Joint X-ray spectroscopic and quantum-chemical study of the electronic structure of pentafluorophenylalkyl ethers

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The high resolution X-ray emission O-Kα spectra of pentafluorophenylalkyl ethers C_6F_5OR (R = Et, Pr^i, and Bu^t) exhibit differences related to a change in the electronic structure of the compounds as R is varied. The search for stable conformers was performed by the semiempirical PM3 method. The most probable structures of C_6F_5OR were determined by the comparison of the experimental and theoretical X-ray spectra plotted for each conformer using *ab initio* calculations in the 6-31G basis set. Substituent R in pentafluorophenylalkyl ethers is situated outside of the ring plane. The fluorination of the benzene ring changes the energy level of the lone electron pair of oxygen relative to the levels of orbitals of the ring and substituent R and leads to an increase in the efficiency of interactions in the σ-system.

Key words: X-ray spectrum, electron density distribution; quantum-chemical calculations, PM3 and *ab initio* methods, structure of electron interactions; pentafluorophenylalkyl ether, conformer.

The study of the influence of different substituents on the electronic structure of benzene derivatives makes it possible to determine the properties of these compounds and predict their reactivity. The electronic structure of several substituted benzenes and fluorobenzenes has been widely studied previously, in particular, by X-ray emission spectroscopy along with quantum-chemical calculations.[1–4] The specific features of the electronic structure due to the interaction of the substituent with the benzene ring and the influence of F atoms on the character of these interactions were studied. It has been shown that in the series of π-donor substituents F, OH, and NH_2, the conjugation of lone electron pairs (LEP) of F, O, or N atoms with the π-system of the benzene ring occurs with participation of all π-orbitals of the benzene fragment.

In perfluorosubstituted benzenes, the π-interaction of the F and C atoms results in a change in the π-system of the ring as compared to the π-system of benzene. The composition of the highest occupied molecular orbital (HOMO), the contribution to which from 2p-atomic orbitals (AO) of the F atom is 20—25%, becomes different, and π-levels appear in the depth of the valence band of the compound.[2] This results in a decrease in the efficiency of the π-bond between the benzene ring and the substituent, but its orientation relative to the cycle plane does not always necessarily change. Anisoles are an example of substituted benzenes, whose molecular structure is distorted on going to perfluorinated analogs. In compounds PhOR, substituent R (excluding R = CMe_3) is localized in the plane of the benzene ring, and it is shifted out of the plane in C_6F_5OR derivatives. This geometric structure of perfluorinated molecules is the reason for several specific features of their electronic structure. First, orbitals in these molecules are not divided distinctly into π- and σ-types. Second, the LEP of the O atom is localized in the plane of the perfluorinated ring and cannot interact with its π-system, due to which the structure of the π-system changes sharply.

Therefore, a question arises about the structure of electronic interactions in the C_6F_5—O—R systems, where the LEP of the O atom is localized in the plane of the benzene ring. The purpose of this work is to study the electronic structure of several pentafluorophenylalkyl ethers (PFPE) C_6F_5OR (R = Et (**1**), Pr^i (**2**), and Bu^t (**3**)) by X-ray emission spectroscopy and quantum-chemical methods and to reveal the reasons for stabilization of these compounds in nonplanar conformations.

Experimental

X-ray O-Kα spectra of vapor of compounds under study were obtained on a Stearat X-ray spectrometer by the electron impact method. The energy of electrons was 4 kV, the current

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[†] Deceased.

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was 0.5 A, and the vapor pressure in the gas jet was ~10^2 Pa. A RbAP single crystal (rubidium biphthalate, $2d$ = 26.6 Å) was used as the dispersing element. Spectra were recorded with a spectrometer resolution of ~0.5 eV using a proportional gas counter. The intensity of O-Kα spectra in the maximum of lines was ~10 pulse s^{-1}. The accuracy of determination of the transition energy was ~0.4 eV. PFPE were synthesized by the known procedure,[5] and their purity was monitored by gas liquid chromatography and ^{1}H and ^{19}F NMR spectroscopy.

Calculation procedure

Stable conformers of ethers were searched for by the semiempirical PM3 method using the GAMESS program.[6] The complete optimization of the geometry of compounds was performed by the BFGS method to a gradient value of 10^{-7} Hartree Bohr^{-1}. The *ab initio* calculations of conformers of C_6F_5OR ethers were performed by the GAUSSIAN-92 program in the 6-31G basis set.

Based on these calculations and Koopmans' theory, we plotted theoretical O-Kα spectra. Separate lines in the spectrum are proportional to the sums of the squares of coefficients with which AO of the O atom enter specific molecular orbitals (MO). Each line was described by the Lorentz curve with a certain width (0.5 eV), and the resulting theoretical spectrum was obtained by summation over all curves.

