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Competitive Hydrogen Bonding and Unprecedented Polymorphism in Selected Chiral Phosphorylated Thioureas

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Abstract

New racemic and enantiopure N-phosphorylated thioureas bearing 1-phenylethyl or tetrahydronaphthalenyl fragments were synthesized. According to NMR data assisted by DFT calculations, the preferred conformation is stabilized by an intramolecular hydrogen bond. This form in solution is in equilibrium with dimeric N-H···S hydrogen-bonded associates, the population depending on the concentration. In the crystalline phase the low-energy conformation with an intramolecular H-bond is realized only in the racemic tetrahydronaphthalenyl derivative. In most crystals various types of intermolecular hydrogen bonding are observed, accompanied by the formation of infinite linear chains or helical structures. Due to the conformational lability of compounds and competitive intermolecular H-bonding, multiple polymorphic modifications are formed. Therefore, crystallization of enantiopure 1-phenylethyl derivatives from various solvents results in concomitant polymorphs at room temperature. One of them undergoes reversible two-step phase transitions from the high-symmetry I41 space group (Z′ = 1, no disorder) via the P41 space group (Z′ = 6) to the monoclinic P21 space group (Z′ = 16) accompanied by drastic concerted conformational changes. Notably, the optimization of the crystal packing is observed upon phase transitions with a gradual reduction of the void space in the unit cell from 4.5% to 0.8%. This is a rare case of several high-Z′ polymorphs for one compound, with chirality playing an important role.

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