Article

Monomolecular films of diacylic diperoxides on the water-air interface

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Abstract: The monomolecular films of diacylic diperoxides on the water/air interface were studied. Their general formula:

$$CH_3\text{-}(CH_2)_m\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}(CH_2)_m\text{-}CH_3$$

The behavior of monomolecular films of diperoxides are affected by the structure of their molecule. The numerical values of the areas of molecules that are extrapolated to zero pressure are different. This indicates a different conformation of the molecules in the monolayer. The optimal geometric structure of the molecule of diperoxide, the total area (*S*), the volume (*V*), the heat of formation ($\Delta_f H^{298}$), the energy of higher occupied (E_{HOMO}) and the lower vacant (E_{LUMO}) molecular orbitals were obtain in the calculations. The optimal geometric structures of peroxides and their electronic properties were calculated by the quantum-chemical method. Calculations of conformational states of the molecule of diperoxides are carried out. Experimental data and quantum-chemical calculations are consistent with each other.

Keywords: diperoxides, monomolecular layers, quantum-chemical calculation, conformation

1. Introduction

Polyfunctional peroxide compounds are successfully used to for obtaining polymer-mineral composites, polymers with special properties, nanomaterials and processing of various surfaces [1–4]. Peroxide initiators are widely used in the processes of emulsion and suspension polymerization [5-8]. Therefore, for the successful use of polyfunctional peroxides information about their behavior at the interface of phases is required.

One of the widely used methods of the study the behavior of the substances on the air-water interface is the preparation of monomolecular films [9]. This method opens up the ability to control the structure of materials, to organize and orientate the molecules in monolayers, providing the maximum efficiency of the chemical reactions [10].

The preparation of Langmuir films is associated with the formation of monolayers of surfactants on the interface between the liquid and the air - when spreading droplets of solution along the surface of the water. Many insoluble amphiphilic substances in the water represent polar molecules of organic substances containing the hydrophilic part – "head" and a hydrophobic part -"tail", capable of spreading over the water surface by a monomolecular layer. Investigating the dependence of the surface pressure from the monolayer area, Langmuir found the existence of various phase states in such films. Monomolecular films of insoluble amphiphilic substances on the surface of the liquid were called Langmuir films [9]. The classic method for obtaining Langmuir films is the use of a special cuvette with a barrier, which serves to regulate surface pressure by changing the area covered by the surfactant. At low pressure, the molecules are in a state of "two-dimensional gas". Increasing the pressure due to bias of the barrier leads to the formation of ordered monolayers of condensed liquid and solid state

In the present work is studding the monomolecular films of diacylic diperoxide initiators formed on the aqueous surface due to the presence of hydrophilic and hydrophobic components in the molecule. The surface pressure of monolayers of diperoxide compounds was determined. The heterogeneous processes are occurring with the participation of these compounds and the results of this study may be useful for prediction the behavior of diperoxide on the phase boundary.

2. Materials and Methods

The diperoxides (DP) were synthesized by the interaction of corresponding peroxycarboxylic acids and dichloride of dicarboxylic acids in the presence of pyridine [7]. The scheme of the reaction:

$$2\ CH_3\text{-}(CH_2)_m\text{-}C(O)OOH + Cl\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)Cl \rightarrow$$

$$\rightarrow CH_3\text{-}(CH_2)_m\text{-}C(O)OO(O)C\text{-}(CH_2)_n\text{-}C(O)OO(O)C\text{-}(CH_2)_m\text{-}CH3\ \ +2\ HCl.$$

The diperoxides were washed with water and recrystallized. The purity of synthesized peroxides, as determined by iodometric analysis [8], was at least 98.5 - 99.5%.

The investigated diperoxide compounds have different carboxylic (R_1) and dicarboxylic (R_2) radicals of varying sizes and flexibility. They general formula and numeration of DP are:

$$CH_3\text{-}(CH_2)_m\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}(CH_2)_m\text{-}CH_3\,,$$

were n=2, m=8 (**I**); n=3, m=8 (**II**); n=4, m=0 (**III**); n=4, m=3 (**IV**); n=4, m=8 (**V**); n=8, m=0 (**VI**); n=8; m=1 (**VII**); n=8, m=8 (**VIII**); C_6H_5, n=4 (**IX**); m=8, *n*-C_6H_4 (**X**). ; n=4: m=5 (**XI**).