Table 1. Total energies (E^{total}) of conformers calculated by PM3 and *ab initio* methods

Conformer	E^{total}/eV	
	PM3	*Ab initio*
1a	−3519.27	−23877.37
1b	−3519.31	−23877.32
1c	−3519.27	−23877.13
1d	−3519.22	−23877.05
2a	−3668.84	−24939.07
2b	−3668.76	−24938.93
2c	−3668.83	−24939.19
2d	−3668.77	−24938.91
3a	−3818.34	−26000.93
3b	−3818.32	−26000.87
3c	−3818.28	−26000.67

Results and Discussion

Molecular structures of PFPE corresponding to the energy minima are presented in Figs. 1—3. The values of total energies obtained are presented in Table 1. The

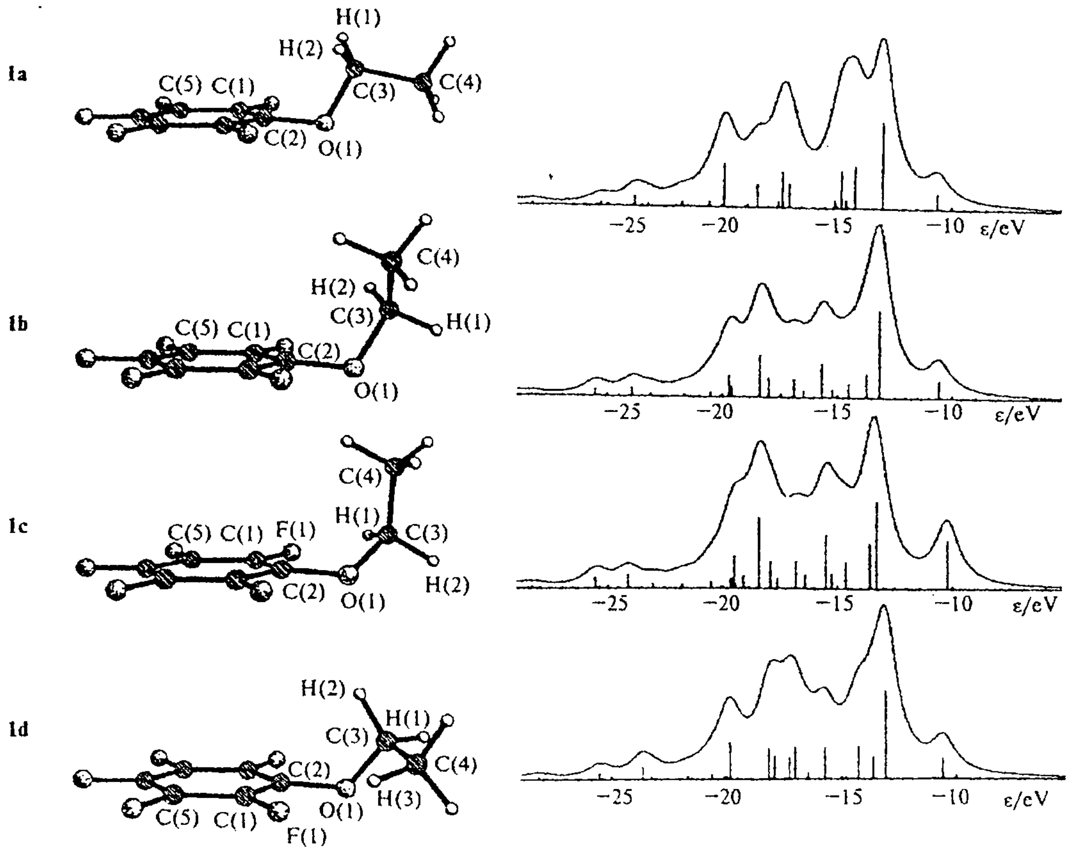

Fig. 1. Structures and theoretical O-Kα spectra of stable conformers of C_6F_5OEt (**1**).

Table 2. Optimized geometric parameters of ethers **1**—**3**

Conformer	Bond length/Å		Angle/deg			
	C(2)—O(1)	O(1)—C(3)	C(1)—C(2)—O(1)	C(2)—O(1)—C(3)	φ_1	φ_2
1a	1.38	1.43	120	113	82	180
1b	1.38	1.42	121	115	78	252
1c	1.37	1.42	124	117	40	262
1d	1.38	1.43	123	116	70	85
2a	1.38	1.43	120	118	86	180
2b	1.37	1.45	118	115	62	21
2c	1.38	1.45	121	114	78	41
2d	1.36	1.44	128	120	10	9
3a	1.38	1.45	120	117	90	180
3b	1.37	1.46	123	117	90	0
3c	1.37	1.46	120	117	76	31

C_6F_5 fragments in all conformers are almost planar with interatomic C—C and C—F distances equal to 1.41 and 1.34 Å, respectively. The O atom is declined from the ring planar by no more than 8°. The parameters determining the position of the O atom relative to the phenyl fragment and R group are presented in Table 2. The C(2)O(1)C(3) plane forms the φ_1 and φ_2 angles with the C_6F_5 plane and the symmetry plane of the alkyl group, respectively.

