SUBSTITUTENT EFFECTS IN HYDRAZIDES OF FLUOROCARBOXYLIC ACIDS

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Intramolecular interaction in hydrazides of fluorocarboxylic acids, $R_F^1 \text{CON}^1 R^2 N^2 R^3 R^4$ (R_F^1 = fluoroalkyl and pentafluorophenyl substituents, R^2 , R^3 , R^4 = H, Alk) was studied by UV and IR spectroscopy. The long wavelength absorption (230-250 nm) in the UV spectra of alkanefluorocarboxylic acids is mainly caused by electron transitions in N-N-C=0 groups. The absorption corresponds to the p, π -conjugation and interaction of lone electron-pairs in the molecule. Different substitution at nitrogen atoms changes the electron transition energy. The NC=0 band intensity and frequency reflect the change in the resonance interaction in CON group.

The ability of hydrazides to self-association via NH---0=C and NH---N bonds also depends on the substitution in the N-N fragment. A remarkable stability of fluoroacyl- $N_1^1N^2$ -dimethyl-hydrazine associates present as NH---N bonded trimer structures even in the gas phase has been established. At the same time, the relative basicity of the oxygen atom of the compounds studied (Δ VOH) is poorly susceptible towards substitution at the nitrogen atom. The Δ VOH value is considerably lower in fluorocarboxylic hydrazides than that of their non-fluorinated analogs.

The intramolecular mutual effect of C_6F_5 and CONN groups in pentafluorophenylhydrazides manifests itself by lower π -order of the C_6F_5 -CO bond and higher torsion angle 3 as compared with hydrocarbon analogs.