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Isomers of Some Vinyl and Allyl Compounds

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Abstract—The structures of two rotational isomers of styrene, methyl methacrylate, *N*-vinylpyrrolidone, and allyl benzoate found by AM1 calculations are discussed. Their formation is indicated by the presence of two minima on the curves of the rotation barriers around the C^1–C^2, C^2–N^3 and C(=O)–O, O–C(H_2) bonds. The structures of the isomers of allyl compounds were detected capable of providing the cyclization reaction and hydrogen atom elimination. It was found that both double bonds were of similar reactivity. The suggested structures of the isomers can participate in intermolecular interactions with the formation of self-associates and heteroassociates (molecular complexes) due to the presence of C=C and C=O groups with different degree of conjugation.

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Traditional unsaturated compounds like as styrene, acrylonitrile, methyl methacrylate, *N*-vinylpyrrolidone, maleic anhydride, allyl benzoate, diallyl phthalate, diethylene glycol, and diallyl carbonate are widely used in industry for producing (co)polymers with a complex of specific properties [1–5]. Kinetics of transformation and the chemistry of their reactions were extensively studied [6–10], but still there is no clear parameters linking the structure of unsaturated compounds with the formation of isomers and evaluation of their role in radical processes. Such studies allow to optimize the conditions for obtaining the final products and to predict the most promising areas for their application. Now these problems can be solved, as there are appropriate methods of quantum-chemical calculations of these molecules and the physicochemical methods for detecting the changes in their functional groups at the interaction.

Isomers can differ by the reactivity, and thereby can affect the rate of the main reaction. It is important to consider this effect in the theoretical study of self-association of unsaturated compounds, in the control over branching, crosslinking, cyclization and reducing the contribution to the degradation chain transfer, especially in the case of allyl compounds. There are a large number of experimental studies on the behavior of these unsaturated compounds in the reactions of (co)polymerization, and therefore it is important to calculate parameters of the structure of their isomers.

In this paper we analyze the spectral properties of certain representatives of vinyl and allyl compounds and identify the most promising structures of the isomers capable of intermolecular interactions or cyclization and hydrogen cleavage reactions, and consider contribution of the isomers to the reactivity of allyl bonds.

Electronic spectra of these compounds contain information on the conjugation of the C=C bonds with the carbonyl group directly, as in methyl methacrylate and maleic anhydride, or via nitrogen atom, as in *N*-vinylpyrrolidone. The absorption band of the C=C bond associated with the π–π^* transition in these compounds in most cases is located at 209–210 nm (Fig. 1a, curves *2*–*4*). Thus, for methyl methacrylate and maleic anhydride the band maxima occur at λ_{max} 209 and 210 nm (Fig. 1a, curves *2* and *3*) with ε 1100 and 8500 l mol^{-1} cm^{-1}. The absorption maximum of *N*-vinylpyrrolidone is shifted to 232 nm due to the increase in the length of the conjugation chain of these groups through the nitrogen atom (Fig. 1a, curve *4*), and it is characterized by the extinction coefficient ε ~ 13500 l mol^{-1} cm^{-1}. In the range of 200–300 nm the allyl benzoate and diallyl phthalate molecules in *n*-

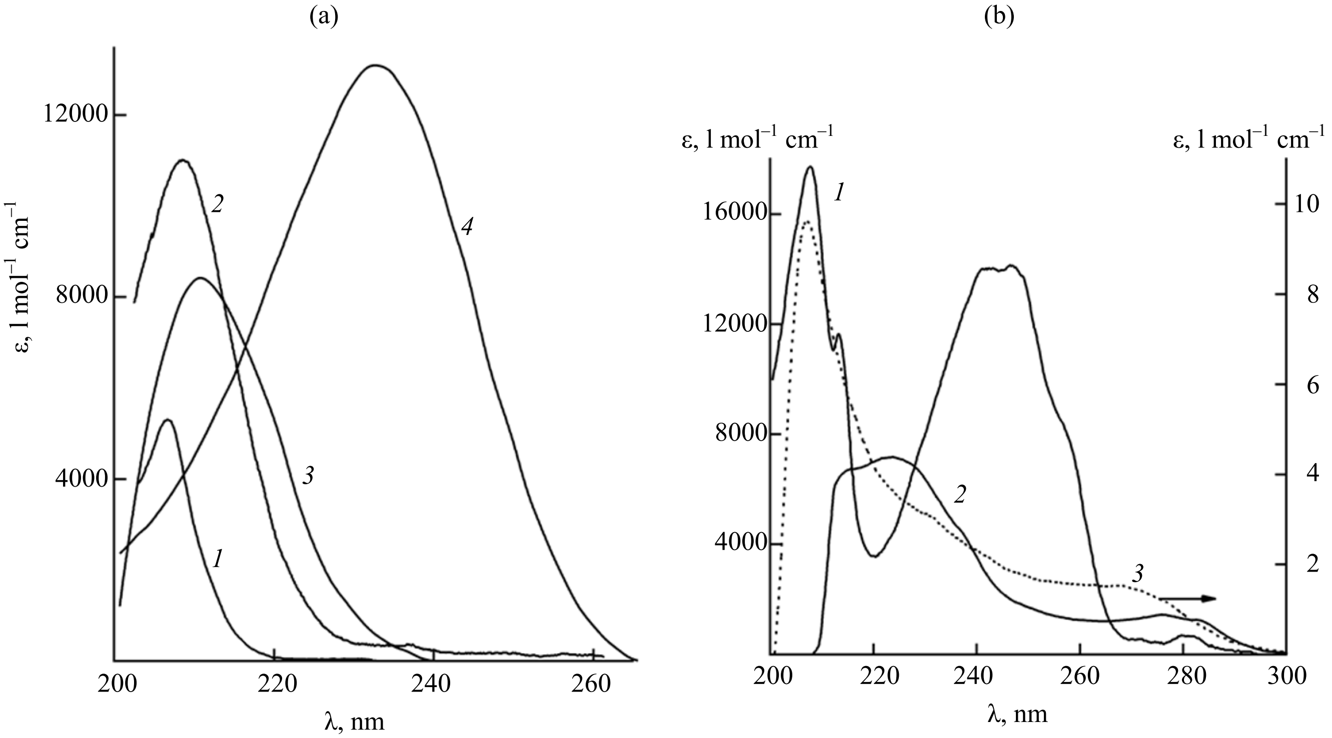
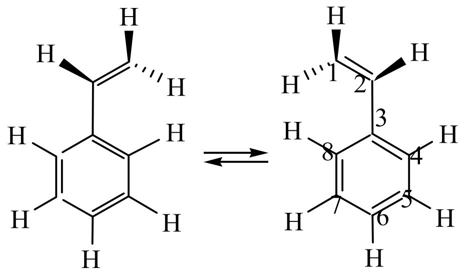


