

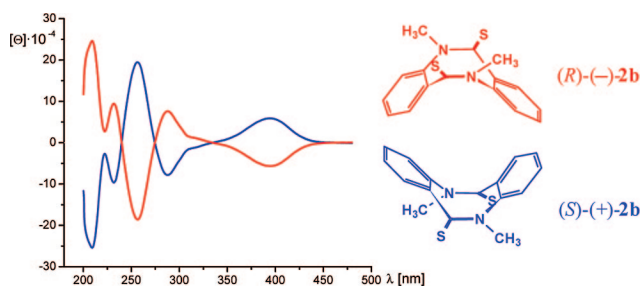
Enantiomeric Resolution of *N,N'*-Dimethyldithiodianthranilide through Diastereomeric Silver(I) Complex. Circular Dichroism Spectra, Racemization Barrier, and Molecular Self-Assembly

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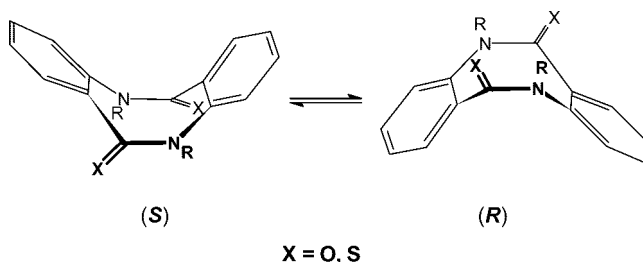


Planar chiral *N,N'*-dimethyldithiodianthranilide (**2b**) was resolved to enantiomers through a diastereomeric complex with easily accessible silver(I) (*1S*)-camphorosulfonate (**3**). The (–)-**2b** enantiomer was assigned the *R* absolute configuration from the X-ray crystal structure of the silver 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– π^* 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



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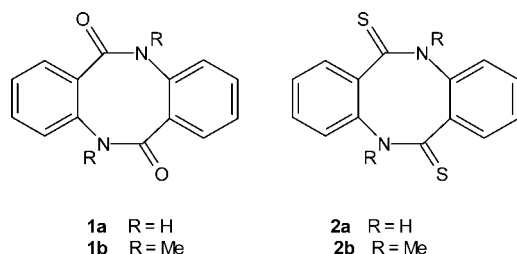
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chiral host systems for molecular recognition studies.⁵ Structurally related dianthranilide {dibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dione} (**1a**) and its dithiono analogue (**2a**) are inherently chiral (planar chirality)⁶ compounds with the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

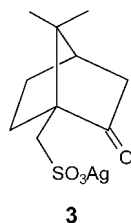
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these compounds are not conformationally locked as Tröger's bases the barriers to ring inversion are sufficiently high (24.1 kcal/mol for **1a** and well over 26 kcal/mol in the case of **2a**) to permit isolation of enantiomers at ambient temperature.⁷ We have recently described the enantiomeric resolution of both compounds.⁷ The dilactam **1a** is configurationally labile and racemized in solution during 24 h (showed a half-life for racemization of 6 h) at 21 °C, whereas the dithiolactam **2a** appeared to be configurationally stable.



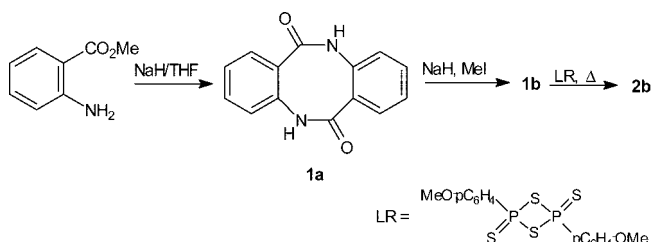
Since thioamides are important class of ligands in coordination chemistry,⁸ the optically active bidentate ligands (bifunctional compounds), like **2a**, offer a considerable potential for construction of chiral coordination polymers, nonlinear optical materials, enantioselective catalysts, or sensors. However, very low solubility of **2a** in majority of organic solvents is a serious obstacle for its intended use, and for this reason, we turned attention to its *N,N*-dimethyl derivative **2b**. Unfortunately, there is no generally applicable method for the *N*-alkylation of thioamides and the optically active compound **2a** cannot be used for preparation of **2b**. Alkyl halides and other alkylating agents react at the S-atom of thioamides to yield *S*-alkylthioimidolium salts.⁹ Similarly, the benzotriazole mediated alkylation methodology proposed by Katritzky et al. is limited to primary thioamides.¹⁰ Thus, the only alternative to the alkylation reaction remains optical resolution of the racemate (\pm)-**2b**. Here we describe a simple method of resolving (\pm)-**2b** through diastereomeric complex with easily accessible silver(I) (1*S*)-camphorsulfonate (**3**) and assignment of the absolute configuration to each optical isomer. In addition, we examine their circular dichroism (CD) spectra and the crystal structures that show their self-assembly mode in the solid state.