The monomolecular films of DP of different types were formed. To measure the surface pressure of monomolecular films, a vertical weight was used, the basis of which was the principle of the action of the Langmuir surface weight [9]. The solvents effects on the area of the peroxide molecules in their monolayer were studied. The surface pressure (π, mN/m) of the monolayers of the peroxides was measured used a vertical installation. Solutions of peroxides in a certain solvent were applied to the aqueous surface of the cuvette in the size from 60 to 16.5 cm. The monolayer was compressed on the surface of the water by a Teflon barrier. All measurements were made at a compressive speed of 1 mm/s and constant temperature 293±0.5 K. To obtain a monomolecular layer, a drop of solution of peroxide from a micropipette was applied on a clean aqueous surface. The monolayer was compressed after 10 minutes. Before applying the monolayer, the water surface was updated by moving the Teflon barrier on it. In all cases, the error did not exceed ± 5% relative in determining the numerical value of the area extrapolated to zero pressure.

Surface pressure isotherms were obtained as a dependence of the pressure π on the area occupied by one molecule of the test substance S. The number of monomer units x of the substance in the monolayer was determined by the formula

$$x=Ng/M, \tag{1}$$

where M is the molecular weight of the monomer unit; N - Avogadro number; g - amount of substance on the substrate surface, g.

Knowing the number of monomer units that are contained on the surface, the area S was determined by the formula

$$S=a/x, \tag{2}$$

where a is the surface area of the monolayer; x is the number of monomer units (mole of a substance in a monolayer).

Surface pressure was determined by the formula

$$\pi=q\Delta P/b, \tag{3}$$

where q - gravitational constant, m/s^2; ΔP - change of load, g; b - perimeter of the plate, m.

Quantum-chemical calculations for diacylic diperoxides were carried out by the semiempirical program MOPAC2016 [11] with the graphical interface Winmostar [12]. To optimize the geometric structure and calculate the heat of molecular structures formation ($\Delta_f H^{298}$), energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals, as well as charges on atoms by Mulliken different semiempirical methods were used.

3. Results and Discussion

The surface pressure of DP compound monolayers was studied for didecanoyldiperphtalate (**X**), diacetyldiperadipinate (**III**), dienanthioyldiperadipinate (**XI**) and didekanoyldiperadipinate (**V**) in different organic solvents. For diperoxides **III**, XI and **V**, the radical between the peroxide groups R_2 is the adipic acid residue $-(CH_2)_4-$, and peroxide **X** has a flat radical $-C_6H_4$-residue of phtalic acid. The final radicals R_1 of peroxide **III** are small. The final radicals R_1 in peroxides **V** and **X** are the same and equal $CH_3-(CH_2)_8-$, diperoxide **XI** finite radical smaller: it is $CH_3-(CH_2)_5-$. The isotherms for the surface pressure of the studied diperoxides were obtained when applying films from chloroform (Figure 1). The behavior of the investigated diperoxides at the water-air interface is different. Diperoxides **XI** and **III** form on the surface of the water monomolecular layers of a condensed type [9], in which it can be argued that the residues of adipic acid in the molecule **III** and phtalic acid in **X** are practically non-flexible.

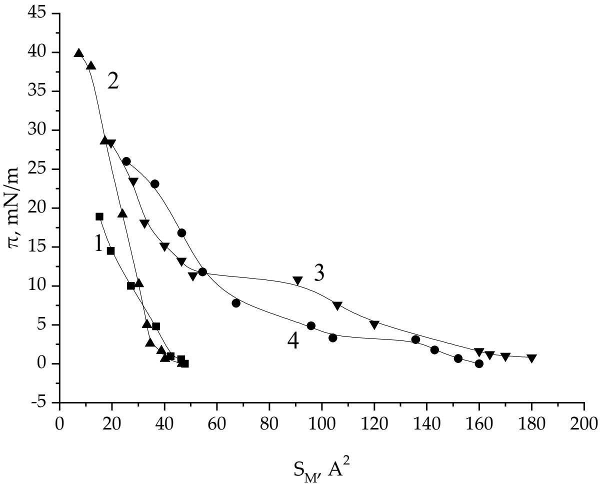


Figure 1. Isotherms of surface pressure monolayers of peroxides 1 - **X**; 2 - **III**; 3 - **V**; 4 - **XI**. Diperoxide was applied to the interface with chloroform.