Fig. 1. Electron absorption spectra *(a)* (*1*) acrylonitrile, (*2*) methyl methacrylate, (*3*) maleic anhydride, and (*4*) *N*-vinylpyrrolidone; (b) (*1*) styrene, (*2*) diallyl phthalate, and (*3*) diethylene glycol diallylcarbonate. The concentration of solutions in heptane, M: (a) (*1*) 0.9×10^{-4}, (*2*) 4.83×10^{-5}, (*3*) 6.8×10^{-5}, (*4*) 4.27×10^{-5}, and (b) (*1*) 2.69×10^{-5}, (*2*) 1.18×10^{-4}, (*3*) 0.0674.

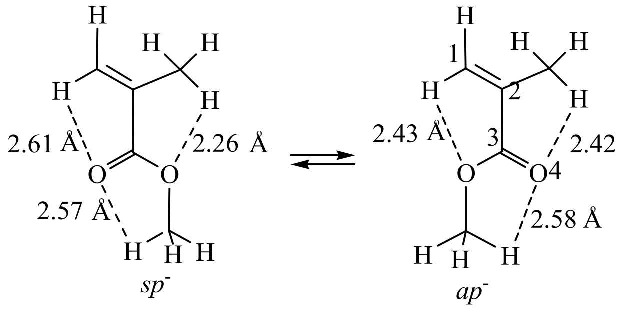
hexane absorb in two regions. The first region contains three bands, at λ 214.6, 225, 236.5 nm and extinction of $\varepsilon\times10^{-3}$ 6.4, 7.8, 4.6 l mol^{-1} cm^{-1}. The second region includes two bands, at λ 276 and 283 nm, with $\varepsilon\times10^{-3}$ 1.1 and 0.9 l mol^{-1} cm^{-1}. The aromatic ring in the molecules of allyl benzoate and diallyl phthalate is conjugated with the oxygen of the carbonyl groups and the carbon of the terminal double bond. These two chromophores are separated by a $CH_2(O)$ fragment and should manifest themselves in the electron spectrum independently. The presence of absorption bands for the allyl benzoate and diallyl phthalate at 225 and 276 nm, respetively, indicates the conjugation of the aromatic rings with the C=O groups. Compounds with nonconjugated chromophores usually show very weak absorption in the range 200–300 nm. For example, absorption of the molecules of diethylene glycol and diallyl carbonate is low, ε is equal approximately to 10 and 2 l mol^{-1} cm^{-1} for the bands at 207 and 268 nm respectively, characterizing the isolation of C=C and C=O bonds separated by methylene groups. In the styrene molecule the C=C bonds of vinyl and phenyl groups are conjugated, and the absorption bands of styrene, p(^1L_a), K-, and benzene (B, ^1L_b α) in a heptane solution exhibit fine splitting at λ_{max} 208, 214, 243, 248 and 272, 280, 289 nm (Fig. 1b, curve *1*) with $\varepsilon\times10^{-3}$ 17.75, 11.6, 14.0, 14.1 and 0.52, 0.51, 0.39 l mol^{-1} cm^{-1}, respectively. For acrylonitrile, the λ_{max} is at 203 nm (Fig. 1a, curve *1*) and ε is somewhat less than in the oxygen-containing compounds, which indicates low electron-donating ability of the multiple bond.

Alongside the electron spectra, we also used for the analysis of these compounds the data on the stretching vibrations of =CH, =CH_2, C=C, and C=O groups and the chemical shifts of these groups obtained by IR, ^{1}H, and ^{13}C NMR spectroscopy [11–14]. The results of spectral analysis in this case are important because the spectral characteristics can be used at the optimization of the selected initial structures of the monomers and their isomers.