Results and Discussion

Optical Resolution. The racemic compound (\pm)-**2b** was obtained by *N*-methylation of dianthranilide (**1a**)¹¹ with methyl

SCHEME 2



iodide followed by thionation with Lawesson's reagent (Scheme 2).¹² The optical resolution of compounds devoid of any additional functional groups always is challenging from an experimental point of view. Since the geometric features of the molecules **2b** ("roof-shaped" structure)¹³ make their efficient packing difficult in the crystal we expected that the separation of enantiomers would be possible by the inclusion crystallization of the racemate with optically active hosts. However, initial attempts of cocrystallization of (\pm)-**2b** with bile acids¹⁴ or TADDOLs¹⁵ were wholly unsuccessful. Thus, bearing in mind good ligand properties of thioamides,⁸ an alternative route of resolution could be an incorporation of **2b** into a diastereomeric metal complex. Chiral platinum or palladium complexes have been used for separation of racemic alkenes,^{16a,b} tertiary phosphines,^{16c} or sulfoxides.^{16d} Since thiocarbonyl ligands are very soft bases and, on the other hand, silver(I) ions can be regarded as extremely soft acids,¹⁷ we tried complexation of (\pm)-**2b** with silver(I) salts of optically active acids. In contrast to photosensitive and insoluble silver salts of carboxylic acids, silver sulfonates are stable and generally well soluble in polar solvents like water, alcohols or acetonitrile. Thus, we chose silver (1*S*)-camphorsulfonate (**3**) that can be easily prepared from (1*S*)-camphorsulfonic acid and silver oxide. Treatment of (\pm)-**2b** with **3** in a 1:2 molar ratio in a mixture of CH₂Cl₂ and acetonitrile afforded a crystalline silver complex in 51% isolated yield. Initially, we attempted to regenerate the optically active ligand (–)-**2b** from the Ag complex by treatment with aqueous sodium sulfide. However, the product was always contaminated with traces of colloidal silver sulfide.

Therefore, bearing in mind a strong affinity of silver to thiosulfate anions,¹⁸ we developed a much simpler and effective procedure for isolation of (–)-**2b** by treatment of the complex with aqueous sodium thiosulfate. It afforded the product with

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FIGURE 1. Photograph of the enantiomer (yellow) and racemate (dark) crystals of **2b**.

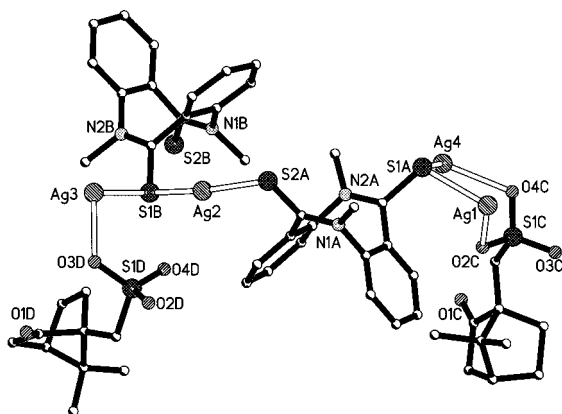


FIGURE 2. Molecular structure of the 1:2 complex of $(-)$ -**2b** with **3**. Hydrogen atoms are omitted for clarity.