For molecule **1**, we found four stable structures (see Fig. 1) in which the φ_1 and φ_2 angles differ substantially from 0°. In conformers **1c** and **1d**, the atoms of the Et substituent are arranged in such a way that the H(1) atom of the CH_2 group in the first conformer (**1c**) and

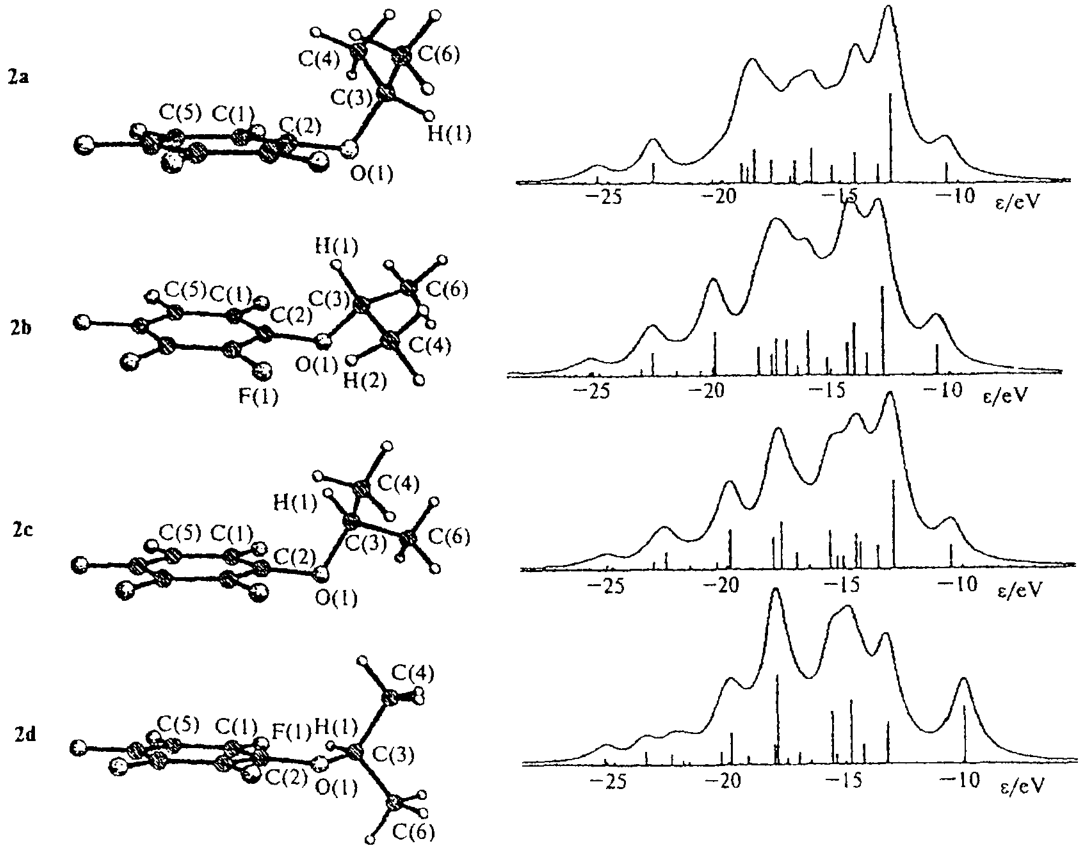

Fig. 2. Structures and theoretical O-Kα spectra of stable conformers of $C_6F_5OPr^i$ (**2**).