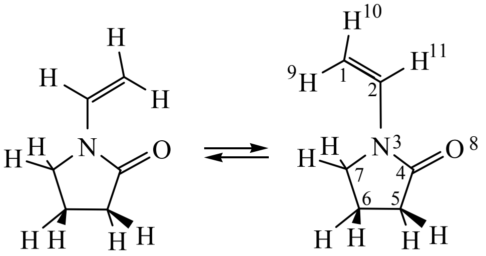
To reveal the structures of the isomers we calculated the magnitude of rotation barrier [15], mostly by AM1 method, for each compound, except for acrylonitrile and maleic anhydride, whose molecules are planar and distinguishing of their isomers is rather difficult. First of all, we have considered the rotation around a single C^1–C^2 bond in the molecules



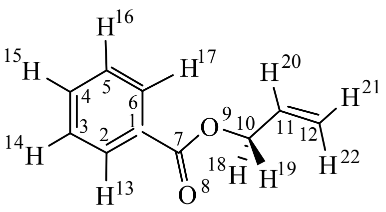
Styrene



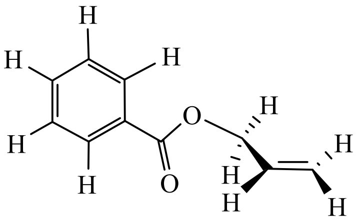
Methyl methacrylate



N-vinylpyrrolidone



Allyl benzoate **Ia**



Allyl benzoate **Ib**

of styrene and methyl methacrylate, and around C^2–N^3 bond in *N*-vinylpyrrolidone or C(=O)–O and O–C(H_2) bonds in allyl benzoate, diallyl phthalate, and diethylene glycol diallyl carbonate, and mostly observed appearance of two minima that indicate the possible formation of two rotation isomers. This is clearly seen from the curves of dependence of the standard heat of formation (H^0_{298}) of an isomer on the angles $C^1C^2C^3C^4$ in styrene, C^1C^2CO in methyl methacrylate, $C^1C^2NC(=O)$ in *N*-vinylpyrrolidone, and $C^2C^1C^7O^9$ in allyl benzoate (Fig. 2).

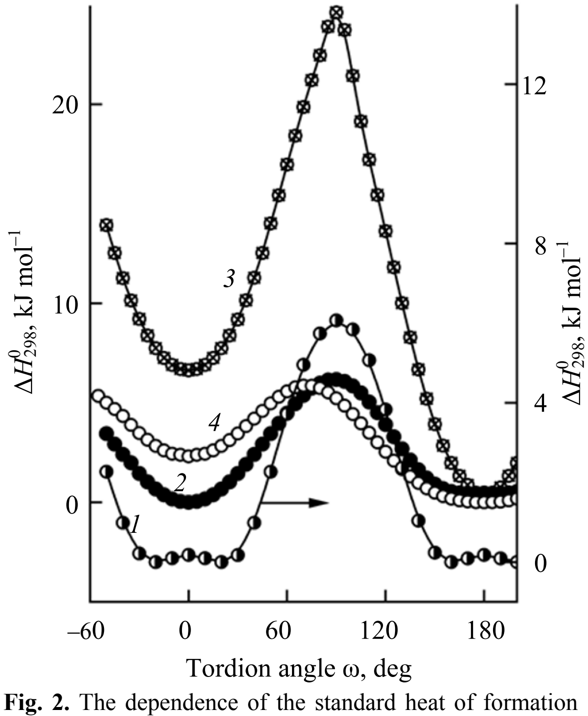


Fig. 2. The dependence of the standard heat of formation (ΔH^0_{298}) of the isomers of (*1*) styrene, (*2*) methyl methacrylate, (*3*) *N*-vinylpyrrolidone, and (*4*) allyl benzoate on the value of the torsion angle (ω, deg.): (*1*) $C^1C^2C^3C^4$, (*2*) $C^1C^2C=O$, (*3*) $C^1=C^2NC(=O)$, (*4*) $C^{12}=C^{11}C^{10}O^9$.

These minima correspond to the angles (ω) ~20° and 340° in styrene (Fig. 2, curve *1*, Table 1), zero and 180° in methyl methacrylate, *N*-vinylpyrrolidone and allyl benzoate (Fig. 2, curves *2*–*4*, Table 1). The magnitude of the potential barrier for styrene at room temperature is less than *RT* (~2.5 kJ mol^{-1}), that is, the thermal motion is sufficient for the free rotation of vinyl and phenyl groups relative to each other. Also, this monomer is nonpolar and its dipole moment is very low (Table 1), and usually it acts as a π-donor. The double bond and the benzoate group lie in different planes.

By comparing the calculated heats of formation of two methyl methacrylate isomers with a *syn-peri*-planar (*sp*) and *anti-peri*-planar (*ap*) location of C=C and C=O bonds (Table 1) we revealed a slight predominance of *ap*-conformer which has a slightly larger dipole moment μ and a negative charge on C^1. The calculated data show that the rotation around C^2–C^3 bond in the $C^1=C^2–C^3=O$ group is restricted due to the intramolecular hydrogen bonding involving both the oxygen atoms and the hydrogen atoms of the three functional groups. In contrast to the methyl metha-

Table 1. Calculated (AM1) parameters of the styrene, methyl methacrylate, *N*-vinylpyrrolidone, and allyl benzoate isomers

Monomer	Izomer	H^0_{298}, kJ mol^{-1}	μ, D	Atomic charges, au		Angle ω, deg[a]	Barrier (ΔH^0_{298}), kJ mol^{-1}
				C^1	C^2		
Styrene	*trans*	160.9	0.021	–0.209	–0.125	–20	1.5
	cis	161.0	0.012	–0.209	–0.124	20	
Methyl methacrylate	*trans*	–319.9	2.05	–0.143	–0.125	180	6.2
	cis	–318.5	1.75	–0.145	–0.125	0	
N-Vinylpyrrolidone	*trans*	–84.2	3.41	–0.312	–0.002	180	24.6
	cis	–78.0	3.97	–0.276	–0.025	0	
Allyl benzoate **Ia**	*trans*	–173.9	2.11	–0.217	–0.167	180	3.6
	cis	–171.5	2.17	–0.193	–0.181	0	