$[\alpha]_D^{20}$ -865 (c 1, CH_2Cl_2) and the high optical purity ($ee > 97\%$ determined by ^1H NMR with use of (S) - $(+)$ -2,2,2-trifluoro-1-anthrylethanol as a chiral solvating agent). It means that the deposited crystals of the Ag complex contained only one diastereomer and that almost complete resolution can be reached after a single crystallization. Furthermore, the second diastereomer did not crystallize from CH_2Cl_2 . Thus, the workup of the mother liquor with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ gave the enantiomer $(+)$ -**2b**. It was not optically pure but after crystallization from CH_2Cl_2 –hexane and a manual picking the large prismatic crystals of the racemate from the needles of the enantiomer it had $[\alpha]_D^{20}$ $+874$ (c 1, CH_2Cl_2). Fortunately, a differentiation between the crystals of the enantiomer and racemate is very easy because they differ not only in shape but also in color since the racemate in contrast to enantiomer is sensitive to light and rapidly becomes dark at the daylight (Figure 1).

The absolute configuration of the coordinated ligand $(-)$ -**2b** was assigned to be *R* based on the X-ray crystal structure of the silver complex (Figure 2). In the triclinic crystal, four symmetry-independent silver(I) atoms, four (1*S*)-camphorsulfonate anions, and two (*R*)-**2b** ligands are assembled into a 2D polymeric structure. The core of the polymer constitutes metal ions coordinated by the sulfur atoms of the bridging (*R*)- $(-)$ -**2b** ligand and by the oxygen atoms of the sulfonate groups, whereas the camphor rests protrude from the layer. The Ag(I) metal centers, which are known to be of a variable coordination

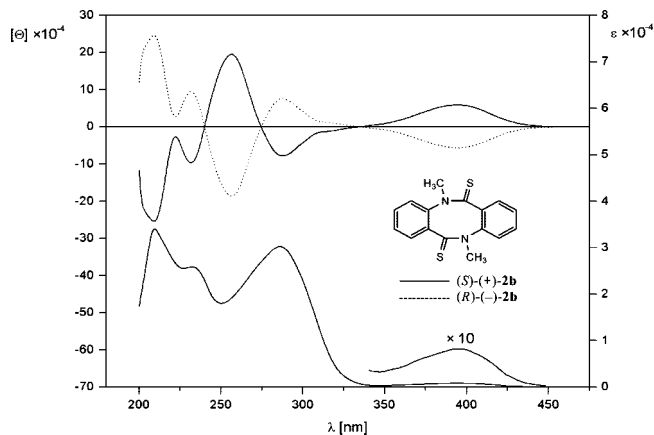


FIGURE 3. CD and UV-vis (lower curve) spectra of enantiomers of **2b** taken in cyclohexane–dioxane (5:1).

geometry, are three- and four-coordinated (see Figure 2S in the Supporting Information).

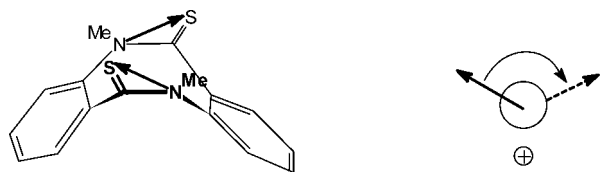
The resolution of **2b** into enantiomers, which are configurationally stable at room temperature, indicates that the inversion barrier is greater than 23 kcal mol⁻¹. Optical activity of $(-)$ -**2b** almost did not change after reflux in toluene solution for 24 h. However, the ring interconversion between two enantiomeric conformations occurs relatively easily on heating in high boiling solvents. The racemization of the compound $(-)$ -**2b** in boiling mesitylene was followed polarimetrically at 589 nm. The first-order rate constant k corresponding to the process is $k = 6 \times 10^{-6} \text{ s}^{-1}$ and the calculated lifetime ($t_{1/2}$) for racemization $(-)$ \rightarrow (\pm) is 32 h, and thus, the activation free energy for the ring inversion in **2b** was evaluated to be $\Delta G^\ddagger = 36.5 \pm 0.2$ kcal mol⁻¹ at 438 K.

