

## ACTION OF THE ATOMIC AND ELECTRONIC STRUCTURE OF PHEROMONE MOLECULES ON THE EFFECTIVENESS OF COMMUNICATION IN XYLOPHAGOUS INSECTS

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The B3LYP/6-31(*p,d*) density functional method is applied to pheromones of the forest xylophagous insects *Ips typographus* L., *Monochamus urusovi* Fisch., and *Monochamus galloprovincialis* Oliv. to calculate the absorption spectra and find excited states. The calculated results are used to assess the possible activity of the molecules when they are affected by solar radiation.

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A popular means for transmitting information in ecological systems is *pheromones*, i.e., odorous substances specifically secreted by insects. This type of communication is, as a rule, a complex system that includes the biosynthesis of a pheromone, its excretion and spreading in the environment, the perception of the pheromone by other individuals, and the analysis of the received signals. This is how pheromone communication is organized in the xylophagous insects of the order *Coleoptera*. A characteristic feature of xylophagous insects is aggregation behavior. When males have found a tree suitable for colonization, they secrete a specific sex pheromone to attract females and an aggregation pheromone to attract other males. The mass colonization weakens the tree and allows the offspring to develop under reduced stem pressure [1, 2].

The effectiveness of pheromone communication depends on many factors [3]. A reduction of the pheromone concentration gradients in the air flow can be due to the overlap of the pheromone jets given a high number of calling individuals, adsorption of the molecules on the surface of plants, or decomposition of the pheromone under the influence of environmental factors. To maintain a pheromone signal at a certain level, the pheromone molecules must be resistant to

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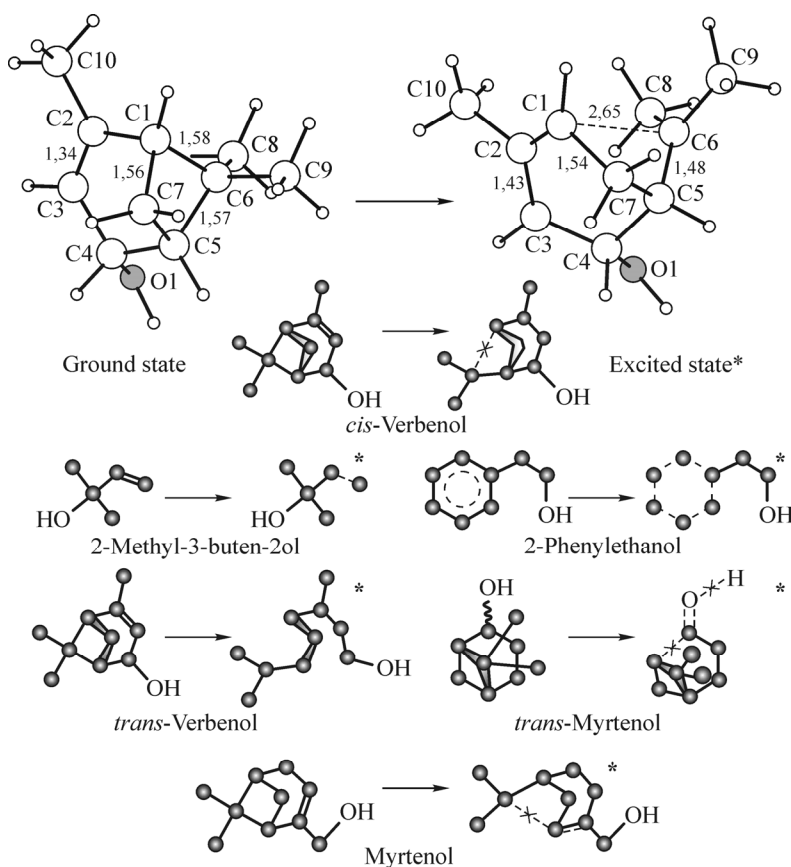
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changes in temperature or to the increase in the intensity of electromagnetic radiation in certain spectral ranges. Changes in the molecule structure may affect the pheromone perception by the antennas of the receiving individuals [4]. In this paper, we use quantum mechanical methods to assess the impact of environmental factors on the structure of pheromone molecules and, as a consequence, on the effectiveness of pheromone communication in xylophagous insects.