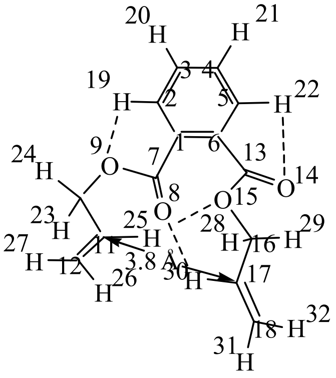
[a] The designations are given in Fig. 2.

crylate isomers whose H^0_{298} values are equal, in the case of the rotation isomers of *N*-vinylpyrrolidone (Table 1) to the minimum value –84.2 kJ mol^{-1} corresponds the *trans*-configuration with the dihedral angle 180°. The advantage of this conformer is provided by the intramolecular hydrogen bond $H^{11}\cdots O^8$, and it is confirmed by experimental data of ^{1}H and ^{13}C NMR spectroscopy, indicating the presence of only one multiple signal for the atoms of hydrogen and carbon in the $=CH_2$ and –HC= groups, as well as a downfield shift of the signal of H^{11} proton in the –HC= group in comparison with the analog without the oxygen atom [13].

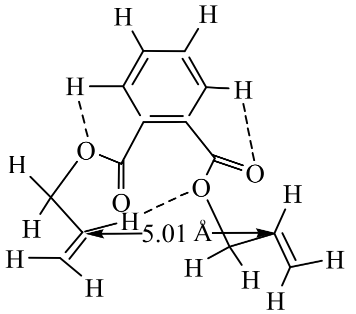
The energy curve at the rotation around the bond between C^1 carbon of benzene ring and C(=O) of the substituent in the molecules of allyl benzoate indicates the existence of to two allyl benzoate isomers, **Ia** and **Ib**, differing by the $C^2C^1C(=O)O$ torsion angle (Fig. 2, curve *4*).

The allyl benzoate isomer **Ia** has a planar structure, and the value of all the torsion angles along the chain of the ester substituent is about 180°. The dependence of potential energy on the $OC(H_2)C(H)=C(H_2)$ angle is similar but with a lower rotation barrier, 0.35 and 1.45 kcal mol^{-1}, respectively. In both cases the rotation around the C(=O)–O and O–C(H$_2$) bonds passes through a deep minimum corresponding to the torsion angle 180°. A possibility of free rotation around these bonds follows from the dependence of potential energy on the values of $C^1C(=O)OC(H_2)$ and $C(=O)OC(H_2)CH$ angles in the range of 70°–290°, the curve is gently sloping. If the angle $C^7C^9C^{10}C^{11}$, which is equal to 180°, is changed to 280°, then the double bond in the structure of allyl benzoate **Ib** becomes located out of the plane of the benzene ring and the carbonyl group.

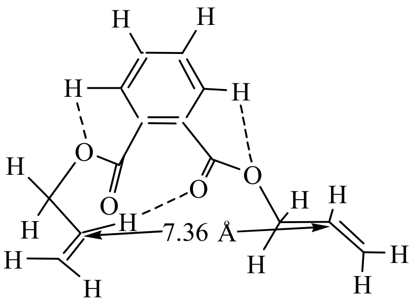
The isomers of allyl benzoate **Ia** and **Ib** have a common and characteristic feature: they do not differ by the magnitude of dipole moments (2.11 and 2.12 D) and have standard heats of formation equal to –41.69 and –41.74 kcal mol^{-1} (174.43 and 174.64 kJ mol^{-1}). The properties of their HOMOs are also similar: the calculated energy is approximately equal to –10.028 eV for the allyl benzoate **Ia** and –10.015 eV for the allyl benzoate **Ib**. This orbital in both isomers has a π-character and consists entirely of p_z-AO of the benzene ring. The closest to it two π-orbitals, HOMO-1, HOMO-2, related to allyl benzoates **Ia** and **IIa** respectively, have very small energy gaps: –10.072, –10.225 and –10.085, –10.265 eV. The contributions of AOs to the HOMO-1 of the planar allyl benzoate isomer **Ia** are distributed mainly over the benzene ring (78.5%) and partly over the C^{11} and C^{12} atoms of the double bond (12.1%), the HOMO-2 is shared between the benzene ring (15.9%) and C=C bond (80.6%). If the double bond is located out of the plane of the main part of the molecule, then 93.5% of the contribution to the HOMO-1 of the allyl benzoate isomer **Ib** consists of p_z-AO of the benzene ring and 4.5% of the carbonyl oxygen, and 84.6% of the HOMO-2 is distributed between the C=C bond and 11.8% for the $C^{10}H_2$ group, that is, HOMO-2 is mainly the π-orbital of the double bond. The analysis of these data leads to a conclusion



