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FLUORO EFFECT IN HEAVY NUCLEAR NMR SPECTROSCOPY OF AROMATIC COMPOUNDS

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Substitution of hydrogen atoms in the benzene ring of aromatic compounds containing nitrogen, oxygen, silicon, germanium, phosphorus, selenium, tin or tellurium, by fluorine leads to increased shielding of ^{13}C, ^{15}N, ^{17}O, ^{29}Si, ^{31}P, ^{73}Ge, ^{77}Se, ^{119}Sn and ^{125}Te nuclei, if the corresponding atom is directly bonded with an aromatic group, and to decreased shielding if there is no direct bonding.[1] This phenomenon is called fluoro effect in NMR spectroscopy of heavy nuclei. The increased shielding of the nucleus of the atom in α-position to the aromatic ring on passing from hydrocarbon analogues to polyfluorinated derivatives may be attributed only to its position with respect to the ring and is independent of the atom state of hybridization, the presence of unshared electron pairs in it, or of its participation in the formation of multiple bonds, i.e. of its valence state. This suggests that the fluoro effect for atom A in α-position to the aromatic ring is determinated not by changes in the local terms σ^{d}_{AA} and σ^{p}_{AA}, but by changes in contributions of the ring to shielding of its nucleus, i.e. by changes in the distant effects.[1] The distant effects related to the ring get quickly reduced in space and the nuclei of atoms in β- and γ-positions to benzene ring are insensitive to them; shielding of the nuclei of these atoms is controlled by changes in the local paramagnetic term σ^{p}_{AA}, reflecting the strong electron-accepting ability of the polyfluorinated phenyl groups.