For diperoxide **V** (figure 1, curve 3), at small surface pressures, the film exists in a two-dimensional gaseous state (G), and further compression translates the film into a stretched liquid state (L_1). The compression of the film in the state (L_1) translates it into a condensed state (L_2). The change in the area of the diperoxide molecule from ~ 90 Å^2 to ~ 50 Å^2 occurs at virtually unchanged surface pressure. On this site, $CH_3-(CH_2)_8-$ radicals R_1 peroxide **V** are squeezed out of the aqueous surface. The behavior of diperoxide **XI** is similar to that of behavior of **V** (figure 1, curve 4).

The isotherms have a different nature (Figure 1). Diperoxides, which contain radical R_2, between the O-O bonds, the remainder of adipic acid, in the monolayer behave differently. That indicate on a low flexibility of the group $-(CH_2)_4-$ in the peroxide molecule. The isotherms are changing with increase the radical R_1. The confirmatory state of the molecule in the monolayer is changing for peroxide. That indicates on the displacement of the radicals $CH_3-(CH_2)_8-$ from the surface of water. The monolayers of diperoxide **X** are rigid. The radical located in the middle of the molecule - the remainder of phtalic acid is flat and stiff.

The various solvents were used when the film applied on the interface of the water-air. It influenced as the nature of the isotherms and as the extrapolated values of the areas corresponding to the molecule in the monolayer (Figure 2).

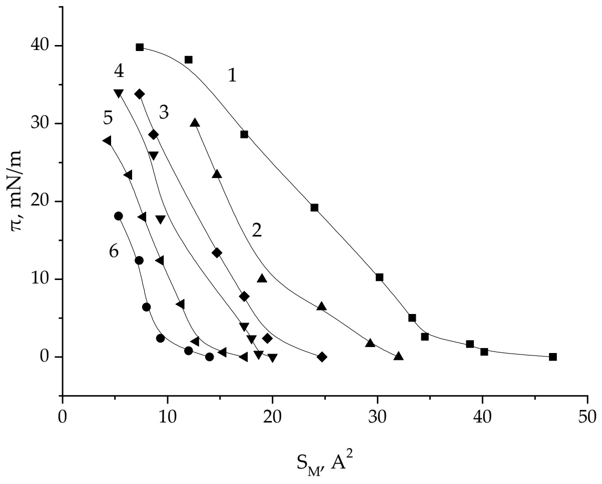


Figure 2. The isotherms of surface pressure of monolayers of diacetyldiperadipinate (**III**) when applied from a solvent: 1- chloroform; 2- tetrachloromethane; 3 - toluene; 4- cyclohexane and butylacetate; 5- benzene and ethylbenzene; 6 - xylene and ethylacetate.

In Figure 2 are shown by the isotherms of surface pressure of monolayers of diperoxide III, which were applied from various organic solvents on the surface of water - air. It should be noted that the isotherms for films of DP III, applied on the surface from solution in xylene and ethyl acetate, are practically identical (curve 6). Similarly, monolayers formed from cyclohexane and butylacetate (curve 4) and benzene and ethylbenzene (curve 5) are the same.

The numerical values of the areas (S_0) that occupy the molecules of the studied diperoxides in the monolayer, which is form from various solvents, are given in Table 1.

