

## Molecular self-assembly and optical activity of chiral thionooxalamic acid esters

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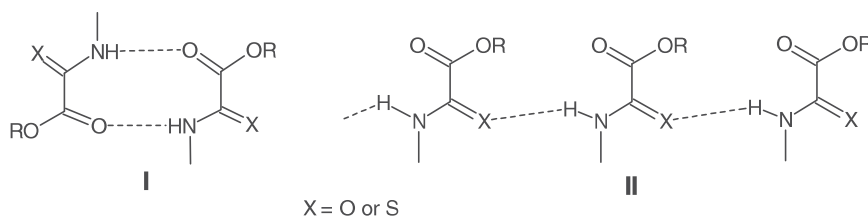
**Abstract**—Three chiral bsthionooxalamides were synthesized by acylation with ethyl or (1*R*)-menthyl chloroacetate of the corresponding diamines and subsequent thionation with Lawesson's reagent. Single crystal X-ray diffraction analysis revealed that products **4b–7b** self-assemble in the solid state by the ring [N–H···O=C,  $R_2^2(10)$ ] or chain [N–H···S=C, C(4)] hydrogen-bond motifs. Only in the case of **4b** was a helical superstructure formed. In racemic compound **6b**, the molecules are connected via N–H···S=C hydrogen bonds into homochiral chains, similar to those formed in **7b**. The solid state CD spectra of chiral bsthionooxalamides are characterized by strong Cotton effects in the region of the thioamide  $n-\pi^*$  transition. Their sign is determined by the helicity of the S=C–C=O unit. © 2007 Elsevier Ltd. All rights reserved.

### 1. Introduction

The construction of complex supramolecular architectures by the self-assembly of a molecular species via weak non-covalent interactions in the solid state is the main goal of crystal engineering.<sup>1</sup> Particularly, attractive targets are helical assemblies that are indispensable structural elements in biological systems. The helical organization of molecules is an ubiquitous phenomenon in Nature and appears to play a critical role in molecular recognition and information storage.<sup>2</sup> In view of the importance of helical chirality as a structural motif, there have been many efforts to introduce helicity into artificial systems.<sup>3</sup> The construction of such systems by self-assembly is a promising alternative to a stepwise covalent synthesis. Among the variety of intermolecular interactions, relatively strong and directional hydrogen bonds appear to be the most important driving force for stabilizing a supramolecular structure.

They can result in the formation of one-dimensional chains or tapes, two-dimensional sheets or layers and various three-dimensional structures.

To explore the possibility of a helix supramolecular architecture, we chose oxalamic esters due to their ability to form self-complementary hydrogen-bonding interactions, motif **I**,<sup>4</sup> very similar to that known for simple oxalamides,<sup>5</sup> which have found wide application as supramolecular building blocks for construction of ordered solid state assemblies,<sup>5,6</sup> *meso*-helicite structures,<sup>7</sup> and gelators yielding thermo-reversible gels.<sup>8</sup> A Cambridge Structural Database (CSD)<sup>9</sup> survey revealed that oxalamic esters also readily form chain motif **II**<sup>10</sup> involving only amide units. In contrast to oxalamides organizing into polymeric tape structures, simple oxalamic acid esters can form only dimers with the use of the hydrogen-bond motif **I**. Thus compounds bearing at least two such functions are required for



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