

Planar Chiral Dianthranilide and Dithiodianthranilide Molecules: Optical Resolution, Chiroptical Spectra, and Molecular Self-Assembly

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Planar chiral dianthranilide (**1**) was resolved to enantiomers with use of (–)-(1*S*,4*R*)-camphanoyl chloride as a chiral derivatizing agent. The (+)-**1** enantiomer was assigned the *S* absolute configuration from the X-ray crystal structure of its *N,N*-dicamphanoyl derivative. Optical resolution of dithionodanthranilide (**2**) was accomplished by inclusion crystallization with (*R,R*)-1,2-diaminocyclohexane, and the X-ray structure of the corresponding adduct revealed the (–)-**2** stereoisomer has the *R* configuration. A slow boat-to-boat ring inversion ($\Delta G^\ddagger = 24.1 \pm 0.1$ kcal mol⁻¹) causes racemization of (+)-**1** in solution as manifested by a gradual decrease of the CD spectrum whereas, (–)-**2** is configurationally stable at these conditions. The analysis of the CD spectra of the title compounds showed that the $n-\pi^*$ Cotton effect signs are determined by the helicity of the skewed benzamide and thiobenzamide chromophores. The solid-state structures of the racemic and homochiral forms of **1** and **2** show different self-assembly patterns: the racemate (\pm)-**1** prefers the cyclic $R_2^2(8)$ hydrogen bond motif, whereas the crystalline DMSO solvates of (\pm)-**1** and (+)-**1** consist of 1D homochiral hydrogen-bonded assemblies generated by the C(6) motif. In the case of dithionolactams (\pm)-**2** and (–)-**2** two types of 1D networks were observed: in the racemate they are generated by the centrosymmetric $R_2^2(8)$ and $R_2^2(12)$ hydrogen bond motifs, whereas the molecules in the homochiral crystals are connected solely with use of the strongly nonplanar $R_2^2(8)$ motif.

Introduction

Molecules incorporating two rigidly oriented amide functionalities are attractive building blocks for construction of ordered supramolecular aggregates.^{1,2} The secondary *cis*-amide groups can participate in strong and highly directional complementary intermolecular hydrogen bonding, facilitating formation of well-defined and stable solid-state architectures. Dilactams possessing molecular chirality in addition can serve as models for the investigation

of chirality-directed molecular self-assembly, and several examples of different superstructures generated from homochiral diamides and from their racemic mixtures have been reported.² For example, the molecules of racemic 2,5-diazabicyclo[2.2.2]octane-3,3-dione self-assemble into infinite undulating tapes, whereas the enantiomeric compound forms a 2D hydrogen bond network composed of catemers and cyclic tetrameric motifs in the solid state.^{2a} Whereas quite a lot of work has been done on the supramolecular chemistry of dilactams,^{1,2} no systematic studies of analogous dithionolactams have been reported. As has been shown by Allen et al.³ the directional and acceptor properties of the C=S function differ from those of the C=O group, and therefore, a self-assembly process of dilactams and their dithiono analogues may result in quite different supramolecular architectures.

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