Table 1. The extrapolated values of the areas that corresponding to the molecule diperoxide in a monolayer

Solvent	**Area per molecule (S_0), Å^2**		
	Diperoxide		
	III	**XI**	**V**
Acetone	12.0	–	31.0
Dioxane	13.0	–	26.0
Benzene	31.5	35.6	40.0
Toluene	30.5	36.6	43.0
Chloroform	42.0	80.0	95.0
Ethylacetate	46.5	10.3	37.0
Tetrachloromethane	50.0	56.3	68.0

The smallest areas in the monolayer have **III** molecules. The area of the **XI** diperoxide in the monolayer is slightly smaller than the corresponding values for the **V**. The numerical values of the extrapolated areas for all investigated diperoxides depend on the solvent from which the monolayer was form. Non-identical numerical values of the areas are corresponding to the diperoxide in the monolayer. It was form from the soluble solvents, and indicated on the possible different packaging of the diperoxide molecules in the monolayer. The hydrophilic peroxide groups are on the boundary of the phase separation. Whereas the hydrophobic terminal hydrocarbon radicals can be located both in the plane of the section and oriented toward the air phase at high pressures in the monolayer. Since the size of the aliphatic radical between the peroxide groups is small, its effect on the change in the area of the molecule in the monolayer when compressed will be low.

Thus, the results of the study of surface pressure of monolayers of diacylic peroxides give information about their behavior at the interface between water-air phases and predict their reactivity in these conditions.

Quantum-chemical calculations can give important information on the structure and electronic properties of the studied diperoxides.

Quantum-chemical calculations we carried out using some of the semiempirical methods: AM1, PM3, PM5, PM6, MNDO and RM1 for the diperoxide **IV** molecule. The numerical values of the heat of formation of diacylic diperoxide **IV** ($\Delta_f H^{298}$) calculated by semiempirical methods are close to the corresponding values. They were obtained based on thermochemical experiments [13]. The numerical values of $\Delta_f H^{298}$ calculated by the PM3 and RM1 best coincide with the experimental data (Table 2). The semiempirical method RM1 has more opportunities compared to others (Table 3). The diperoxide compound **IV** is polar according to the obtained calculations. The dipole moments (μ) for it are calculated by different methods (1.993 - 6.073 D). The numerical values of the ionization potential (I_x) of diperoxide **IV** and the associated energy parameter HOMO are close (-11.089 to -10.717 eV). The numerical values of the energy of LUMO vary in the wider range from -1.133 to 0.453 eV. The numerical values of the total squares of molecules (***S***) and the volume of molecules (***V***) are close and depend on the calculation method.

Table 2. The results of calculations of physical-chemical parameters for diperoxide **IV** by semi-empirical quantum-chemical methods

Method	**$\Delta_f H^{298}$, kJ/mol**	**μ, D**	**HOMO, eV**	**LUMO, eV**	**η, eV**	**S, Å^2**	**V, Å^3**
AM1	-1038.1	5.089	-11.089	0.348	5.719	395.2	426.64
PM3	-1106.9	3.914	-11.440	-0.760	5.600	398.26	440.37
PM5	-1044.7	1.992	-10.717	-1.133	4.792	393.32	432.86
PM6	-1044.7	1.993	-10.717	-1.133	4.792	393.32	432.87
MNDO	-986.9	3.419	-11.041	0.358	5.699	413.54	446.11
RM1	-1079.1	6.073	-11.018	0.453	5.736	393.79	426.75

*The experimental value $\Delta_f H^{298*}$ is thermochemical determined -1206.9 kJ/mol.

Table 3. The results of calculation of physical and chemical parameters of investigated diperoxides by semiempirical method RM1

Diperoxide	**$-\Delta_f H^{298}$, kJ/mol**	**$-\Delta_f H^{298*}$, kJ/mol**	**I_x, eV**	**HOMO, eV**	**LUMO, eV**	**η, eV**	**S, Å^2**	**V, Å^3**
I	1214.7	1365.0	10.833	-10.833	0.250	5.542	542.3	590.7
II	1246.1	1347.6	10.915	-10.915	0.194	5.555	544.4	632.1
III	977.9	1080.1	11.151	-11.151	0.441	5.796	287.1	294.9
IV	1079.1	1206.9	11.018	-11.018	0.454	5.736	393.8	426.8
V	1240.4	1406.9	10.663	-10.663	0.387	5.525	554.2	635.5
VI	1046.3	1161.3	11.212	-11.212	0.508	5.860	356.0	381.7

VII	1063.0	1206.1	10.975	-10.975	0.540	5.758	358.9	429.3
VIII	1364.7	1488.1	11.061	-11.061	0.499	5.780	673.1	748.2
IX	693.2	-	9.913	-9.913	-0.633	4.640	395.1	435.4
X	1076.7	-	10.340	-10.340	-0.936	4.702	536.5	662.9
XI	1214.7	-	11.179	-11.179	0.818	5.999	487.7	510.0

*Thermochemical data [13].