Circular Dichroism (CD) Spectra. The electronic absorption spectrum and CD curves of $(+)$ -**2b** and $(-)$ -**2b** are shown in Figure 3. The UV-vis spectrum of **2b** taken in cyclohexane–dioxane (5:1) shows a relatively weak band at 393 nm that shifts by 15 nm to the blue upon changing the solvent to methanol. It can unequivocally be assigned to the forbidden thioamide $n-\pi^*$ electronic transition.¹⁹ Much stronger absorption bands at 285 and 231 nm are only slightly dependent on the solvent changes and correspond to the allowed $\pi-\pi^*$ and $\sigma_{\text{C-S}}-\pi^*$ excitations, respectively.^{19c,d} The CD curves of the enantiomers $(+)$ -**2b** and $(-)$ -**2b** are perfect mirror images of each other reflecting the opposite configuration of the inherently chiral skeletons (Figure 3). The CD spectrum of $(-)$ -**2b** closely resembles that of the previously reported for (R) -**2a**,⁷ though the intensities of the Cotton effects are stronger. The negative long wavelength Cotton effect at 393 nm is due to the $n-\pi^*$ transition and reflects the helicity of the twisted thiobenzamide chromophore. According to the X-ray structure of $(-)$ -**2b**, it is twisted in the *M* sense [the $\text{S}=\text{C}-\text{C}=\text{C}$ angles are of $-54.5(2)$ and $-59.7(2)^\circ$], whereas the thioamide function itself is nearly planar [the $\text{S}=\text{C}-\text{N}-\text{C}$ angles are of $-3.5(3)$ and $3.1(3)^\circ$].

There is a close analogy to α,β -unsaturated carbonyl systems, where the *P*-helicity of the chromophore leads to the positive $n-\pi^*$ Cotton effect sign whereas the *M*-helicity causes the

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SCHEME 3



negative one.²⁰ A sequence of the positive and negative Cotton effects at 288 and 256 nm, respectively, in the region of the $\pi-\pi^*$ transition can be attributed to the exciton coupling between two thioamide chromophores. According to Hosoya et al.,²¹ the $\pi-\pi^*$ electric transition moment in thioacetamide follows near the direction through the sulfur and nitrogen atoms. Thus the geometry of (–)-**2b** implies the right-handed screwness (clockwise orientation) of the $\pi-\pi^*$ transition moments in agreement with the observed sequence of the maximum at the longer wavelengths and the minimum at the shorter wavelengths (positive exciton coupling,^{7,22} Scheme 3). A strong positive CD band at 208 nm is probably due to the aromatic 1L_a excitation.

Molecular Self-Assembly. As already mentioned, V-shaped or roof-shaped molecules are often unable to achieve efficient crystal packing by themselves and therefore can form self-assembled supramolecular structures or act as lattice inclusion hosts.^{4c,23} The intermolecular interactions in the crystals of **2b** should be relatively weak, and one may expect some influence of C–H $\cdots\pi$, $\pi-\pi$ stacking or C–H \cdots S interactions on the molecular assembly mode of the molecules. The compound (\pm)-**1b** being the oxo analogue of (\pm)-**2b** has been reported to crystallize in two monoclinic polymorphic forms.²⁴ In the polymorph I, the methyl group involved in C–H $\cdots\pi$ interactions is hidden in a concavity of the V-shaped molecule,^{24b} whereas in the form II the molecules assemble into dimeric units via interdigitation and the aryl rings are involved in the C–H $\cdots\pi$ and $\pi-\pi$ stacking interactions.²⁴

The racemic compound (\pm)-**2b** was also obtained in two crystal modifications: its crystallization from methanol yielded crystals of the solvent free compound in the monoclinic space group $P2_1/c$ with two molecules of **2b**, designated as A and B, in the asymmetric unit, whereas a crystallization from toluene afforded crystals of a 2:1 solvate in the triclinic space group $P-1$. In the triclinic crystals, the *R* and *S* the molecules of **2b** form centrosymmetric dimers through the $\pi-\pi$ stacking interactions, and thus, the solvent molecules cannot be included in hydrophobic cavities of the host. Instead, the disordered toluene molecules occupy cages formed between the adjacent (–101) layers of the dimeric host (Figure 4). In the monoclinic form of (\pm)-**2b** an achiral chain is formed by the B molecules by placing

