The electronic structure of the $C_6F_6$ and $C_6F_5NO_2$ molecules has been investigated on the basis of data from X-ray emission spectroscopy and MNDO calculations. A fragment-by-fragment analysis of their $\pi$ systems has been carried out. It has been shown that the fluorine $2p_{\pi}$ AOs interact not only with the occupied $\pi$ orbitals of the benzene ring, but also with orbitals which were vacant in the hydrocarbon analogs. The quantum-chemical calculations point out an increase in the effectiveness of the $\pi$ interaction of the NO$_2$ group with the aromatic ring upon the transition from nitrobenzene to pentafluoronitrobenzene.

The introduction of fluorine atoms into the benzene ring causes the appearance of a number of peculiarities in the chemical behavior of polyfluorinated aromatic compounds in comparison to the hydrocarbon analogs. The need to understand these peculiarities prompted the performance of investigations involving detailed studies of the electronic structure of polyfluorinated derivatives of benzene.

It was concluded on the basis of data from the F K$_\alpha$ spectra of fluorinated aromatic compounds [1] that the contribution of the fluorine $2p_{\pi}$ AO's to the upper $\pi$ MO's is small and that the main interaction of the fluorine $2p$ AO's with the MO's of the benzene ring is realized by means of the deep $\pi$ and $\sigma$ levels. It was shown in [2, 3] that the efficiency of the interaction of the nonbonding electron pairs of the heteroatomic SR and PR$_2$ substituents in a polyfluorinated benzene ring with its $\pi$ system is reduced in comparison to the hydrocarbon analogs. Nevertheless, it is very interesting to reveal the laws governing the interaction of the $\pi$ system of a polyfluorinate benzene ring with substituents whose $\sigma$ orbitals are at significantly deeper positions along the energy scale than the highest filled level of hexafluorobenzene. The elucidation of the structure of the chemical bond in hexafluorobenzene is also of interest for understanding the "perfluoro effect," i.e., the preferential stabilization of the $\sigma$ levels in comparison to the $\pi$ system upon the transition from aromatic compounds to the polyfluorinated analogs, which is known from photoelectron-spectroscopic data [4, 5].

The purpose of the present work was to investigate the electronic structure of hexafluorobenzene and pentafluoronitrobenzene on the basis of data from X-ray and X-ray photoelectron spectroscopy and semiempirical quantum-chemical calculations.

EXPERIMENTAL

The O K$_\alpha$, C K$_\alpha$, and F K$_\alpha$ X-ray spectra were obtained on a Stearat ultralong-wavelength X-ray spectrometer. Single crystals of salts of organic acids (2d = 26.6 and 52.4 Å) and mica and its cleavage plane (2d = 19.9 Å) served as the dispersing elements. The radius of the Rowland circle was 0.25 m. The resolution of the spectrometer in the regions of the O K$_\alpha$ and C K$_\alpha$ spectra was no poorer than 0.3 eV, and in the region of the F K$_\alpha$ spectrum it was...
no poorer than 0.5 eV. The X-ray spectra of the gaseous substances were obtained by the electron impact method. The energy of the electrons was 3-4 keV, the current was 0.5 A and the pressure of the vapor in the flow was \( \sim 0.5 \) torr. The C K\( \alpha \) spectra were obtained according to the method described in [6]. Some difficulties appeared during the treatment of the C K\( \alpha \) spectra of the polyfluorinated aromatic compounds. It was found that the intensity of the first maximum in the C K\( \alpha \) spectrum of the C\( _6 \)F\( _5 \)NO\( _2 \) molecule (\( E_{hv} = 285 \) eV) depends on the energy of the exciting electrons and is minimal when the energy of the electrons is greatest (Fig. 1).

When the energy of the electrons was increased to 8-10 keV, the intensity of the X-ray lines decreased only slightly despite the decrease in the cross section for the interaction of the electron with the atoms, since there was additional excitation of the emission by the bremsstrahlung of the copper anode, which was noted at a distance of \( \sim 10 \) mm from the center of the flow. In the case of fluorescence excitation, the contribution of the satellites due to multiple ionization to the total emission is known to be minimal. Therefore, the C K\( \alpha \) spectra presented in this communication were obtained with an energy of the electron beam equal to 8 keV. The F K\( \alpha \) spectrum of the solid compound C\( _6 \)F\( _5 \)NO\( _2 \) was obtained by the fluorescence method [7]. The spectra were recorded by a proportional counter filled with methane at a pressure of 0.2 atm. The window of the counter was made from a Mylar film with a thickness of 1 \( \mu \). The intensity of the 0 K\( \alpha \) and C K\( \alpha \) spectra was equal to \( \sim 10 \) counts/sec.