The structure of the investigated diperoxides in the basic state of the molecule is a rod-shaped (Figure 3). All DPs have many conformations at the expense of the flexibility of hydrocarbon radicals. Different conformational states of the DP molecules are characterized by practically the same energy and can substantially change the dipole moment.

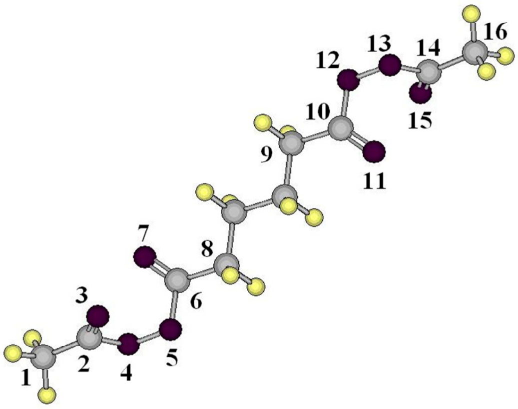


Figure 3. The optimal geometrical structure of diperoxide **III.**

The physicochemical parameters for the atoms that are part of the O-O groups and are located near them were calculated. The reactivity of the diperoxide molecules is due to the presence of peroxide groups in their composition. The numbers of heavy atoms (C and O) shown in Figure 3. The parameters of carbon atoms, which are in positions away from peroxide groups, are practically the same. For diperoxides (**III, VI, IX**), at the ends of which the CH_3 group or the phenyl group C_6H_5 are located, the constant of the thermal decay rate is lower than for all other compounds, where the final radical is large [9]. The calculation of charges on heavy atoms (C and O) in the molecules of diperoxides indicates on that. Thus, for the DP at the ends of the molecule is the CH_3 group (**III, VI**). The numerical value of the charge on atoms 1 and 16 is -0.224 - -0.253. For all other compounds at the ends of which the molecules contain longer hydrocarbon radicals, the value is slightly lower and lies within -0.153 - -0.183 (Table 4). In the case of compound **IX,** the stabilizing effect of the phenyl radical explained by the coupling effect of the electrons of the peroxide group and the substituent. The length of the peroxide bonds in the molecules of the studied DPs are close (1.3640-1.4139 Å). The length of the O-O bond in crystalline benzoyl peroxide is 1.46 Å according to the literary data [1]. The length of the connection of C-O in the carbonyl group of DP, containing aliphatic radicals, is same and equal to 1.2093 – 1.2205 Å.

All four carbonyl groups in compound **IX** have the largest length of 1.2550 Å. The length between carbon atoms and oxygen in carbonyl groups is 1.2255 Å for a DP containing a phenyl nucleus between the peroxide groups (**X**).