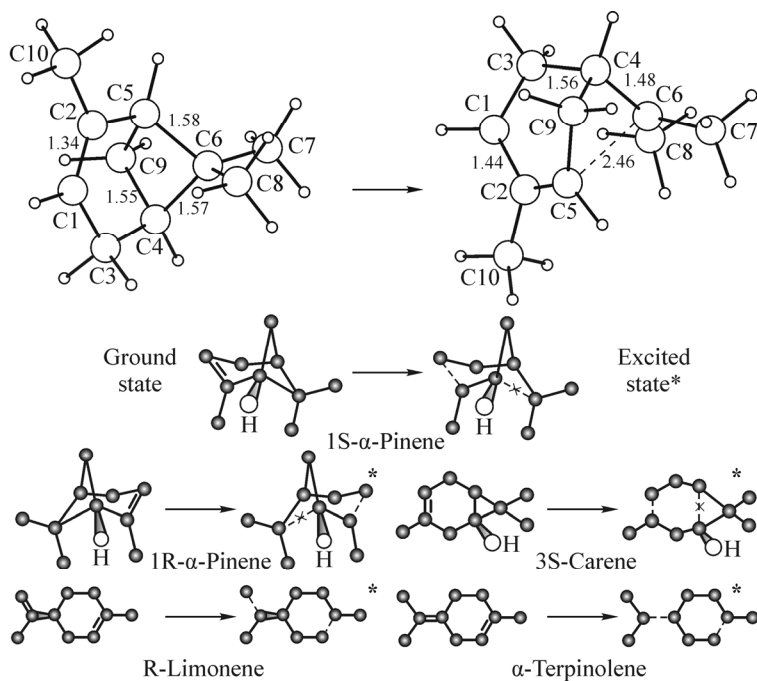
## SUBJECTS AND METHODS OF RESEARCH

The subject of this study is the pheromones of three species of xylophagous insects: the European spruce bark beetle *Ips typographus L.*, black fir sawyer beetle *Monochamus urussovi Fish*, and black pine sawyer beetle *Monochamus galloprovincialis Oliv.* Population outbreaks of the bark beetle and fir sawyer beetle cause enormous damage to forests in Europe, Siberia, Mongolia, Northeast China, Korea, and Japan [5, 6]. The black pine sawyer beetle *M. galloprovincialis* inhabits pine forests in North America, Asia, and Europe [7].

For each of the species of xylophagous insects selected for this study, pheromones are a mixture of highly volatile synergistic substances that mutually reinforce their action. Most of the compounds belong to the group of terpenes and terpenoids [8-10], which are related to odorous resin substances. The reason is that compounds of this type are relatively easily synthesized in insects, which have to secrete pheromones during long periods of time while waiting for the partner's reaction. The species specificity of pheromones is achieved through the synthesis of structural and optical isomers. The composition of the pheromone secreted by the bark beetle *Ips typographus L.* includes alcohols such as 2-methyl-3-buten-2-ol, *cis*-verbenol, *trans*-verbenol, 2-phenylethanol, mirtenol, and *trans*-mirtenol (Fig. 1). The pheromone of the fir sawyer beetle *Monochamus*