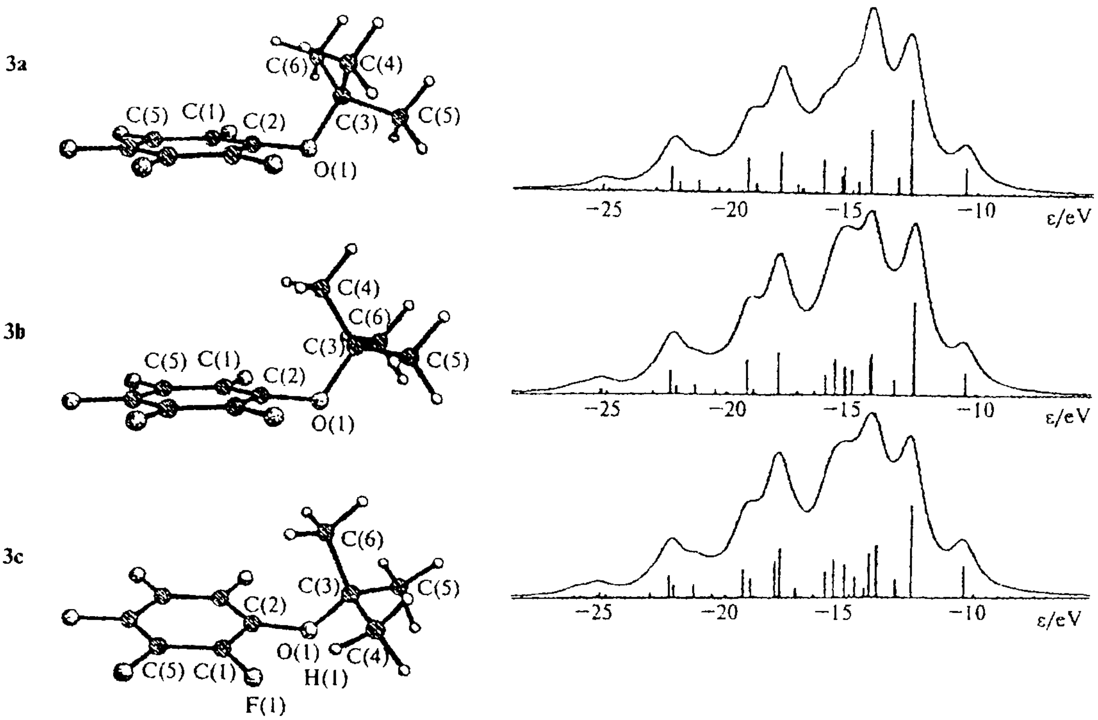

Fig. 3. Structures and theoretical O-Kα spectra of stable conformers of $C_6F_5OBu^t$ (3).

the H(3) atom of the Me group in the second conformer (**1d**) are virtually in the plane of the phenyl fragment, the distance between the H(1) and F(1) atoms in molecule **1c** is 1.88 Å, and the distance between the H(3) and F(1) atoms in molecule **1d** is 1.84 Å.

Four stable conformers of molecule **2** are presented in Fig. 2. In structure **2d**, the torsion φ_1 and φ_2 angles are close to 0°. The C(3) and H(1) atoms of substituent R are arranged almost in the plane of the phenyl ring, and a six-membered cycle is formed. The distance between the H(1) and F(1) atoms is equal to 1.81 Å.

The optimization of the geometry of molecule **3** gave three stable conformers presented in Fig. 3. In structure **3b**, the φ_2 angle is equal to 0°, and the C(5), C(3) (substituent R) and O(1), C(2) (ring) atoms are arranged in the same plane; φ_1 = 90°, *i.e.*, the plane of the C_6F_5 fragment is perpendicular to the local symmetry plane of the R group. Conformer **3c** is less symmetrical as compared to others.

Electronic structure of PFPE. To choose the most preferable molecular structure for our experimental conditions, the O2p-electron density distributions in the valence band were studied for each conformer and compared with the experimental X-ray O-Kα spectra. The theoretical O-Kα spectra of the compounds plotted according to the results of *ab initio* calculations are presented in Figs. 1—3.

The experimental X-ray O-Kα spectra of ethers demonstrate different states of the O atom in the series of compounds studied (Fig. 4). First, the intensity of the short-wave extension *A'* in the spectra increases on going from derivative **1** to **2**. For system **3**, the extension along with the *A* component forms a short-wave shoulder of maximum *B*. Second, the intensity of the *A* maximum decreases and approaches the *B* maximum. Third, in the series of the spectra of PFPE, the *C* maximum is shifted to the short-wave region. It is noteworthy that maximum *W* in the O-Kα spectra is attributed to nondiagram lines and is caused by the manifestation of satellites with multiple ionization in the region of increased efficiency of reflection of the crystal-analyzer RbAP near the O-K-edge of absorption. In order to take into account the influence of satellites on the X-ray emission spectrum, the long-wave part of this band is designated by the dotted line (see Fig. 4).

The best agreement between the theoretical and experimental spectra was obtained for conformers **1a**, **2b**, and **3a** (see Fig. 4). The regular change in charges (according to Mulliken) on the O atom and related C atoms as well as lengths and orders of bonds between O and C_6F_5 and R is observed in the series of PFPE conformers under study (Table 3).

To study in detail the electronic structure of ethers C_6F_5OR, we used fragment analysis. In terms of this method, MO of molecules can be presented as a linear combination of MO of fragments.[7,8] Three fragments were distinguished for molecules considered in this work: C_6F_5, the O atom, and the hydrocarbon substituent R. The results of fragment analysis of conformers **1a**, **2b**, and **3a** are presented in Figs. 5—7. The orbitals affect-

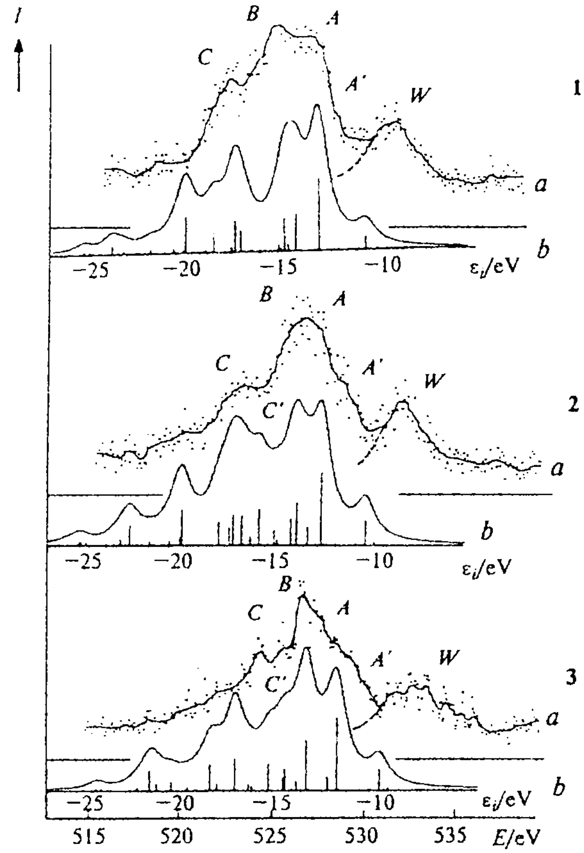

Fig. 4. Experimental emission O-Kα spectra (*a*) and theoretical X-ray spectra (*b*) of C_6F_5OEt (**1**), $C_6F_5OPr^i$ (**2**), and $C_6F_5OBu^t$ (**3**).