Table 4. The charges on atoms by Mulliken for the studied diperoxides

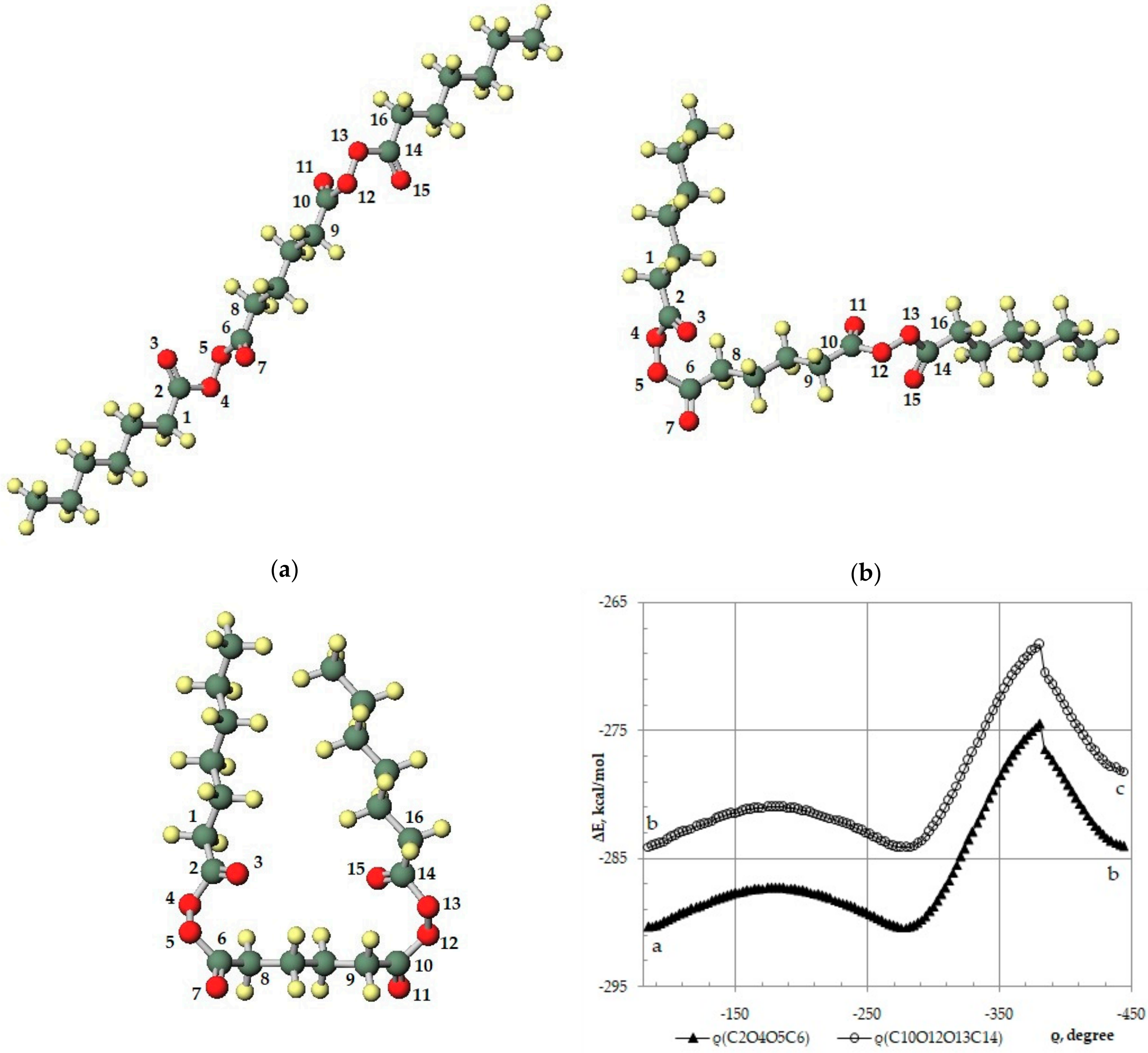
Atom	Diperoxide							
	I	**II**	**III**	**VI**	**VIII**	**IX**	**X**	**XI**
C(1)	-0.183	-0.179	-0.227	-0.253	-0.175	-0.163	0.153	-0.157
C(2)	0.330	0.328	0.334	0.342	0.327	0.367	0.330	0.334
O(3)	-0.280	-0.288	-0.313	-0.288	-0.291	-0.318	-0.313	-0.321
O(4)	-0.119	-0.122	-0.154	-0.117	-0.116	-0.152	-0.157	-0.139
O(5)	-0.150	-0.152	-0.118	-0.155	-0.156	-0.115	-0.111	-0.136
C(6)	0.316	0.325	0.330	0.324	0.322	0.337	0.361	0.334
O(7)	-0.297	-0.310	-0.285	-0.313	-0.310	-0.295	-0.275	-0.322
C(8)	-0.152	-0.162	-0.183	-0.158	-0.159	-0.163	-0.114	-0.158
C(9)	-0.144	-0.103	-0.155	-0.154	-0.176	-0.153	-0.097	-0.158
C(10)	0.324	0.324	0.334	0.331	0.328	0.334	0.361	0.334
O(11)	-0.289	-0.310	-0.320	-0.320	-0.288	-0.315	-0.274	-0.322
O(12)	-0.158	-0.151	-0.138	-0.135	-0.117	-0.137	-0.130	-0.136
O(13)	-0.115	-0.120	-0.137	-0.138	-0.152	-0.129	-0.135	-0.139
C(14)	0.324	0.334	0.345	0.346	0.321	0.377	0.337	0.334
O(15)	-0.280	-0.287	-0.317	-0.321	-0.309	-0.335	-0.321	-0.321
C(16)	-0.183	-0.174	-0.224	-0.224	-0.154	-0.153	-0.151	-0.157