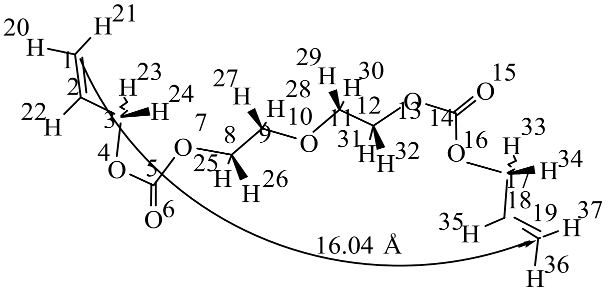
Diallyl phthalate **IIa**



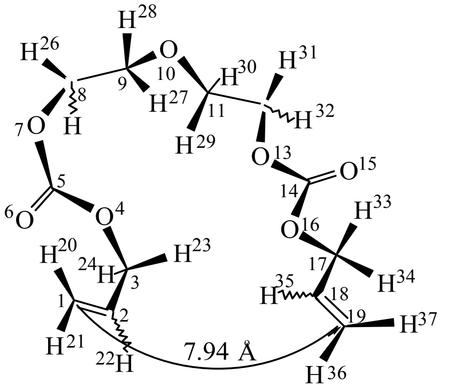
Diallyl phthalate **IIb**



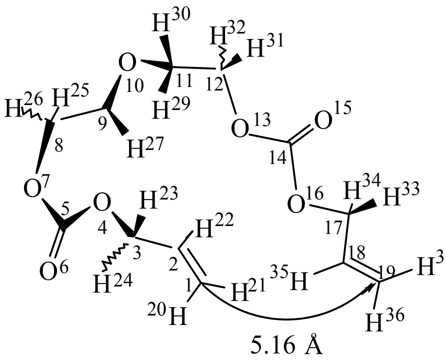
Diallyl phthalate **IIc**



Diethylene glycol diallyl carbonate **IIIa**



Diethylene glycol diallyl carbonate **IIIb**



Diethylene glycol diallyl carbonate **IIIc**

that deviation of the double bond from the plane of the benzene ring changes the distribution of the contributions of AOs to the functional groups of allyl benzoate **Ib**.

Proceeding from the data for allyl benzoate **Ia** and **Ib**, let us consider the possibility of the formation of the diallyl phthalate isomers whose substituents have four axes of internal rotation: $C^1(C^6)$–C(=O), C(=O)–O, O–$C(H_2)$ and $C(H_2)$–C(= C), providing an opportunity of free rotation of the chain. Accounting for the existence of two substituents in the *ortho*-position of benzene ring we have used the allyl benzoate molecule as a model to describe the isomers. These compounds differ little by reactivity [14], suggesting that the second ester group has no significant influence of on the reactivity of the first one, possibly because of the lack of conjugation between the double bond in the substituent and the aromatic fragment of diallyl phthalate. The difference is in non-planar arrangement of oxygen atoms of the diallyl phthalate carbonyl

Table 2. Calculated (AM1) values of the standard heat of formation (H^0_{298}), dipole moment (μ) and the distance between the carbon atoms of the double bonds of two allyl groups (*1*, *2*) for the optimized molecules of diallyl phthalate and diethylene glycol diallyl carbonate isomers

Isomer	C=C–CH$_2$–O angle,[a] deg		$-H^0_{298}$, kJ mol^{-1}	μ, D	Distance between the terminal atoms, Å			
	1	*2*			C^{12} and C$^{18\,b}$	C^{11} and C$^{18\,b}$	C^{12} and C$^{17\,b}$	C^{11} and C$^{17\,b}$
IIa	145.9	174.8	415.1	2.99	5.2	4.6	4.7	3.8
a	147.8	341.8	411.2	2.76	4.9	4.1	4.9	4.2
b	335.2	174.1	411.0	3.16	5.0	5.7	4.1	4.8
c	3.4	18.8	405.2	3.41	4.6	4.4	3.6	5.2
IIb	150.0	138.9	412.9	2.91	5.8	5.7	5.4	5.0
IIc	153.2	170.7	413.8	3.08	8.9	8.2	8.2	7.4
IIIa	180.0	180.0	1141.6	1.19	16.0	14.7	15.2	14.0
IIIb	–156.7	–169.1	1156.5	3.21	7.9	6.7	6.9	5.6
IIIc	–4.2	–168.7	1158.8	3.16	5.2	5.7	4.1	4.5

[a] The torsion angle in the diallyl phthalate isomers: (*1*) $O^9C^{10}C^{11}C^{12}$, (*2*) $O^{15}C^{16}C^{17}C^{18}$; diethylene glycol diallyl carbonate isomers: (*1*) $C^1C^2C^3O^4$, (*2*) $O^{16}C^{17}C^{18}C^{19}$. [b] Indicated is the numbering of atoms in the isomers of diallyl phthalate, for the diethylene glycol diallyl carbonate is indicated the distance between the atoms C^1 and C^{19}, C^2 and C^{19}, C^1 and C^{18}, C^2 and C^{18}, respectively.

groups, as indicate the values of the torsion angles $C^2C^1C^7O^8$ and $C^5C^6C^{13}O^{14}$, both differing from zero and 180°.

At the calculation, we optimized three structures to achieve maximal absolute value of the standard heat of formation: the diallyl phthalates **Ia–Ic**. Based on the energy and geometric parameters (Tables 2–4) we conclude that diallyl phthalate **Ia** is the most energetically favorable, although the difference with diallyl phthalates **Ib** and **Ic** is less than 1 kcal mol^{-1}. The calculated dipole moments of these structures (~3 D) and the distribution of charges on the atoms of the two substituents (Table 3) are also similar. Despite the fact that the diallyl phthalate isomers **Ia** and **Ib** differ by their spatial structures and location of double bonds with respect to one another and to the plane of the benzene ring, they have similar charge on their atoms and the atoms of the substituents in the isomer **Ib.** A special feature of the latter is the location of the double bond out of the main plane of the molecule. The similarity of the allyl benzoate isomer **Ib** and diallyl phthalate isomers **IIa–IIc** is manifested in the properties of the HOMO and next four MOs with energies in the range –10.0 to –10.4 eV, which all are of π-character and the range of their localization is rather narrow. The first two of these MOs are localized on the *p*-electrons of the carbon atoms of double bonds of the two allyl groups of diallyl phthalate isomers, the contributions are ~85% and ~ 69%, while the other two are localized on the carbon atoms of benzene ring with the contributions ~98% and ~93%. Based on this distribution of electron density in the MOs of the isomers, we can assume that the π-orbitals of the aromatic system and the allyl group of the substituent do not interact with each other.