Table 3. Results of *ab initio* calculations of PFPE

Conformer	Charge of atom			Bond order	
	O(1)	C(2)	C(3)	O(1)—C(2)	O(1)—C(3)
1a	−0.688	0.285	0.212	0.90	0.68
2b	−0.693	0.296	0.090	0.92	0.66
3a	−0.703	0.269	−0.011	0.92	0.66

ing the formation of the O-Kα spectra of PFPE are considered.

Conformer **3a** is related to the point group of the C_s symmetry, and its symmetry plane coincides with the local symmetry plane of the *tert*-butyl group and is perpendicular to the plane of the C_6F_5 fragment. Conformer **1a**, to some arbitrary extent, can also be related to the point group of the C_s symmetry, and the φ_1 angle in it is close to 90°. For structure **2b**, the degree of deviation from the symmetrical configuration is more significant, but for convenience of comparison of the interaction of the O atom with the C_6F_5 and R fragments in different ethers, MO were also assigned, in this case, to irreducible representations of local point groups of the C_s symmetry. The MO of the C_6F_5 and R fragments corresponded to irreducible representations of local point groups of the C_{2v} and C_s symmetry. The *x* axis is directed along the O(1)—C(2) bond (see Figs. 1—3), the *y* axis is arranged in the plane of the aromatic ring, and the *z* axis is perpendicular to this plane. The $2p_x$- and $2p_z$-AO of oxygen can participate in σ-coupling with the C_6F_5 and R fragments, and $2p_z$-AO can conjugate with the π-system of the fluorinated ring. The axis of the orbital of the LEP of the O atom in the conformers considered is perpendicular to the C(2)O(1)C(3) plane and directed along the *y* axis in the system of coordinates chosen.

In the diagrams (see Figs. 5—7), the energy levels of $2p_y$-AO of the O atom and $10b_2$- and $9b_2$-MO of the C_6F_5 fragment are arranged in the left part. These orbitals, interacting with each other and orbitals of the a″ symmetry of the R substituent, compose the MO system of ether and are transformed by the irreducible representation a″. The levels of $2p_z$-AO of the O atom and $5b_1$-, $4a_2$-, $4b_1$-, and $11a_1$-MO of the C_6F_5 fragment are arranged in the right part of the diagrams. These MO, excluding $4a_2$, interact with $2p_z$-AO of the O atom and orbitals of the R substituent, mainly of the a′ symmetry, and compose the MO system of ether transforming by the irreducible representation a′. The figures above thin lines indicate the percentage participation of the specified MO of the fragment in the formation of MO of C_6F_5OR. Contributions of less than 4% are not marked in the diagrams.

The $2p_z$-AO of the O atom, interacting with the $5b_1$-MO of the C_6F_5 fragment, contributes to the HOMO of ethers. The *A′* maximum, which can be compared to the short-wave *A′* extension in the experimental O-Kα spectra, corresponds to the X-ray transition from this MO to the 1s-AO of the O atom in the theoretical spectra. The intensity of the *A′* maximum for compounds **2** and **3** is somewhat higher than that for **1**, which is reflected in the experiment. The degree of participation of the $2p_z$-AO of the O atom in the formation of HOMO in PFPE depends only on the position of the O—R bond relative to the plane of the benzene ring. The interaction of the $2p_z$-AO of the O atom with the $5b_1$-MO of the C_6F_5 fragment is maximum when the C(3) atom of the R substituent is localized in its plane, as, *e.g.*, in conformer **2d** (see Fig. 2). The $4a_2$-MO of the C_6F_5 fragment remains "antibonding" and only somewhat changes its energy in the C_6F_5OR molecule.

The π-type molecular orbitals next in energy (16a″, 17a″, and 19a″ of molecules **1**, **2**, and **3**, respectively) are antibonding relative to the interactions of the $2p_y$-AO of the O atom and MO of the R substituent (see Figs. 5—7). The *A* maxima in the O-Kα spectra of ethers correspond to the X-ray transitions from these MO. In this case, MO 15a″, 16a″, and 18a″, to which MO of the C_6F_5 fragment makes a minor (5%) contribution, are bonding. The *B* maxima in the O-Kα spectra