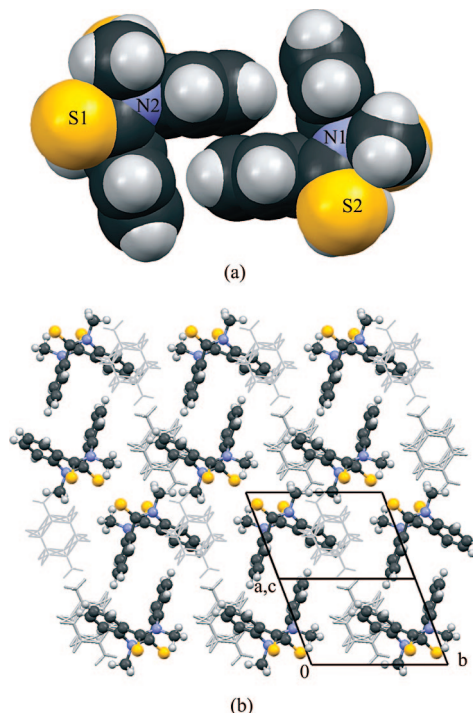


FIGURE 4. (a) Centrosymmetric dimer via $\pi-\pi$ stacking interactions in $[(\pm)\text{-2b}]_2\cdot\text{C}_7\text{H}_8$ and (b) crystal packing showing the layer of **2b** dimers and included toluene molecules.

one of two methyl groups in the hydrophobic cavity of the neighbor whereas the A molecules embrace this chain by including the remaining methyl substituents of B inside their concaves. In each case, the interacting molecules are heterochiral (Figure 5) and this is an important difference from the molecular assembly mode in the polymorph I of (\pm)-**1b** where the C–H $\cdots\pi$ interactions between the methyl groups and aromatic rings of the hydrophobic cavities generate a homochiral chain.

Similar chiral chains were found in the homochiral crystals of **2b** where the 1D assembly is additionally stabilized by the C–H \cdots S interactions with a H \cdots S distance of 2.74 Å (Figure 7S in the Supporting Information).

Since aryl (electron-rich) and perfluoroaryl (electron-deficient) rings are known for their strong attractive $\pi-\pi$ interactions and aryl–perfluoroaryl stacking combined with hydrogen bonding interactions²⁵ has been proven to be useful in controlling crystal structure of supramolecular assemblies we attempted complexation of **2b** with such a strong hydrogen bond donor as pentafluorophenol (**pfp**). Indeed, cocrystallization of (\pm)-**2b** with **pfp** from hexane afforded yellow prisms of a 1:2 complex in the monoclinic space group $C2/c$. The crystals are characterized by a layered structure composed of rows containing the alternating enantiomers of **2b** and pairs of antiparallel stacked **pfp** molecules with an intercentroid distance of 3.58 Å (Figure 6). The centroids of the benzene and **pfp** rings are separated by 3.84 Å and an interplanar angle is of 21.9°. The O–H \cdots S hydrogen bond links the **pfp** units and **2b** molecules belonging to adjacent layers.

In summary, planar chiral *N,N'*-dimethyldithiodianthranilide (**2b**) due to a relatively high inversion barrier of the central eight-membered ring is a configurationally stable compound. Owing