While considering the calculated distance 2.2–2.8 Å between the oxygen and hydrogen atoms in the ester substituents of the diallyl phthalate isomers **IIa–IIc**, we see that the distance is less than the sum of the respective atomic radii. This fact and the theoretical concepts in [16] allow us to assume that in the diallyl phthalate isomers **IIa, IIb,** and **IIc** intramolecular hydrogen bonds formed, the numbers of the bonds are 9, 8, and 7, respectively (Table 4). The atoms H^{25} and H^{30} of the first and second allyl groups, respectively, and the oxygen O^{15} of the second ester group in the diallyl phthalate isomers **IIa** and **IIb,** or O^{14} and O^8 in the first substituent in the isomer **IIc** form the H-bonds of the length 2.58, 2.65, 2.39, and 2.39 Å (Table 4) that brings together the double bonds holding the skeleton of the molecule in a more compact state. This is particularly true for the isomer **IIa**, in which the

Table 3. Effective charges by Löwdin on the atoms of allylbenzoate isomer **Ia**, **Ib** and on first and second ester groups (*1, 2*, respectively) of diallyl phthalates **IIa**–**IIc**

Atom	Charge magnitude, au							
	IIa		**IIb**		**IIc**		**Ia**	**Ib**
	1	*2*	*1*	*2*	*1*	*2*		
C(=O)	0.355	0.351	0.352	0.348	0.349	0.350	0.350	0.347
=O	–0.339	–0.338	–0.331	–0.344	–0.325	–0.346	–0.357	–0.356
–O–	–0.265	–0.275	–0.268	–0.267	–0.264	–0.275	–0.279	–0.275
C(H_2)	0.014	0.010	0.013	0.016	0.013	0.014	0.014	0.015
–*C*(H)=	–0.187	–0.194	–0.184	–0.187	–0.184	–0.169	–0.167	–0.186
=*C*(H_2)	–0.213	–0.213	–0.215	–0.209	–0.220	–0.214	–0.217	–0.210
C(=O)[a]	0.403	0.403	0.397	0.392	0.397	0.393		
=O[a]	–0.338	–0.342	–0.342	–0.386	–0.339	–0.387		
–O–[a]	–0.222	–0.289	–0.291	–0.242	–0.294	–0.237		
C(H_2)[a]	0.021	0.026	0.014	0.018	0.024	0.018		
–*C*(H)=[a]	–0.173	–0.176	–0.193	–0.176	–0.201	–0.176		
=*C*(H_2)[a]	–0.211	–0.207	–0.199	–0.205	–0.198	–0.207		

[a] The charges on the atoms in the molecules of diethylene glycol diallyl carbonate isomers.

distance between the atoms C^{11} and C^{17} is 3.8 Å, which may be a precondition for its participation in the cyclization reaction. Apparently, the appearance of cyclic structures in polydiallylphthalate [6] evidences that the diallyl phthalate **IIa** is involved in the polymerization. At turning one or both groups HC= and =CH_2 in the structure of this isomer around the CH_2–CH bond by 180° (from 190° to 144°), we obtain the structures *a–c* of the diallyl phthalate **IIa** isomers (Table 2), in which the atoms C^{11} and C^{18} (*a*) or C^{12} and C^{17} (*b, c*) can approach each other to the distances of 4.1 (*a, b*) or 3.6 (*c*) Å. This fact, as well as the presence in the MOs of common AOs of the two groups of double bonds with energy of about 35.50, 22.14 and 14.77 eV (Figs. 3a–3c) suggest more convincing the involvement of diallyl phthalate isomers **IIa** and **IIb** in the cyclization reaction.

It is hoped that this process will become real if the diallyl phthalate isomers **IIa** and **IIb** would be in larger proportion in the reaction mixture than **IIc**. In the presence of free radicals in the mixture of diallyl phthalate isomers **IIa** and **IIb** can be involved in reactions of abstraction of the hydrogen atoms from the positions H^{28} or H^{29}. However, these reactions should be somewhat hindered due to the presence in the structures of the isomers of intramolecular hydrogen bonds, which are typical for all the compounds containing double bonds and the groups C=O (diallyl phthalate, diethylene glycol diallyl carbonate), methyl, methoxy group (methyl methacrylate), aromatic ring (diallyl phthalate), a ring and nitrogen atom (*N*-vinylpyrrolidone). Undoubtedly, the H-bonds change the values of the torsion angles $C^{13}O^{15}C^{16}O^{17}$ and $O^{15}C^{16}C^{17}C^{18}$ (Table 4) mainly in the second substituent in the diallyl phthalate isomers **IIa** and **IIb** by 183° and 36°. At the same time it was found for the first substituent that all its angles are close in value, and it occupies the same position relative to the plane of the aromatic ring. The angles $C^5C^6C^{13}O^{14}$ and $C^5C^6C^{13}O^{15}$ in the second substituent of these isomers are also virtually equal, which indicates the same orientation of the fragment C(=O)–O to the benzene ring. The diallyl phthalate isomers **IIa** and **IIb** differ only in the orientation of the terminal fragment of the second substituent, the allyl group.

