$	1.046	LPO→BD*(C-C)	40
	C-N	1.984	$Sp^{2,41}$	0.759	LPCl→BD*(C-C)	15
	C-Cl	1.985	$Sp^{3,25}$	1.068	LPN→3C*(C-C)	51
	C=O	1.995	$Sp^{2,25}$	1.717		
		1.956	P			
	N-C	1.984	$Sp^{1,71}$	1.029		
	LPO _H	1.970	$Sp^{1,31}$			
		1.851	P			
	LPO	1.979	$Sp^{0,71}$			
		1.885	P			
	1.727	P				

A continuation of Table 2.

Molecule	bond (NEP)	The population, e	Hybridization	The Wiberg Index	The interaction of orbitals	$E_{ij}^{(2)}$, kcal/mol
TS2	C=O	1.995	Sp ^{2,25}	1.722	LPO _H →BD*(C-Cl)	30
		1.957	P		LPO→BD*(C-C)	41
	C-Cl	1.985	Sp ^{3,30}	1.060	LPCl→BD*(C-G)	14
	C...Cl	1.964	Sp ^{7,14}	0.801	LPN→BD*(C-C)	42
	C-N	1.983	Sp ^{2,38}	1.098		
	C-O N-	1.991	Sp ^{3,33}	1.032		
	C	1.980	Sp ^{1,87}	0.983		
	LPO _H	1.969	Sp ^{1,31}			
		1.858	P			
	LPO	1.979	Sp ^{0,71}			
		1.885	P			
	1.786	P				
TS3	C=O _H	1.994	Sp ^{2,51}	1.499	LPO _H →3C*(C-C-H)	85
		1.970	P		LPO _H →BD*(C-C)	
	C=O	1.995	Sp ^{2,23}	1.733	LPO→BD*(C-C)	11
		1.942	P		LPCl→BD*(C-C)	42
	C-N	1.975	Sp ^{2,34}	1.091	LPN→3C*(C-C-H)	18
	N-C	1.983	Sp ^{1,98}	1.106	LPN→BD*(C-C)	33
	C-Cl	1.986	Sp ^{3,11}	1.118		23
	N-H	1.952	Sp ^{2,65}	0.601		
	LPO _H	1.952	Sp ^{1,48}			
		1.759	Sp ^{4,05}			
	LPO	1.979	Sp ^{0,72}			
	1.883	P				
	1.737	P				