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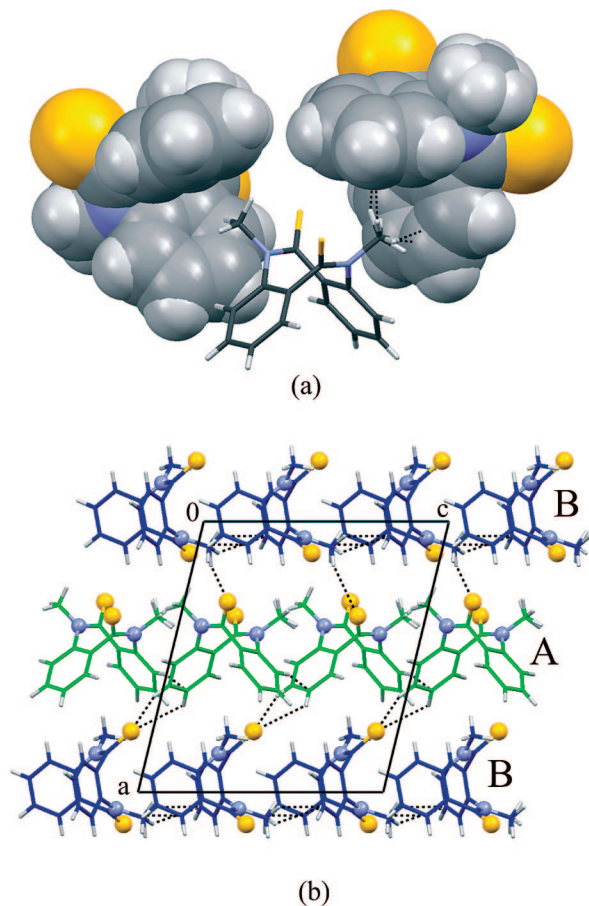


FIGURE 5. (a) Fragment of the crystal structure of (\pm)-**2b** showing interaction of the methyl groups of the molecule B with the aromatic rings lining the hydrophobic cavity of two neighboring molecules. (b) Crystal packing of (\pm)-**2b** showing achiral chains of the B molecules embraced by the A molecules. The dashed lines represent short C–H \cdots C and C–H \cdots S contacts.

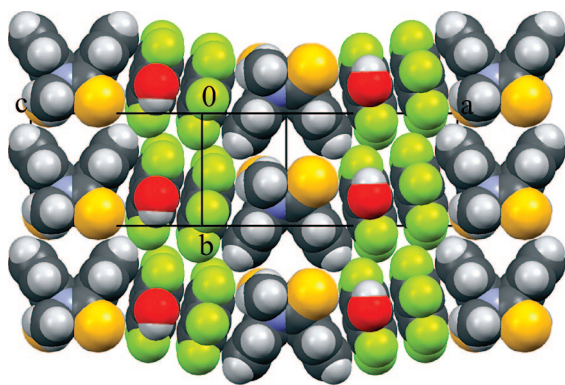


FIGURE 6. Layer formed via stacking interactions between the pentafluorophenol (**pfp**) molecules and stacking interactions of pentafluorophenol and benzene rings in the crystal structure of (\pm)-**2b**·(**pfp**)₂.

to good ligand properties of the thiocarbonyl function it can be resolved to enantiomers through diastereomeric complex with easily accessible and inexpensive silver(I) (*S*)-camphorsulfonate (**3**). The absolute configuration of the chiral ligand can be easily deduced from the crystal structure of the complex and confirmed by the CD spectrum on the basis of the long-wavelength $n-\pi^*$ Cotton effect sign. We believe that this simple entirely new

method of resolution opens access to other enantiopure thiocarbonyl compounds on a preparative scale.

Due to the unique roof-shaped geometry the molecules of **2b** are unable to achieve efficient crystal packing by themselves and easily form inclusion complexes with toluene or pentafluorophenol.

Experimental Section

¹H and ¹³C NMR spectra were obtained at 500 and 125 MHz, respectively, and the deuteriated solvents were used as an internal lock.

5,11-Dimethyldibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dione (1b). Sodium hydride (0.58 g, 24 mmol) was added to a stirred solution of dilactam **1a**¹¹ (2.38 g, 10 mmol) in DME (10 mL), and after the reaction ceased (ca. 15 min), methyl iodide (2 mL) was added dropwise. The reaction mixture was stirred for an additional 30 min and poured into water. The product was extracted with CH₂Cl₂, dried (Na₂SO₄), and evaporated to dryness. The residue was crystallized from toluene–hexane to obtain 1.82 g of **1b**: mp 208–210 °C (lit.^{24b} mp 133 °C); IR (KBr) ν_{\max} 1651, 1598, 1377 cm⁻¹; ¹H NMR (CDCl₃) δ 7.32–7.07 (complex m, 8H), 3.45 (s, 6H); ¹³C NMR (CDCl₃) δ 168.0, 140.2, 134.3, 130.6, 128.1, 127.6, 124.0, 36.6. Anal. Calcd for C₁₆H₁₄N₂O₂ (266): C, 72.16; H, 5.30; N, 10.52. Found: C, 72.27; H, 5.25; N, 10.52.

