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Spectroscopic and thermal studies on 2- and 4-phenyl-1*H*-imidazoles

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ABSTRACT – The polarized IR spectra of isotopically neat and isotopically substituted monocrystalline samples of 2-phenyl-1*H*-imidazole (2PI) and 4-phenyl-1*H*-imidazole (4PI) were recorded at two temperatures of 293K and 77K. The room-temperature ATR-FTIR and Raman spectra of 2PI and two polymorphic forms of 4PI were also recorded. Theoretical analysis of the vibrational spectra of selected imidazole derivatives reflected similar characteristics of their hydrogen-bond networks and allowed us to obtain the information about the mechanism of the H/D isotopic "*self-organization*" phenomenon. The distribution of protons and deuterons in the lattices of the isotopically diluted crystalline samples of 2PI and 4PI was found to be non-random. In the crystals of the hydrogen- and deuterium-bonded imidazole derivatives the strongest vibrational exciton interactions favored the intrachain ("*tail-to-head*")-type exciton coupling widespread at 77K *via* the π-electrons. At room temperature a weak interchain ("*through-space*")-type exciton coupling was also partially responsible for the IR spectra generation. Differential scanning calorimetry (DSC) measurements showed that the two polymorphic forms of 4PI exhibit an extensive supercooling of crystallization process and cold crystallization on reheating. Additionally, both polymorphic modifications of 4PI are monotropically related. 2PI exhibits only the crystallization and melting processes.

KEYWORDS: Hydrogen bond; Polarized IR spectra; H/D exchange; Supercooling; Polymorphism.

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