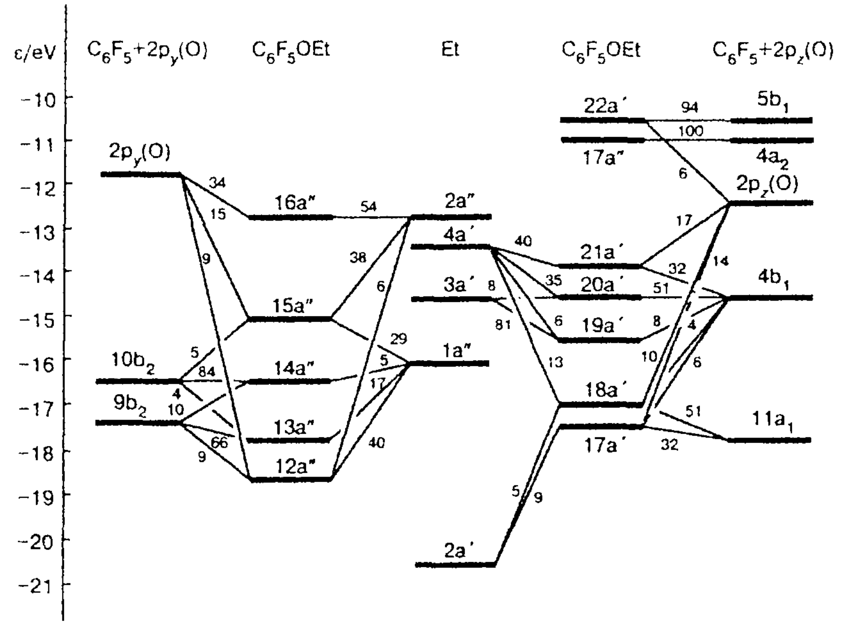

Fig. 5. Diagram of interactions of MO of the C_6F_5 and Et fragments and 2p-AO of the O atom in the C_6F_5OEt molecule.

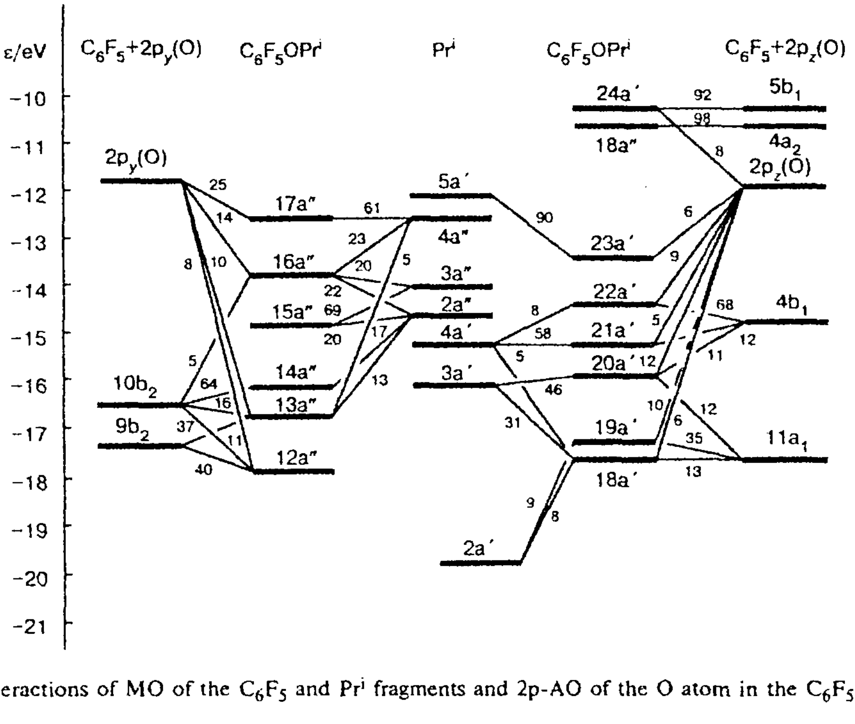

Fig. 6. Diagram of interactions of MO of the C_6F_5 and Pr^i fragments and 2p-AO of the O atom in the $C_6F_5OPr^i$ molecule.

of ethers correspond to the X-ray transitions from these MO. The MO of the a′ symmetry also participate in the formation of the *B* band: for molecule **1**, MO 21a′, for **2**, MO 23a′ and 22a′, and for **3**, MO 24a′ and 23a′.

Despite the fact that the *B* maximum corresponds to X-ray transitions from the group of MO and the *A* maximum corresponds to the transition from one MO, the distance between these maxima depends on the difference between the energies of MO 16a″ and 15a″ (for compound **1**), MO 17a″ and 16a″ (**2**), and MO 19a″ and 18a″ (**3**). As has been mentioned, the interaction of the LEP of the O atom with mainly R corresponds to these MO. The greater stabilization of the 15a″-MO of compound **1**, as compared to the 16a″-MO of derivative