5,11-Dimethyldibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dithione (2b). Dilactam **1b** (1.33 g, 5 mmol) and Lawesson's reagent (2.42 g, 6 mmol) were refluxed in dry toluene (10 mL) for 90 min. The solvent was evaporated at reduced pressure, and the product crystallized after addition of methanol 1.40 g (91%): mp 198–199 °C; IR (KBr) ν_{\max} 1474, 1377, 1301, 1097 cm⁻¹; ¹H NMR (CDCl₃) δ 7.24–6.98 (complex m, 8H), 3.81 (s, 6H); ¹³C NMR (CDCl₃) δ 197.2, 140.8, 139.9, 129.9, 128.7, 123.3, 43.8; UV (MeOH) λ_{\max} 382 nm (ϵ 475), 300 (18000). Anal. Calcd for C₁₆H₁₄N₂S₂ (298): C, 64.39; H, 4.73; N, 9.39; S, 21.49. Found: C, 64.50; H, 4.70; N, 9.49; S, 21.27.

Silver(I) (1*S*)-Camphorsulfonate (3). To a suspension of 2.32 g (10 mmol) of Ag₂O in 5 mL of water was added a solution of (1*S*)-camphorsulfonic acid (5.00 g, 20 mmol) in 10 mL of water. During 30 min of stirring and gentle heating, the black suspension was gradually dissolved. The unreacted black powder of Ag₂O was filtered off, and the filtrate was concentrated in vacuo and diluted with acetone. The product crystallized in colorless needles which were collected, washed with acetone, and dried: mp 246–248 °C; [α]_D²⁵ +14.5 (c 4, H₂O) [lit.²⁶ [α]_D²⁵ +14.6 (c 4, H₂O)].

Optical Resolution of 5,11-Dimethyldibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dithione (2b). To a solution of racemic dithionolactam (\pm)-**2b** (1.20 g, 4 mmol) in CH₂Cl₂ (30 mL) was added silver(I) (1*S*)-camphorsulfonate (**3**) (2.72 g, 8 mmol) dissolved in 3 mL of MeCN. After 48 h at room temperature, the precipitated crystals were filtered and washed with CH₂Cl₂ to obtain 1.95 g of the silver complex. The crystals of the complex were suspended in CH₂Cl₂ (20 mL) and washed with 20% aqueous solution of Na₂S₂O₃ (10 mL). The organic layer was dried (Na₂SO₄) and evaporated to dryness and the residue crystallized from CH₂Cl₂–hexane to obtain 480 mg of (–)-**2b**: [α]_D²⁵ –865 (c 1, CH₂Cl₂); ee > 97% was assigned by ¹H NMR using (*S*)-(+)-2,2,2-trifluoro-1-anthrylethanol as a chiral solvating agent.

An analogous workup of the filtrate from the crystallization of the silver complex afforded the enantiomer (+)-**2b** (570 mg), which after crystallization and discarding big prismatic crystals of the racemate (200 mg) had [α]_D²⁵ +874 (c 1, CH₂Cl₂).

X-ray Structure Analyses. X-ray data were collected with a KM4CCD diffractometer with the exception of (\pm)-**2b**·C₇H₈, which was measured using a Kuma KM4 diffractometer. The crystal

(26) Pope, W. J.; Gibson, C. S. *J. Chem. Soc.* **1910**, 97, 2211.

structures were solved by direct methods with SHELXS97²⁷ and refined by full-matrix least-squares SHELXL97.²⁶