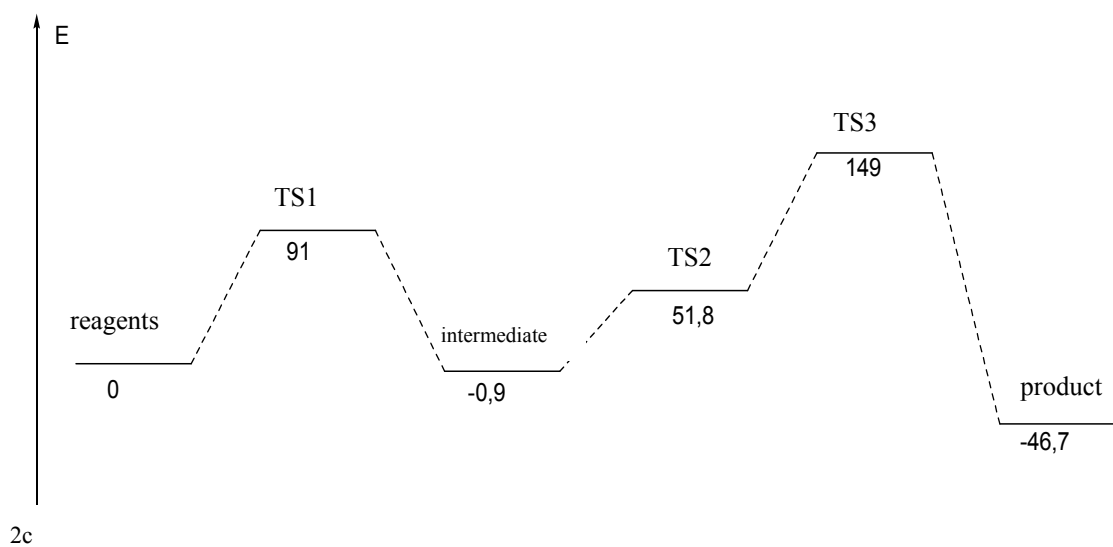
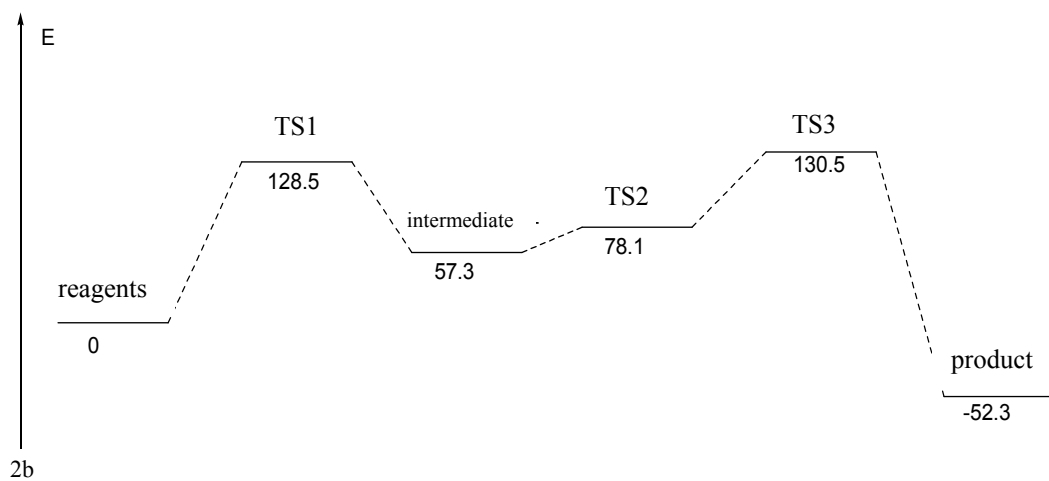
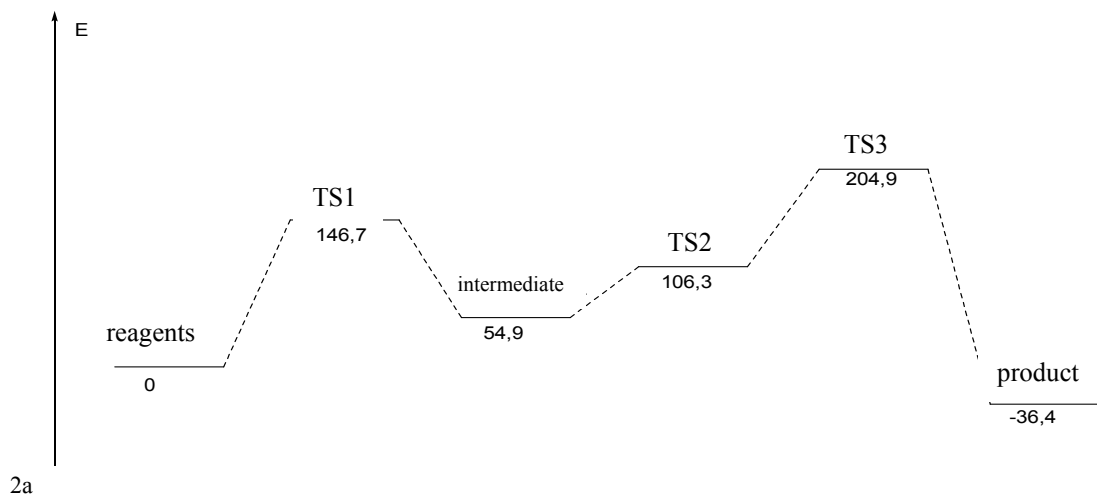
The process of replacement of chlorine in the molecule of naphthoquinones is a multistage and included studying the formation of the intermediate via the first transition state, which then turns into the product through the second and third transition states (Fig. 2).

In Fig. 2 shows the results obtained for the total energy of the reactants, intermediates, transition states and products of the reactions.

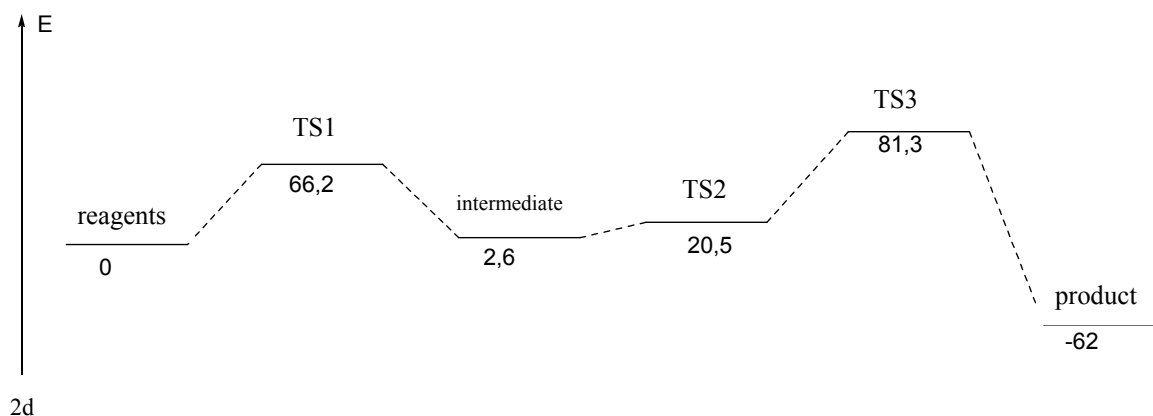
From the point of view of perturbation theory to second order [25] that the naphthoquinones in the first transition state, the interaction between bonds is between the lone electron pairs of the oxygen atoms (LP) and anti-bonding C-C orbital (BD*), which seem to indicate mostly electrostatic interaction between components.