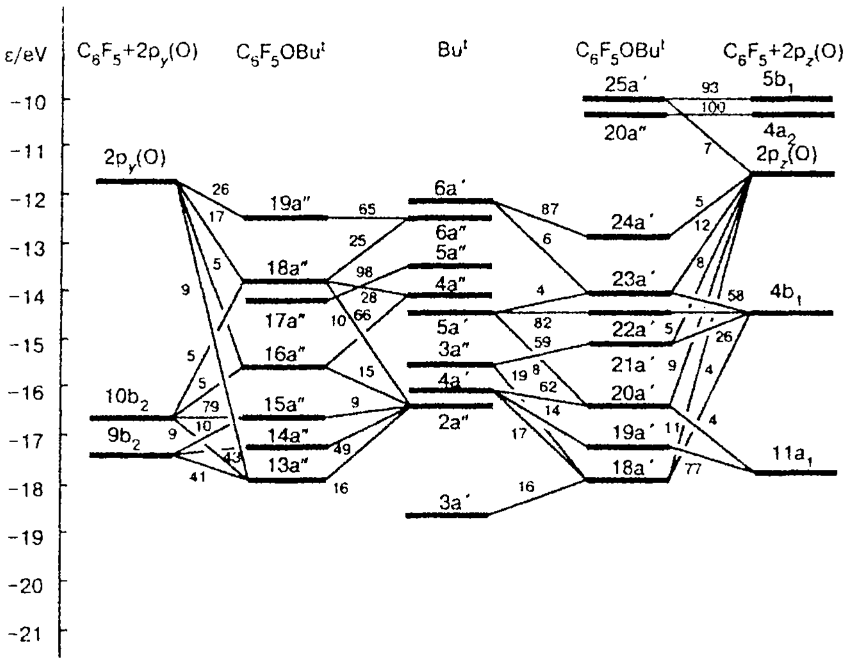

Fig. 7. Diagram of interactions of MO of the C_6F_5 and Bu^t fragments and 2p-AO of the O atom in the $C_6F_5OBu^t$ molecule.

2, is due to the fact that the 1a"-MO of the Et fragment participates in the formation of the first MO, and it has a considerably lower energy than MO 3a" and 2a" of the $CHMe_2$ group, which contribute to the MO 16a" of molecule 2. This is reflected in the experimental spectra of the two ethers under study (approach of the *A* and *B* maxima) and is the result of an increase in the number of atoms in the hydrocarbon substituent and, as a consequence, the appearance of contributions to its MO of additional orbitals, which can be mixed according to the π-type with the 2p-AO of the O atom.

In the theoretical O-Kα spectrum of derivative 3, unlike the spectra of other ethers, the *B* maximum is more intense than the *A*. This is due to the fact that the energies of MO 18a" and 23a' of molecule 3 corresponding to the *B* maximum are almost equal. At the same time, the *A* maximum is broader, since it is related to two MO: 19a" and 24a". Thus, in the experimental spectrum of compound 3, the *A* maximum can be observed as a short-wave shoulder of the *B* maximum.

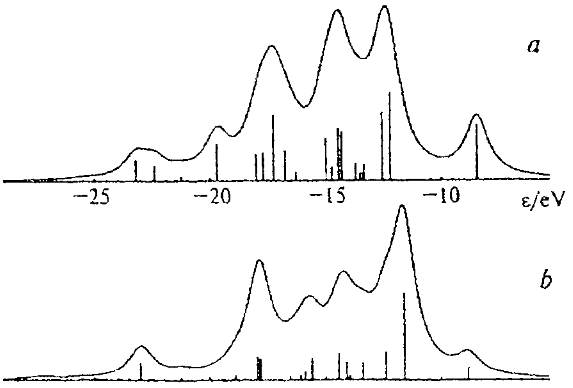

Fig. 8. Theoretical O-Kα spectra of "planar" (*a*) and "nonplanar" (*b*) conformers of the $PhOPr^i$ molecule.

The *C* maximum in the O-Kα spectrum of ether 1 corresponds to the X-ray transitions from MO 18a' and 17a', which are formed with participation of the 11a'-MO of the C_6F_5 fragment, $2p_z$-AO of the O atom, and MO 4a' and 2a' of the Et group (see Fig. 5). These MO can be compared (by the character of interactions between fragments of the molecule) to MO 19a' and 18a' of compounds 2 and 3 (see Figs. 6 and 7). The energies of these MO in the ether series remain almost unchanged and range within −(17—18) eV. The short-wave shift of the *C* maximum in the experimental spectra can be assigned to the appearance of the *C'* maxima in the theoretical spectra of conformers **2b** and **3b**.

The *C'* maximum in the theoretical O-Kα spectrum of compound 2 is localized at −16.5 eV in the energy scale and corresponds to the transitions from MO 13a" and 20a'. In the spectrum of molecule 3, the *C'* maximum is localized at −15.5 eV and corresponds to the transitions from MO 21a', 20a'; and 16a". The appearance of these maxima is associated with additional contributions of the 2p-AO of the O atom to MO of ethers. The additional interactions between O, R, and C_6F_5 occur due to an increase in the number of MO in the Et, Pr^i, and Bu^t series.

The study of several PFPE confirmed that these compounds have "nonplanar" conformations. The search for stable structures for derivative **2** gave the conformer in which the C(3) atom of the hydrocarbon substituent is located in the plane of the fluorophenyl ring. This conformer (**2d**), according to the nonempirical calculations (see Table 1), has the highest total energy (E^{total}) among conformers of compound 2.