Crystal data for $(R)-(-)-2b \cdot 3_2 \cdot H_2O \cdot CH_2Cl_2$: $M = 1079.65$, triclinic, space group $P1$, $a = 10.9118(7) \text{ \AA}$, $b = 13.9513(9) \text{ \AA}$, $c = 16.0627(10) \text{ \AA}$, $\alpha = 103.793(5)^\circ$, $\beta = 108.602(6)^\circ$, $\gamma = 103.178(5)^\circ$, $V = 2124.4(2) \text{ \AA}^3$, $T = 130 \text{ K}$, $Z = 2$, $\rho_x = 1.688 \text{ g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.298 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 15915 reflections measured, 11051 unique ($R_{\text{int}} = 0.0195$). Final residuals for 1049 parameters were $R_1 = 0.0453$, $wR_2 = 0.1095$ for 9516 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0523$, $wR_2 = 0.1139$ for all data; Flack parameter $x = 0.01(2)$.

Crystal data for $(R)-(-)-2b$: $M = 298.41$, orthorhombic, space group $P2_12_12_1$, $a = 7.9798(5) \text{ \AA}$, $b = 10.2973(9) \text{ \AA}$, $c = 17.5711(14) \text{ \AA}$, $V = 1443.82(19) \text{ \AA}^3$, $T = 130 \text{ K}$, $Z = 4$, $\rho_x = 1.373 \text{ g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.359 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 10915 reflections measured, 2934 unique ($R_{\text{int}} = 0.0381$). Final residuals for 183 parameters were $R_1 = 0.0330$, $wR_2 = 0.0606$ for 2543 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0417$, $wR_2 = 0.0636$ for all data; Flack parameter $x = 0.01(7)$.

Crystal data for $(\pm)-2b$: $M = 298.41$, monoclinic, space group $P2_1/c$, $a = 13.9899(8) \text{ \AA}$, $b = 17.6632(9) \text{ \AA}$, $c = 12.3039(6) \text{ \AA}$, $\beta = 103.639(5)^\circ$, $V = 2954.6(3) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 8$, $\rho_x = 1.342 \text{ g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.351 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 21624 reflections measured, 6014 unique ($R_{\text{int}} = 0.0260$). Final residuals for 367 parameters were $R_1 = 0.0392$, $wR_2 = 0.0946$ for 4468 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0616$, $wR_2 = 0.1026$ for all data.

Crystal data for $[(\pm)-2b]_2 \cdot C_7H_8$: $M = 688.96$, triclinic, space group $P-1$, $a = 8.5694(8) \text{ \AA}$, $b = 9.811(2) \text{ \AA}$, $c = 11.707(2) \text{ \AA}$, $\alpha = 107.36(2)^\circ$, $\beta = 95.12(1)^\circ$, $\gamma = 101.21(2)^\circ$, $V = 910.0(3) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 1$, $\rho_x = 1.257 \text{ g} \cdot \text{cm}^{-3}$, $\mu(\text{Cu K}\alpha) = 2.648 \text{ mm}^{-1}$, $\lambda = 1.54178 \text{ \AA}$, 3030 reflections measured, 3030 unique. Final residuals for 247 parameters were $R_1 = 0.0501$, $wR_2 = 0.1393$ for 2445 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0660$, $wR_2 = 0.1503$ for all data. The toluene molecule is disordered around inversion center.

Crystal data for $(\pm)-2b \cdot (C_6F_5OH)_2$: $M = 666.55$, monoclinic, space group $C2/c$, $a = 21.417(3) \text{ \AA}$, $b = 7.5864(8) \text{ \AA}$, $c = 17.247(2) \text{ \AA}$, $\beta = 95.493(12)^\circ$, $V = 2789.5(6) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 4$, $\rho_x = 1.587 \text{ g} \cdot \text{cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 0.289 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, 5998 reflections measured, 2449 unique ($R_{\text{int}} = 0.0168$). Final residuals for 204 parameters were $R_1 = 0.0442$, $wR_2 = 0.1286$ for 1685 reflections with $I > 2\sigma(I)$, and $R_1 = 0.0649$, $wR_2 = 0.1413$ for all data.

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Supporting Information Available: ORTEP plots for the reported crystal structures and packing digrams for $(R)-(-)-2b \cdot 3_2 \cdot H_2O \cdot CH_2Cl_2$ and $(R)-(-)-2b$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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