The calculations showed that for all reactions the first transition state close to the structures, which is a weakening of the bonds between the chlorine and carbon atoms of the naphthoquinones and the formation of weak bonds between the carbon atom of the naphthoquinones and the nitrogen atom of the amino group of arylamine (~1.8 Å). This condition is really transitional because it has one negative vibration frequency (~ -350 cm⁻¹), characteristic for transition state and representing the valence fluctuation of the C...N bond.

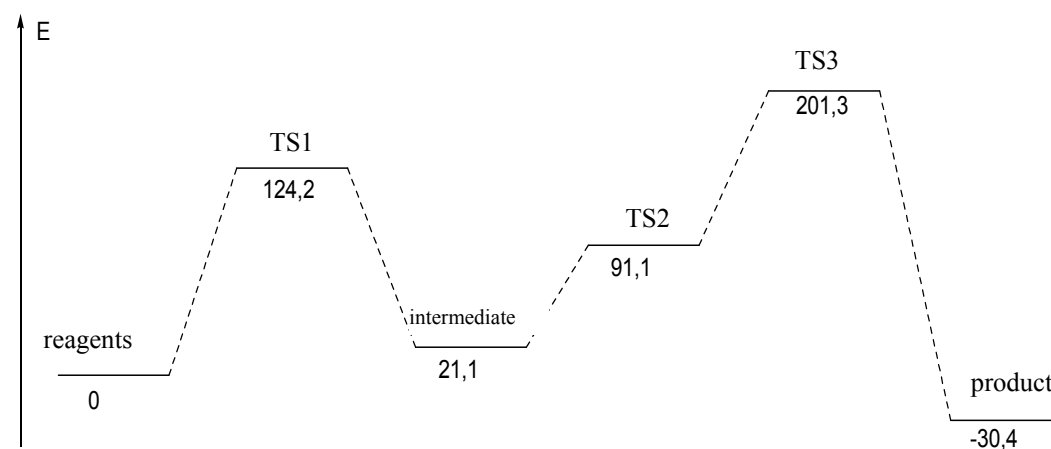
Our analysis method of natural bond orbital [25] (table. 2, Fig. 1) shows that with the approach of the aniline to dichlorojuglone the polarization of the bonds in the past with a significant decrease in the effective negative charge on the nitrogen atom and a slight modification of the Wiberg indices and the hybridization of the orbitals.



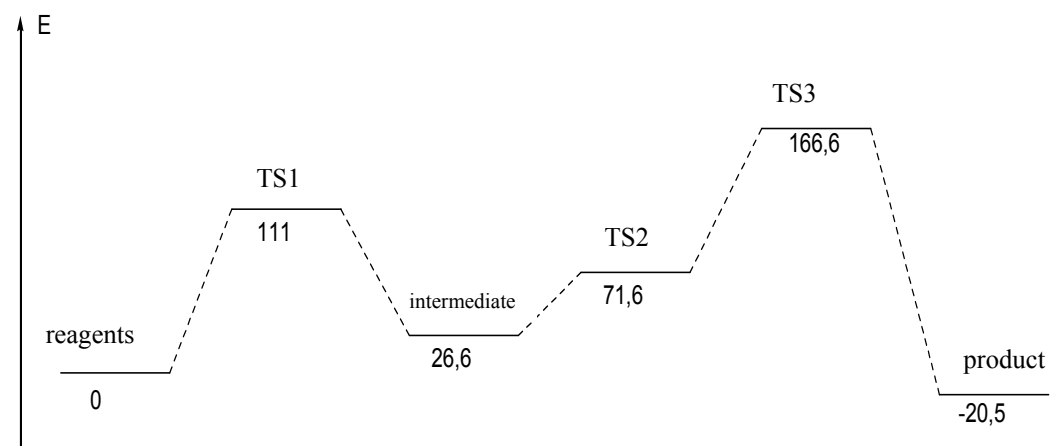
A continuation of Fig. 2



2d



2e



2f

Figure 2 - The full energy profile of the amination reaction of dichloronaphthalene (a) ΔG in gas phase, (b) ΔG in the solution of alcohol, (c) ΔH in gas phase, (d) ΔH in the solution of alcohol, (e) ΔE in gas phase, (f) ΔE in the solution of ethanol (kJ/mol)

