THE INVESTIGATION OF THE ELECTRONIC EFFECTS OF POLYFLUORO-ARYL GROUP BY MEANS OF NMR SPECTROSCOPY

G.G. Furin, A.I. Rezvukhin, G.G. Yakobson
Institute of Organic Chemistry, 630090, Novosibirsk, U.S.S.R.

The relationship between NMR ^{15}N, ^{17}O, ^{31}P, ^{77}Se, ^{13}C spectral parameters and electronic structure of number of polyfluoroaromatic compounds has been discussed. The increase of the nuclei shielding has been found in all classes of investigated polyfluorinated compounds in respect to the corresponding hydrocarbon analogues. That effect has been discussed in terms of decrease of the conjugation between the unshared electron density of heteroatoms and the π-system of polyfluorinated benzene ring. The conductivity of substituent electronic effects on the π-system of the polyfluoroaryl group by the heteroatom has been estimated from NMR ^{13}C data. The sensitivity of nuclei shielding towards interamolecular electronic effects has been noticed to increase from oxygen to selenium and the analysis of the influence of the intramolecular electronic effects on the ^{17}O and ^{77}Se shifts has been given. The influence of the substituents either in pentafluorophenyl ring or adjacent to heteroatom have been shown to correspond those in the hydrocarbon analogues.

The conclusion about the influence of polyfluoroaryl group on the character of bonds between different atoms in functional group has been made from the NMR ^{17}O and ^{15}N data for aromatic nitro-derivatives. Polyfluorophenyl group in respect to phenyl one deshields the oxygen atom and shields the nitrogen atom. The same effect of pentafluorophenyl group has been observed by other spectral methods.

The different screening of ^{17}O, ^{15}N, ^{31}P and ^{77}Se nuclei due to the action of substituents adjacent to the element and variation of the coordination number of heteroatom have been used to the solvation of a number of problems in chemistry of the heteroanalogues of carbenium ions and the detail investigation of the mechanism of electrophylic substitution in the field of polyfluoroaromatic compounds.