The both peroxide groups in the molecule of DP have the same reactivity. The rigidity (η) of the studied DPs are low (Tables 2, 3). That indicates on the possibility of reactions of these compounds with both electrophilic and nucleophilic reagents.

The solvent affects both the nature of the isotherms and the extrapolated values of the areas which corresponding to the molecule in the monolayer. The data obtained the nature of most isotherms belongs to the condensed type.

The conformational analysis of the DP **XI** was performed by changing the placement of the terminal radicals R_1 by rotating around the O-O axis of the peroxide groups. In the main state, the diperoxide molecule is placed planarly on the water-air interface and is in a two-dimensional gaseous state (Figure 4a). Peroxide groups -C(O)-O-O-C(O)- are located on the surface of water. The energy of the molecule at the same time is minimal (Figure 4d).

With an increase in surface pressure, one of the radicals R_1 is displaced from the phase separation. Due to the change in the torsion angle C(2)O(4)O(5)C(6), from (-84 °) to (-444 °) the position of the carbonyl groups C(2)=O(3) and C(6)=O(7), while the energy of the molecule increases. Figure 4b depicts a peroxide molecule for this case, and Figure 4d shows the transition path from the state (**a**) to the state (**b**).



(**a**) (**b**)

(**c**) (**d**)

Figure 4. Conformational states of the DP **XI** molecule: the two-dimensional gaseous state (**a**); film in the expanded liquid state (**b**); film in a condensed state (**c**). The paths of conformational transitions when the torsion angles (ϱ) of the groups C(2)O(4)O(5)C(6) and C(10)O(12)O(13)C(14) are changed (**d**).

With further increase of surface pressure from the surface of the phase separation, the second radical R_1 is superseded by changing the torsion angle C(10)O(12)O(13)C(14) from (-84 °) to (-444 °), as well the position of the carbonyl groups C(10)=O(11) and C(14)=O(15) changes (Figure 4c). The energy of the DP **XI** molecule increases even more, and the path of this change is shown in Figure 4d.

4. Conclusions

The monolayers of 11 diperoxides of different structure were formed on water-air interface by means of Langmuir method. The solvent affects both the nature of the isotherms and the extrapolated values of the areas which corresponding to the molecule in the monolayer. The nature of most isotherms belongs to the condensed type.

From the investigation of behavior of diperoxide monomolecular films on the water-air interface was found a different conformation of the molecules in the monolayer. Diperoxides with small radicals CH_3-$(CH_2)_m$-, form on the surface condensed monolayers. The radical located between peroxide groups

-$(CH_2)_n$- is stiff. Hydrophilic peroxide groups are located on the surface of the water, and hydrophobic hydrocarbon radicals can squeeze from surface to air.

The conformational analysis of the studied peroxides indicates that the area of the molecule at the interface take different values. The correspondence of theoretically calculated and experimental data indicates on the correctness of the used semiempirical quantum-chemical methods. The numerical values of the calculated areas are correlate with the corresponding values found for the molecules of the diperoxides in the monolayer. The results of this study may be useful for prediction the behavior of diperoxide on the phase boundary in heterogeneous processes with the participation of these compounds.

Author Contributions: Conceptualization, V.D. and O.A.; methodology, V.D.; software, Y.K.; validation, N.O. and Y.K.; formal analysis, N.O.; investigation, Y.K.; resources, Y.K.; data curation, N.O. and O.A.; writing—original draft preparation, V.D.; writing—review and editing, O.A.; visualization, Y.K.; supervision, O.A.; project administration, V.D.; funding acquisition, O.A.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflict of interest.

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