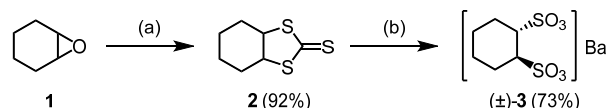


Starting from cyclohexene, a five step synthesis of enantiomerically pure 1,2-cyclohexanedisulfonic acid was developed. The key step of this sequence was the formation of a cyclic trithiocarbonate intermediate, which could directly be oxidized to the corresponding racemic acid. Optical resolution with optically active 1,2-diaminocyclohexane in two additional steps led to enantiomerically pure product in good yield. The solid state structures of racemic and optically active potassium salts show significant differences.

Synthesis of racemic 1,2-cyclohexanedisulfonic acid

Since the relative configuration of trithiocarbonate **2** was established to be *trans* by X-ray crystallography we considered it to be a convenient starting material for the synthesis of racemic disulfonic acid **5**. Preparation of the intermediate product **2** from cyclohexene oxide (**1**) and CS₂ was already reported in the literature^[1] and succeeded in good yields. Direct oxidation to the corresponding sulfonic acid proceeded by an excess of H₂O₂. Barium sulfonate was precipitated by addition of BaCl₂ and removed from the mixture. Further treatment with BaCl₂ furnished the barium salt (\pm)-**3** in 73% yield.



Scheme 1. Synthesis of the racemic barium salt (\pm)-**3**. Reagents and conditions: (a) 3.0 eq. CS₂, 2.5 eq. KOH, MeOH, 23°C, 4 h; (b) 1. 20 eq. H₂O₂ (30% in H₂O), AcOH, 23°C, 20 h; 2. 1.9 eq. BaCl₂ · 2 H₂O.

Solid state structures of potassium salts

Treatment of the free acids **5** with KHCO₃ led to crystalline materials suitable for X-ray single structure analysis. The structure of racemic coordination polymer K₂[(\pm)-1,2-CDS] is shown in Figure 2. A significant difference between the crystal structures of racemic and optically active coordination polymer K₂[(+)-1,2-CDS] (Figure 3) can be observed. While the racemic structure is built of one-dimensional chains the enantiomerically pure structure shows a three-dimensional architecture with channels inside.

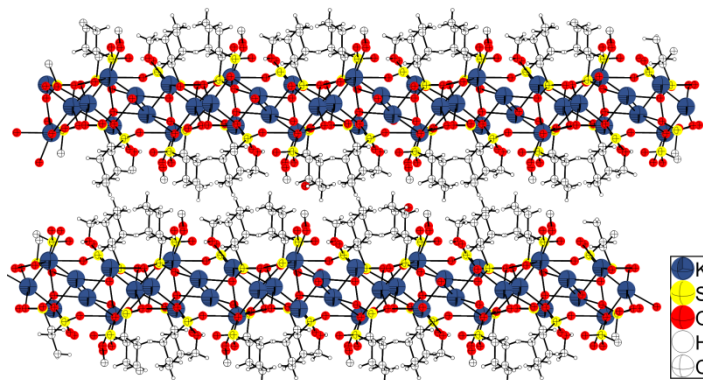
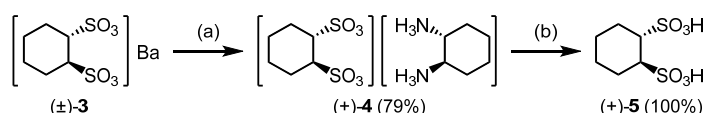


Figure 2. Racemic structure K₂[(\pm)-1,2-CDS].

Optical resolution

Resolution of racemic 1,2-cyclohexane disulfonic acid **5** was accomplished via the ammonium salt. Ba-salt (\pm)-**3** was protonated with ion exchange resin Amberlyst 15 and then treated with (–)-(*R,R*)-1,2-diaminocyclohexane. The resulting diammonium salt (+)-**4** was recrystallized. The absolute configuration of the sulfonate could be established to be (*S,S*) by X-ray crystallography since the absolute configuration of the amine was known (Figure 1). The free acid (+)-**5** was obtained as the dihydrate by protonation of compound (+)-**4** with Amberlyst 15 and evaporation of water.



Scheme 2. Resolution of *trans*-cyclohexanedisulfonic acid **3**. Reagents and conditions: (a) 1. Protonation with Amberlyst 15; 2. 0.4 eq. (–)-(*R,R*)-1,2-cyclohexanediamine; (b) protonation with Amberlyst 15.

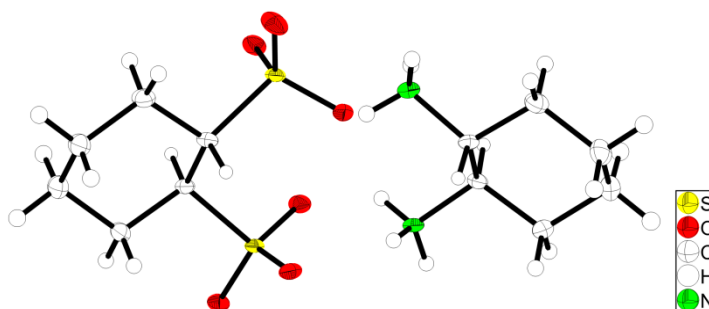


Figure 1. Structure of diammonium salt (+)-**4**.

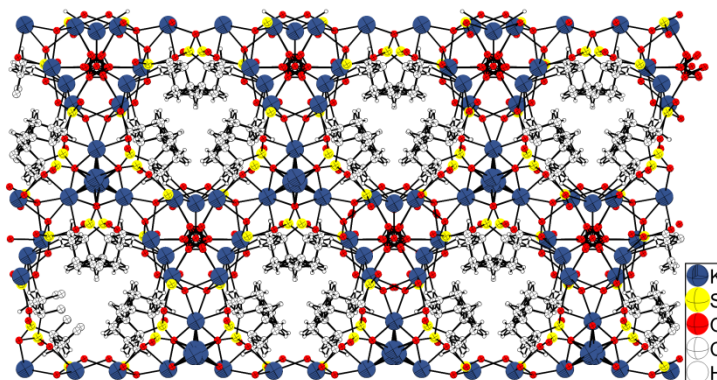


Figure 3. Optically active structure K₂[(+)-1,2-CDS].