

Generation of chirality in 4,4'-azopyridine by co-crystallization with optically active dicarboxylic acids

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ABSTRACT

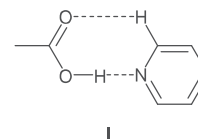
The co-crystals of *anti*-4,4'-azopyridine **apy** with optically active 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid **1** and *trans*-1,2-cyclohexanedicarboxylic acid **2** were prepared and their solid state CD spectra were measured. The positive Cotton effect sign, corresponding to the lowest energy $n-\pi^*$ transition, was correlated with the *M* helicity of the twisted Ar-N=N chromophore. The absolute sense of the twist of the guest **apy** molecule was deduced from the X-ray structures of the (*S,S*)-**1-apy** and (*S,S*)-**2-apy** complexes.

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1. Introduction

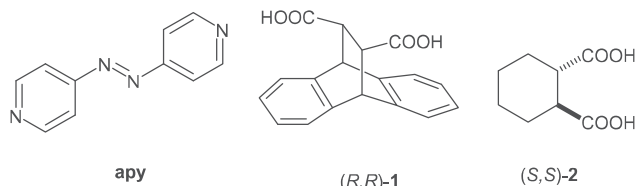
A phenomenon of induced optical activity arises when an achiral guest molecule is complexed by a chiral host. The guest becomes optically active due to a dissymmetry created by a chiral environment or generation of an excess population of two rapidly interconverting chiral conformers.¹ An asymmetric perturbation of the chromophore leads to induced circular dichroism (ICD), whose magnitude depends on the mutual arrangement of the host and guest molecules.² Optical activity can be induced upon dissolution of an achiral solute in a chiral solvent or by inclusion complexation of an achiral guest in the cavity of a chiral host. One well-known example is ICD observed in symmetric cyclohexanones, benzophenone, or azo dyes upon complexation with cyclodextrins.^{3,4} Solid state CD measurements of crystalline inclusion complexes in combination with X-ray studies have recently emerged as an exceptionally useful technique for the elucidation of the mechanisms of induction of optical activity.^{5,6} In particular, crystal lattices of naturally occurring cholic and deoxycholic acids are able to accommodate many types of organic guest molecules that make them versatile hosts for ICD studies.⁶ Recently, we have shown that the *anti*-azobenzene trapped in the crystal lattices of these bile acids exhibits strong CD in the region of the $n-\pi^*$ electronic transition.⁷

Azo dyes, particularly azobenzene, undergo a photoinduced *syn-anti* isomerization that is responsible for their potential application in optical switches and sensors, reversible data storage,⁸ photoreversible supramolecular systems,⁹ or liquid crystalline polymers.¹⁰ Control of supramolecular chirality is often a decisive factor in molecular recognition, assembly, or catalysis. In this context, we explored the new possibility of inducing optical activity by using supramolecular hydrogen-bonded assemblies of *anti*-4,4'-azopyridine **apy** with optically active dicarboxylic acids **1** and **2**. The motivation for this study was that the pyridine unit can form a stable cyclic hydrogen bond motif **I**.¹¹ Herein, we report X-ray studies of the co-crystals **1** and **2** with **apy** and their solid state CD spectra.



2. Results and discussion

The reported procedures for the asymmetric synthesis or chiral resolution of **1** are rather elaborate and suffer from low yields.¹² We found that the racemic acid **1** can be easily resolved to its enantiomers via the use of the diastereomeric cinchonine salt. Acid **2** was resolved with quinine according to the literature method.¹³ Diffraction quality co-crystals of **apy** with optically active dicarboxylic acids **1** and **2** were grown from ethanol at ambient temperature using a 1:1 molar ratio of components. The X-ray structure of the complex (*S,S*)-**1-apy** revealed that the crystals (space group $P2_12_12_1$) are built of polymeric zig-zag chains with the alternating component molecules connected by strong O-H...N hydrogen



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