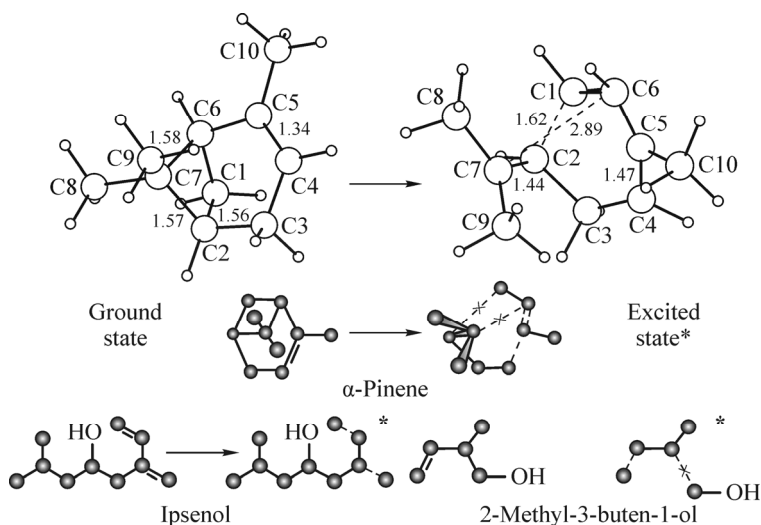
**Fig. 1.** Pheromone molecules of the European spruce bark beetle *Ips typographus L.* The \* symbol is used to indicate molecules in the excited state; the dashed lines show the bonds whose lengths increase during the transition of the molecules into the excited state; and the dashed line with a cross shows the breaking of the bonds.



**Fig. 2.** Pheromone molecules of the black fir sawyer beetle *Monochamus urussovi* Fish. See the note to Fig. 1.

*urussovi* Fish. consists of five substances, among which there are no oxygen-containing compounds: 1S- $\alpha$ -pinene, 1R- $\alpha$ -pinene, 3S-carene, R-limonene, and  $\alpha$ -terpinolene (Fig. 2). The pheromone of the pine sawyer beetle *Monochamus galloprovincialis* Oliv. has three main components: ipsenol,  $\alpha$ -pinene, and 2-methyl-3-buten-1-ol (Fig. 3) [11-18].

The atomic and electronic structure of the pheromone molecules was studied by quantum-chemical methods. The geometry and energy characteristics of the molecules were calculated using the popular B3LYP method with the 6-31(*p,d*) basis. In the calculations of the geometry and energy data for organic compounds of various classes (alcohols, amines, hydrocarbons, etc.), this method shows good convergence with different experimental data [19-24]. The energies of transitions into the excited state were calculated by the TD (time-dependent) method [25, 26]. All the calculations were made in the GAMESS software [27].



**Fig. 3.** Pheromone molecules of the black pine sawyer beetle *Monochamus galloprovincialis* Oliv. See the note to Fig. 1.

**TABLE 1.** Spectral Characteristics of the Pheromone Molecules of Xylophagous Insects

Pheromone	D	$\lambda$ , nm	OS	MO*	
<i>Ips typographus</i>					
2-Methyl-3-buten-2-ol	1.66	157	0.41	HOMO	LUMO
<i>cis</i> -Verbenol	1.45	204	0.08	HOMO	LUMO
		184	0.08	HOMO-1	LUMO
<i>trans</i> -Verbenol	1.45	189	0.12	HOMO	LUMO
2-Phenylmethanol	1.68	174	0.64	HOMO-1	LUMO+1
Myrtenol	1.67	198	0.09	HOMO	LUMO
<i>trans</i> -Myrtenol	1.4	144	0.02	HOMO-1	LUMO
		140	0.02	HOMO	LUMO+1
<i>Monochamus urussovii</i>					
1S- $\alpha$ -Pinene	0.15	190	0.16	HOMO	LUMO
1R- $\alpha$ -Pinene	0.15	190	0.16	HOMO	LUMO
3S-Carene	0.18	174	0.17	HOMO-2	LUMO
R-Limonene	0.65	166	0.42	HOMO-1	LUMO
$\alpha$ -Terpinolene	0.19	181	0.64	HOMO	LUMO
<i>Monochamus galloprovincialis</i>					
Ipsenol	1.24	219	0.16	HOMO-1	LUMO+1
$\alpha$ -Pinene	0.15	190	0.16	HOMO	LUMO
2-Methyl-3-buten-1-ol	1.58	160	0.25	HOMO	LUMO

\* Molecular orbitals participating in a given electronic transition.

Note. Absorption wavelength  $\lambda$ ; dipole moment D; OS, a dimensionless variable; MO, molecular orbital participating in a given electronic transition.