The total energy of a molecule can be presented as the sum of electron (E^{el}) and nuclear (E^{nuc}) interactions. A lower E^{nuc} component and a higher E^{el} component correspond to structure **2d** compared to **2a—c**. This implies that the "planar" molecular conformation exhibits a gain in the nuclear contribution and a loss in the electron contribution, and the latter is more substantial. Therefore, the more efficient electron interaction is the reason for the stabilization of PFPE in "nonplanar" conformations.

Electron components of interactions in substituted benzenes can be divided into two types (σ and π). In conformer **2d**, the LEP is localized on the $2p_z$-AO (on the $2p_y$-AO in structures **2a—c**). As a consequence, the O atom can interact more efficiently with the fluorophenyl π-system, which appears as an increase in the contribution of its 2p-AO to HOMO of the molecule (see Fig. 2, conformer **2d**). In the planar structure, the efficiency of the σ-interaction of the $2p_y$-AO of the O atom with the C_6F_5 fragment increases. In the theoretical spectrum, it appears as a decrease in the contributions of the 2p-AO of the O atom in MO of the σ-type (see Fig. 2). It follows from the results of fragment analysis of conformer **2d** that the interaction of the 2p-AO of the O atom with π-MO $5b_1$ and $4b_1$ of the C_6F_5 fragment increases, and that with σ-MO $10b_2$, $9b_2$, and $11a_1$ it decreases. Since it follows from the structural and calculated data that the PFPE molecules have "nonplanar" conformations, it can be concluded that electron interactions in the σ-system of these compounds are more efficient than in the π-system.

The position of the LEP of the O atom relative to orbitals of the aromatic ring and substituent R results in differences in the electron interactions in "planar" and "nonplanar" conformers. Therefore, hereinafter we consider interactions of precisely the LEP of the O atom with MO of molecular fragments. The reasons for the structural differences between PFPE and their structural analogs were revealed for $C_6F_5OPr^i$ and $PhOPr^i$. The optimization of the geometry of conformers of the $PhOCHMe_2$ molecule similar to structures **2a** and **2d** and the corresponding *ab initio* calculations in the 6-31G basis set were performed by the PM3 method. The theoretical O-Kα spectra of these conformers are presented in Fig. 8. According to the data of the PM3 method, the "planar" structure of $PhOPr^i$ is more stable.

In order to understand why pentafluorophenyl ether is more stable in the "nonplanar" form and its hydrocarbon analog is more stable in the "planar" form, changes in the electronic structure of the molecule upon replacement of H atoms by F atoms should be revealed. The replacement results in the separation in energy of the higher π- and σ-orbitals of the benzene ring ("perfluoro-effect").[9] According to the X-ray electron, photoelectron,[10] and calculated data, the charge on the O atom also changes, resulting in an increase in the ionization potential (IP) of the orbital of its LEP. However, these changes are insufficient for the "nonplanar" conformer to make it preferable. For example, phenol and pentafluorophenol molecules exist in planar conformations. The interaction of the LEP of the O atom with the hydrocarbon substituent substantially affects the geometric structure of ethers.

According to quantum-chemical calculations, in the planar conformer of $PhOPr^i$, the orbital of the LEP is localized between the π-MO of the benzene ring and is substantially higher than MO of the R fragment. The IP of the orbital, which has the maximum contribution from the 2p-AO of the O atom, is 12 eV for $PhOPr^i$. The orbital of the LEP of the O atom in the planar conformer of **2d** is energetically lower than the MO of the R fragment, which can interact with it. Due to this interaction, the IP of the orbital with the maximum contribution of the 2p-AO of the O atom is in the region of 17—18 eV. This MO reflects π-conjugation between C_6F_5, O, and R. The contribution of orbitals of the C_6F_5 fragment to this MO is low, due to which the efficiency of interaction over the π-system between RO and C_6F_5 is low. The energy gain is achieved when the molecule is transformed into the "nonplanar" conformer in which the orbital of the LEP of the O atom interacts efficiently with MO of the ring and R substituent arranged in the σ-plane of the system.

The theoretical O-Kα spectra of "nonplanar" conformers of $PhOPr^i$ (see Fig. 8) and **2a** (see Fig. 2) resemble each other both in the number of bands and their relative intensity. Therefore, the electron states of the O atom in these structures are close. This is explained by the fact that in both cases, the orbital of the LEP of the O atom is arranged energetically higher than all MO of the σ-type of the ring and hydrocarbon substituent. The IP of the orbital with the maximum contribution of the 2p-AO of the O atom for these molecules is in the region of ~11—12 eV.

Thus, a more efficient interaction of the orbital of the LEP of the O atom with σ-MO of the ring and substituent is one of the reasons for the high stability of "nonplanar" conformers of PFPE, unlike their hydrocarbon analogs. The parameters of σ-bonds in PFPE and their hydrocarbon analogs are similar, whereas a considerable difference is observed for π-conjugation. An unwarranted high IP related to orbitals of the LEP of O atoms should be observed for planar structures of PFPE.

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