Table 4. The geometrical parameters of the optimized diallyl phthalate isomers calculated by AM1 method

Angle, ω	The angle values, deg			H-bond	CH···O distance, Å		
	IIa	**IIb**	**IIc**		**IIa**	**IIb**	**IIc**
$C^2C^1C^7O^9$	–56.3	–53.1	–70.7	O^8H^{23}	2.411	2.385	2.370
$C^1C^7O^9C^{10}$	–175.0	–174.6	–173.5	O^8H^{25}	2.684	2.799	2.907
$C^7O^9C^{10}C^{11}$	75.5	78.2	80.1	O^8H^{30}	2.385	5.402	6.561
$O^9C^{10}C^{11}C^{12}$	145.9	150.0	153.2	O^9H^{19}	2.585	2.702	2.970
$C^2C^1C^7O^8$	121.3	124.1	106.3	O^9H^{25}	2.754	2.555	2.544
$C^{10}C^9C^7O^8$	7.2	7.9	9.3	$O^{14}H^{22}$	2.654	2.641	3.882
$C^7C^1C^6C^{13}$	–2.9	–2.8	–3.7	$O^{14}H^{28}$	2.280	2.399	2.580
$C^5C^6C^{13}O^{14}$	–30.9	–29.8	155.5	$O^{14}H^{29}$	3.603	3.673	2.513
$C^{16}C^{15}C^{13}O^{14}$	–7.5	–4.2	1.1	$O^{14}H^{30}$	3.622	2.674	2.401
$C^5C^6C^{13}O^{15}$	146.0	148.4	–23.5	$O^{15}H^{22}$	3.877	3.889	2.427
$C^6C^{13}O^{15}C^{16}$	175.4	177.4	–179.8	$O^{15}H^{25}$	2.583	2.654	4.630
$C^{13}O^{15}C^{16}C^{17}$	–95.2	81.9	176.6	$O^{15}H^{30}$	2.475	2.629	2.408
$O^{15}C^{16}C^{17}C^{18}$	174.8	138.9	170.7				

For the diallyl phthalate isomer **IIc** the values of torsion angles in the first substituent are close to those in **IIa** and **IIb** except for the angles $C^2C^1C^7O^8$ and $C^2C^1C^7O^9$, which are by 15° less and by 18° larger, respectively, than those in diallyl phthalate **IIb**. Despite this fact, the orientation of the substituent in general can be considered coincident in the three optimized isomeric structures. The values of the related torsion angles $C^5C^6C^{13}O^{14}$ and $C^5C^6C^{13}O^{15}$ in the second substituent of the diallyl phthalates **IIb** and **IIc** differ by 185° and 172°, respectively, that is, the substituents are directed oppositely relative to the plane of benzene ring. The consequence of this arrangement is a considerable distance between the two allyl groups in the diallyl phthalate isomer **IIc** (Table 2). The calculation of dependence of the potential on the torsion angles of the diallyl phthalate isomers showed that it is difficult to find general rules for the rotation around each flexible bond for all the structures of the isomers. This is probably due to the mutual influence of two substituents differing by configuration, as well as the formation of a "net" of the intramolecular hydrogen bonds.

In all the structures (Table 3) the charges on the atoms C^{11}, C^{12} and C^{18} change slightly, therewith, the

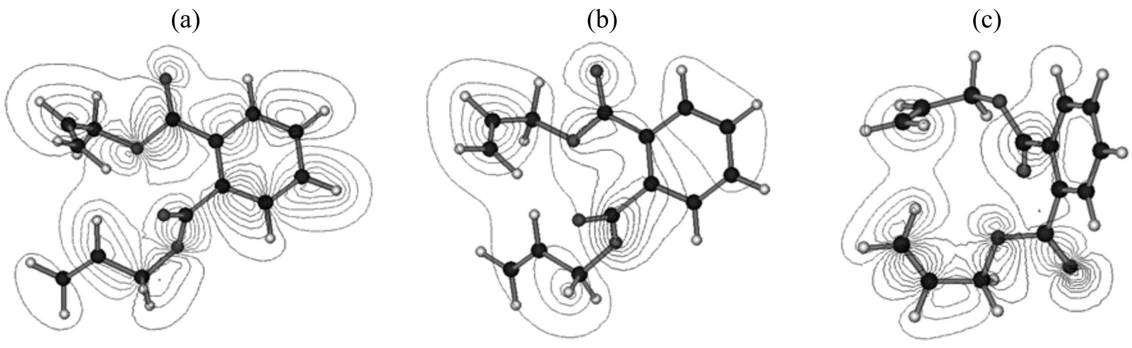


Fig. 3. The molecular orbitals with common orbitals of the groups of double bond in the diallyl phthalate **IIa** with the following energy of orbitals (E_{MO}, eV): (a) 35.504, (b) 22.140, and (c) 14.775.

negative charge on the atom C^{17} decreases in the diallyl phthalate **IIb** and particularly in **IIc** compared with the isomer **IIa.** This leads to an increase in the charge difference on the atoms of the double bond of the second substituent from 0.019 in **Ia** and 0.022 in **Ib** up to 0.045 in **IIc**. This means that the formation of an isomer with more compact configuration is connected with a decrease in the double bond polarization of the isomers and hence in their activity in organic reactions.

The most difficult task was to describe the isomers (conformers) of diethylene glycol diallyl carbonate. Almost 1/3 of the skeleton occupy oxygen atoms contributing to a high flexibility of the molecules and providing their existence in the form of a ball with a central fragment: $O^6C^8C^9O^{10}C^{11}C^{12}O^{13}$. In this study we primarily considered a completely expanded structure of the diethylene glycol diallyl carbonate **IIIa**, containing the skeleton and C=O group in a same plane. Even in this form, the isomer comprises 18 events of approachment of the oxygen and hydrogen atoms to the distance of 2.4–2.7 Å (Table 2). We found that O^7 and O^{10} are involved in the formation of four hydrogen bonds, and the atoms H^{25}, H^{26}, H^{31}, and H^{32} each form two H-bonds increasing the total number to 8. Thus, due to the location near the oxygen atoms and the CH_2 groups a "net" is formed of the intramolecular hydrogen bonds, and their total number in these isomers virtually does not differ from that in the original molecules of the diethylene glycol diallyl carbonate.