## RESULTS AND DISCUSSION

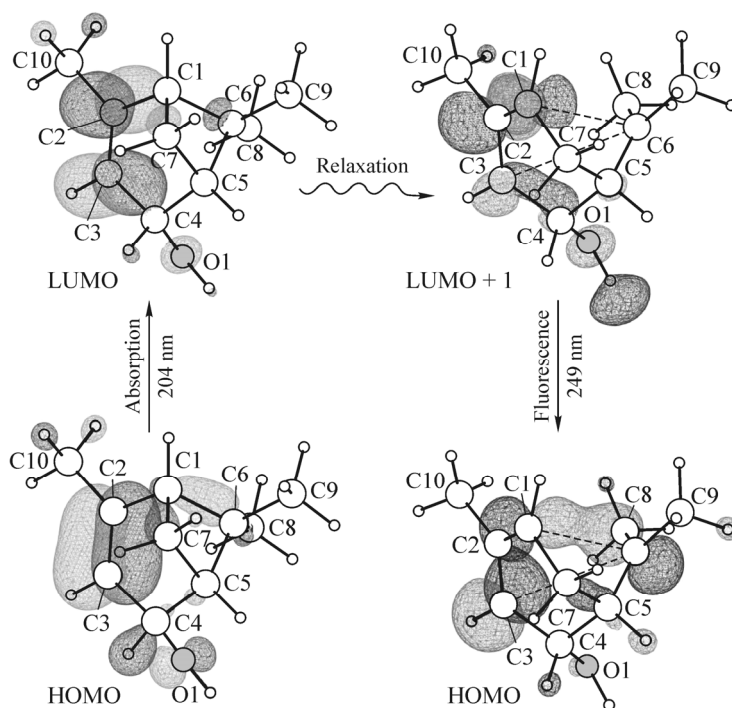
In this study, we simulated the pheromone molecules, performed the geometry optimization procedure, and calculated the dipole moments (D) and absorption wavelengths ( $\lambda$ ) corresponding to dipole-allowed transitions of electrons from the occupied molecular orbital to vacant ones. The calculated data are shown in Table 1; the wavelengths are given with the corresponding oscillator strength (OS; dimensionless variable). A high OS corresponds to the most intense transitions in the absorption spectrum.

It follows from Table 1 that the dipole moments of terpene molecules are 0.15 D to 0.65 D; those of molecules of unsaturated alcohols lie in the range of 1.2 D to 1.7 D. The polarity of the oxygen-containing pheromone molecules suggests their possible interaction with the polar molecules contained in air, e.g., with water molecules, the dipole moment of which is 1.85 D. The interaction of pheromone molecules with water reduces the concentration of these molecules in air and, hence, the power of the pheromone signal. Thus, air humidity can have a substantial impact on the effectiveness of pheromone communication in fir sawyer beetles because all the pheromones secreted by these beetles are oxygen-containing compounds. In turn, the concentration of the pheromones of the pine sawyer beetle is least affected by air humidity because all of its pheromones have a low dipole moment.

The absorption wavelengths of all the molecules being studied lie in the ultraviolet spectral range 140-219 nm. For the majority of the molecules, energy absorption leads to substantial changes in the atomic structure. The pheromone molecules containing two cycles show a substantial increase in bond lengths, which leads to the possible breaking of the bonds and opening of the cycles. Fig. 1 shows the structure of the bicyclic *cis*-verbenol molecule in the ground and excited states. The six-membered ring of the molecule is formed by the atoms C1, C2, C3, C4, C5, and C6; the small ring is formed

