

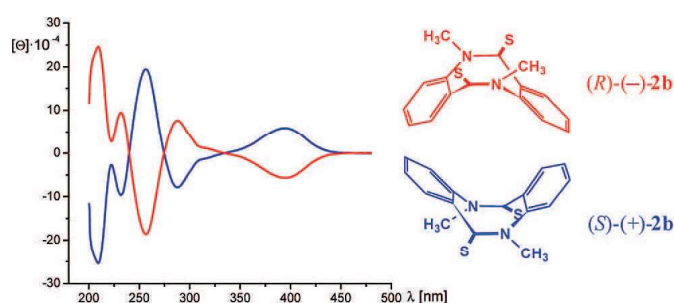
Enantiomeric Resolution of *N,N'*-Dimethyldithiodianthranilide through Diastereomeric Silver(I) Complex. Circular Dichroism Spectra, Racemization Barrier, and Molecular Self-Assembly

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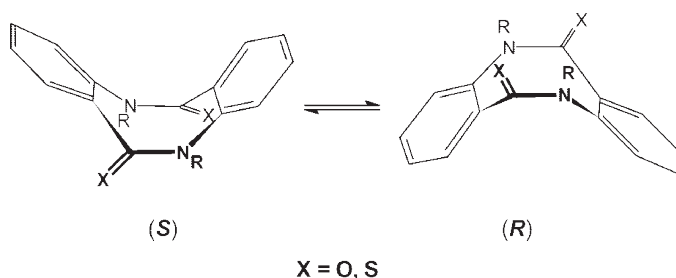


Planar chiral *N,N'*-dimethyldithiodianthranilide (**2b**) was resolved to enantiomers through a diastereomeric complex with easily accessible silver(I) (1*S*)-camphorosulfonate (**3**). The (–)-**2b** enantiomer was assigned the *R* absolute configuration from the X-ray crystal structure of the silver complex. The compound is configurationally stable and its racemization occurs through boat-to-boat ring inversion ($\Delta G^\ddagger = 36.5 \pm 0.2$ kcal mol⁻¹ at 438 K). The analysis of the CD spectrum of the title compound showed that the $n-\pi^*$ Cotton effect sign is determined by the helicity of the skewed thiobenzamide chromophore. The molecules of **2b** are unable to achieve efficient crystal packing by themselves and easily form inclusion complexes with toluene or pentafluorophenol.

Introduction

Dissymmetric concave shape molecules have both theoretical and practical interest as molecular receptors,¹ chiral solvating agents,² chiral modifiers, and catalysts in enantioselective reactions³ and as molecular building blocks in the construction of new functional materials.⁴ A well-known example is Tröger's base and its analogues used for the construction of a number of

SCHEME 1



chiral host systems for molecular recognition studies.⁵ Structurally related dianthranilide {dibenzo[*b,f*][1,5]diazocine-6,12(*5H*,11*H*)-dione} (**1a**) and its dithiono analogue (**2a**) are inherently chiral (planar chirality)⁶ compounds with the unique V-shaped geometry. Two enantiomeric forms may interconvert through a slow boat-to-boat ring inversion process (Scheme 1). Although

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