Intermediate is a structure where the chlorine atom, in contrast to the first transition state, has a greater distance from the ring of naphthoquinones, and the hydrogen atom of the amino group is transferred to one of the oxygen atoms of the naphthoquinones. A characteristic difference from the first

intermediate transition state from the point of view of interaction between orbital is less of a polarization of relations, and the emergence of additional inter-actions between the unshared electron pairs of chlorine atoms and nitrogen disintegrating orbital of the C-C bonds, indicating a greater contribution of the orbital interactions in comparison with electrostatic.

The second transition state in the reactions of 2,3-dichloro-1,4-naphthoquinones with aniline, p-toluidine, p-chloroaniline, as well as in the reactions of condensation dichlorojuuglone with p-chloroaniline, p-anisidine, m-toluidine are similar in geometry with the appropriate intermediates, has a small negative vibration frequency ($\sim 50 \text{ cm}^{-1}$), and in fact is not transition, as evidenced by the IRC method.

On the basis of the calculated data shows that in all cases, a third transition state formed during the direction of a hydrogen atom from the oxygen atom of the second transition state is indeed a transition, as it has one negative vibration frequency ($\sim 1000 \text{ cm}^{-1}$) and in accordance with the method of the IRC. From the point of view of energy interactions of the second order ($E_{ij}^{(2)}$), unlike the rest of the calculated states, appear very strong orbital interaction, including three center C-C-H bond (3C*), which mainly stabilized this transition state. For comparison, the calculated thermodynamic parameters at the B3LYP/6-31G(d) method we also conducted calculations of the energy profile of the second reaction method BP86/TZ2P+ from the ADF.

We can see that the calculated by ADF energy parameters are close enough to thermodynamic parameters in GAUSSIAN, despite the different functional and basis states. This indicates that the density functional methods, incorporated in both schemes of the calculation works well when we study the mechanism of some organic reactions.

Conclusion

1. It is shown that the used method of calculation B3LYP/6-31G(d) gives adequate results in the prediction of geometrical parameters, IR, UV and NMR spectra of reagent amination reactions of the naphthoquinones. We have found the transition states and calculated their electronic and spatial structure. It is shown that the amination reaction takes place via formation of an intermediate and two transition states.

2. We have calculated the activation energies in the gas phase and solution for the amination reactions of various amines. It is shown that the use of solvent leads to smaller activation energies. The analysis of orbital bond in the investigated structures from the point of view of perturbation theory of the second order was used. We have explained the observed variation of transition states on the basis of orbital interactions.

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ИССЛЕДОВАНИЕ МЕХАНИЗМА РЕАКЦИИ АМИНИРОВАНИЯ ДИХЛОРНАФТОХИНОНОВ НА ОСНОВАНИИ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ

Аннотация. Проведен анализ термодинамических параметров реакции аминирования в газовой фазе и в растворе на основании расчетов методом функционала плотности с использованием полно-электронного базисного набора 6-31G(d) в программном пакете GAUSSIAN'03 и TZ2P+ в программе «Амстердамский функционал плотности». Показана термодинамическая и кинетическая возможность реакции дихлорюглона с анилином. Рассчитаны переходные состояния, энергии активации и проведен анализ орбитальных взаимодействий.

Ключевые слова: теория функционала плотности; B3LYP/6-31G(d); нафтохиноны; механизм реакции, натуральные орбитали связи.

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ТЫҒЫЗДЫҚТЫҢ ФУНКЦИОНАЛ ТЕОРИЯСЫНЫҢ НЕГІЗІНДЕ ДИХЛОРНАФТАХИНОНДАРДЫҢ АМИНДЕУ РЕАКЦИЯСЫНЫҢ МЕХАНИЗМІН ЗЕРТТЕУ

Аннотация. Газды фазада және ерітіндіде аминдеу реакциясының термодинамикалық параметрлері «Амстердамский функционал плотности» бағдарламасында және GAUSSIAN'03 и TZ2P+ бағдарламалық пакетінде толық электронды базисті жинақты 6-31G(d) қолданып тығыздық функционалы тәсілімен есептеу көмегімен талданды. Дихлорюглоның анилинмен конденсациялану реакциясының термодинамикалық және кинетикалық мүмкіндіктері көрсетілді. Конденсирлеу реакциясы үшін ауыспалы күйі, активтендіру энергиясы және жылдамдық константасы есептелді.

Тірек сөздер: тығыздықтың функционал теориясы; B3LYP/6-31G(d); нафтохинондар; реакция механизмі, байланыстың табиғи орбитальдары.

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