by four atoms – C1, C7, C5, and C6. The hexatomic ring contains one double bond between the atoms C2 and C3 with a length of 1.34 Å. The single bonds between the atoms in the ring are strained, e.g., the lengths of the C1–C6 and C6–C5 bonds are 1.58 Å and 1.57 Å, respectively. The C1 and C6 atoms are also part of the small ring of the molecule. The valence angle C1–C7–C5 in the tetratomic ring is 85.6°. The transition of the molecule to the excited state leads to a strong increase in the C1–C6 bond, which might lead to the breaking of the bond. Since the C1 and C6 atoms are part of both rings, the breaking has a marked effect on the initial structure of the entire molecule: the tetratomic ring opens up, and the hexatomic one is formed by the atoms C1, C2, C3, C4, C5, and C7. The length of the C2–C3 bond increases to 1.43 Å, which corresponds to a transition from a double to one-and-a-half bond. The valence angle C1–C7–C5 after the excitation of the molecule is 104.3°. Fig. 2 shows the changes in the structure of the pheromone molecule associated with the pine sawyer beetle (1S- $\alpha$ -pinene in the excited state is rotated for a better view). Like *cis*-verbenol, 1S- $\alpha$ -pinene contains hexa- and tetratomic rings. Since the molecules have a similar structure, the changes in the molecule of 1S- $\alpha$ -pinene after the excitation follow the same scheme. The length of the bond between the carbon atoms that are part of both of the molecule rings increases substantially, which might lead to the breaking of the bond, opening of the tetratomic ring, and formation of a new hexatomic ring (Fig. 2). The double bond between the carbon atoms in the hexatomic ring transforms into a one-and-a-half bond; when the small ring opens up, the valence angle C5–C9–C4 increases from 85.9° to 102.2°. The  $\alpha$ -pinene (the pheromone of pine sawyer beetles) molecule also contains tetra- and hexatomic rings, but, unlike *cis*-verbenol and 1S- $\alpha$ -pinene, the hydrogen atoms at one of the carbon atoms in the small ring are replaced by two methyl radicals (Fig. 3). The excitation of the  $\alpha$ -pinene molecule leads to a substantial increase in the length of the C6–C7 bond (both big and small rings) and C1–C2 bond (small ring). A further increase may lead to the breaking of the bonds and, hence, the formation of new structures containing no rings. Like in the above examples, the double bond between the carbon atoms in the big ring transforms into a single one by stretching from 1.34 Å to 1.47 Å. The strained single bond C2–C7 transforms into a one-and-a-half bond by shortening from 1.57 Å to 1.44 Å.

Apart from studying the changes in the geometry of the molecules under excitation, we also considered the electronic structures of the molecules under absorption and fluorescence. Fig. 4 shows, as an example, the molecular orbitals of the *cis*-verbenol molecule, which are involved in electronic transitions.



**Fig. 4.** Molecular orbitals of the *cis*-verbenol molecules participating in electronic transitions under absorption and fluorescence.

Under absorption, the most likely transition is from the highest occupied molecular orbital (HOMO) to the lower unoccupied molecular orbital (LUMO). In the ground state, electron density is concentrated at the C2 and C3 atoms, which are linked by a double bond. As shown in the figure, the transition from the HOMO to LUMO corresponds to that from the bonding orbital to the antibonding one. The changes in the electronic structure of the molecule lead to the corresponding changes in its atomic structure, in particular the C2–C3 double bond increases to transform into a one-and-a-half bond. The process of optimizing the geometry of the excited structures involves drastic changes in the molecule geometry, leading to a substantial rearrangement of the molecular orbitals, which are, in fact, responsible for a new substance. For example, the LUMO for *cis*-verbenol are the nonbonding orbitals of carbon atoms. Then, the resulting structure has several ways of development: either further transformation of the molecule into a new substance or return to the ground state with the possible radiation from the excited state. The possible fluorescence may be accompanied by the transition from the LUMO+1 to HOMO. Judging by the type of the HOMO, we can assume that the atomic structure of the molecule will not return to its original state and will transform into a more stable structure containing no stretched bonds.

## CONCLUSIONS

The calculations showed that the pheromone structure can be affected by external factors such as air humidity and solar radiation intensity. Water molecules in the air can interact with the polar molecules of the pheromones, and this process leads to a decrease in the pheromone concentrations. Solar radiation (UV part of the spectrum) excites pheromone molecules; the excitation manifests itself in changes in the bond lengths and valence angles and, possibly, in the breaking of the bonds and opening of the rings in the molecules. If we associate the molecule excitation process with communication in the insects, we can assume that the pheromone molecule in the excited state may not be captured by the insects' sensors (because the effectiveness of pheromone binding within the receptor depends on its atomic structure), resulting in a decrease the intensity of the pheromone signal.

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