The H-bonds formed at the approach of the hydrogen and oxygen atoms H^{29} and O^4 of the two parts of the molecule relative to the central atom O^{10} in both isomers, and H^{23} with O^{13} or O^{14} in the **IIIb** isomer, H^{22} with O^{14} in the **IIIc** isomer are rather stable. Apparently this is the reason why the H^0_{298} of the expanded isomer **IIIa** only differs by about 4 kcal mol^{-1} from the respective value for the diethylene glycol diallyl carbonates **IIIb** and **IIIc**.

The terminal carbon atoms C^1 and C^{19} in the isomers **IIIa, IIIb and IIIc** are separated by the distances of 16, 8, and 5 Å, respectively. At the isomerization of the flexible molecules of diethylene glycol diallyl carbonate the bond lengths vary only slightly (Table 2), approximately by 0.01 Å, but the bond O^4–C^5 is the longest and C^5–O^7 is the shortest in the **IIIb** and **IIIc** isomers as compared with the isomer **IIIa**. For virtually all angles forming the molecule skeleton a change by 3°–6° is characteristic as well as for the angles that fix the position of the carbonyl atoms O^6 and O^{15} relative to the planes of neighboring bonds. The values of the central and neighboring angles, such as $C^5O^7C^8C^9$, $C^8C^9O^{10}C^{11}1$, $C^9O^{10}C^{11}C^{12}$, and $O^{10}C^{11}C^{12}O^{13}$, suffer changes by 90°–100° (Table 4). In addition, the molecules of the more compact diethylene glycol diallyl carbonates **IIIb** and **IIIc** differ significantly from **IIIa** by the electron density distribution, whereas the charges on their atoms are close to each other. Therewith, the negative charge on the O^4 atom of the isomer **IIIa** is by 0.070 au higher and on the O^7 by 0.075 au less in **IIIa** than in **IIIb** and **IIIc.** The negative charges on the atoms C^8, C^9, and C^{12} and positive charge on the atoms H^{27}–H^{30} are higher by 0.33 and by 0.20–0.030 au, respectively, in **IIIa** than in **IIIb** and **IIIc**. The differences in the charges on the oxygen atoms of isomers of diethylene glycol diallyl carbonate **IIIb** and **IIIc** are comparable (Table 2) due to the constant relation between the number of the hydrogen atoms approaching O^4 and removed from O^7. Since the charge on the C^1 atom of both **IIIb** and **IIIc** isomers is higher by 0.011 au and on C^2 is less by 0.020 au in **IIIb** and 0.028 au in **IIIc** than in the diethylene glycol diallyl carbonate **IIIa** isomer, the allyl bonds are depolarized, and the charges on the atoms C^1 and C^2 are almost equal. The analysis of the charge distribution on the atoms of the isomers suggests that the well-known fact about equal reactivity of the allyl double bonds of diethylene glycol diallyl carbonate molecule before the reaction is due to the predominance of structures **IIIb** and **IIIc** in the mixture.

Thus, the study of spectral properties of some vinyl and allyl compounds and the calculation of the rotation barrier (AM1) resulted in elucidation of the structure of styrene, methyl methacrylate, *N*-vinylpyrrolidone, allyl benzoate, diallyl phthalate and diethylene glycol diallyl carbonate isomers most promising for the study of intermolecular interactions. Calculation of electronic and energy parameters, charge distribution on atoms and molecular orbitals on the functional groups showed that diallyl phthalate **IIa** in which the distance between the terminal atom C^{11} and C^{17} is 3.8 Å, can enter the cyclization reaction. This fact for the first time allows the suggestion that the occurrence of cyclic structures in polydiallylphthalate is due to the presence of isomer **IIa** in the reaction mixture. In addition, if the system contains free radicals and the diallyl phthalates with structures **IIa** and **IIb**, then the reactions of hydrogen abstraction from the sites H^{28}

and H^{29} are probable. The observed depolarization of allyl bonds in the diallyl phthalate with the structures **IIb** and **IIc** apparently causes their equal reactivity before the reaction of one of them and testifies to the predominance of these isomers in the initial diallyl phthalate.

The data obtained and analysis of charge distribution on atoms C^1 and C^2 of the diethylene glycol diallyl carbonate with structures **IIIb** and **IIIc** also indicate the depolarization of allyl bonds, which makes them almost equal. In the case of diethylene glycol diallyl carbonate one can assume that for allyl bonds this is due to the prevalence of the isomers **IIIb** and **IIIc** among the original molecules. Owing to the presence of C=C and C=O groups with different degrees of conjugation, the suggested structures may participate in the intermolecular interactions with the formation of self- and heteroassociates (molecular complexes).

EXPERIMENTAL

We used freshly distilled styrene, acrylonitrile, and methyl methacrylate. Maleic anhydride was twice sublimated. *N*-Vinylpyrrolidone from Merck was dried over potassium hydroxide and distilled twice in a vacuum. All compounds after purification by commonly used methods had characteristics consistent with the published data, and the content of the main substance was at least 99.98%. Diallyl phthalate and diethylene glycol diallyl carbonate from Fluka and Aldrich were used without further purification. Heptane was purified from traces of benzene by shaking with sulfuric acid followed by washing to remove the acid, dried over calcium chloride, and distilled.

The UV spectra of the heptane solution of compounds were recorded on a Specord UV-VIS instrument at 298 K in the range 200–300 nm using quartz cells with a layer thickness 10 mm.

For the quantum-chemical calculations of individual molecules of unsaturated compounds and the isomers we used semiempirical AM1 method (software package MOPAC 6) [17]. The molecular geometry optimization was performed with respect to all independent parameters at the gradient norm 0.002, the frequency analysis was performed in the harmonic approximation.

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