Syntheses, Absolute Configurations, and UV/Vis Spectroscopic Properties of New Chiral Tri- and Pentamethinium Streptocyanine Dyes with 4-Aminophenyl 4-Methylphenyl Sulfoxide Endgroups[‡]

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Dedicated to Prof. Dr. Douglas M. Lloyd on the occasion of his 80th birthday

Keywords: Chirality / Cyanines / Dyes / Polymethines / UV/Vis spectroscopy

Starting with monochiral 4-aminophenyl 4-methylphenyl sulfoxides **3a** and **3b**, the absolute configurations of which were determined by X-ray analysis, we have synthesized the new chiral C_2-symmetrical tri- and pentamethinium streptocyanine dyes **5a** and **5b** and **7a** and **7b** with sulfinyl groups as stereogenic centers in the two endgroups. Deprotonation of the trimethinium dyes **5a** and **5b** gave the intramolecularly H-bonded neutral streptocyanines **6a** and **6b**; the molecular structures and absolute configurations of **5b** and **6b** were also confirmed by X-ray analyses. For comparison, the corresponding achiral tri- and pentamethinium streptocyanine dyes **11**–**13**, with sulfonyl moieties instead of sulfinyl groups in the two endgroups, were synthesized from 4-aminophenyl 4-methylphenyl sulfone (**10**). The UV/Vis spectroscopic and chiroptical properties of the new polymethinium streptocyanine dyes have been studied.

Introduction

Together with aromatic and polyenic conjugated π-systems, polymethine dyes represent a third, independent type of conjugated π-systems with their own specific intrinsic chemical and physical properties.[3−6] As so-called *functional dyes*[7] they have found various practical applications, particularly as sensitizers for silver halide emulsions used in photography.[8] Whereas chiral aromatics (such as helicenes) and chiral polyenes (such as carotenoids) are well known, chiral polymethine dyes have only recently attracted more interest because of their potentially interesting chiroptical properties.[9] The first chiral polymethine dyes were obtained by König et al.[10] as early as 1928 and by Götze[11] in 1938, although published only in two rather short communications. Some natural dyes, such as the orange-red fungus dye Musca-aurine I (from the fly agaric, *Amanita muscaria*)[12] and the red-violet betalain dye betanin (responsible for the color of red beets, *Beta vulgaris*)[13] contain chiral pentamethinium chromophores with endgroups originating from monochiral[14] L-α-amino acids.

Because of its historical importance,[9] and also because of the insufficient elaboration of synthetic and spectroscopic details, the mostly unknown enantiomeric purities, and absolute configurations of the stereogenic centers, as well as in continuation of our own work on chiral polymethine dyes,[15−21] we have repeated and significantly improved on some of the work of König[18,21] and Götze.[17] Further work on inherently chiral polymethine dyes has also been done recently by Grahn et al.,[22] Wolf et al.,[23] and particularly Buß et al.[24−30] The observation by Dähne, Kirstein, et al.,[31−34] that achiral trimethinium cyanine dyes with long *N*-alkyl groups spontaneously form chiral J-aggregates with optical activity in solution should also be mentioned in this context.

Most of the known monochiral[14] polymethinium dyes either contain asymmetrically substituted carbon atoms in the two heterocyclic endgroups as their stereogenic centers or (and) are helically twisted for steric reasons. In this paper, we describe for the first time syntheses, partly based on preliminary, unpublished results obtained in 1935 by König and Liewald, [10c] of new chiral C_2-symmetrical tri- and pentamethinium streptocyanine dyes with sulfur atoms as stereogenic centers in the two endgroups. Chiral compounds with sulfur as stereogenic centers include sulfonium salts and sulfoxides (containing sulfinyl groups).[35] In this work, we deal with the well-known chiral sulfoxides,[36] such as suitably 4,4′-disubstituted diphenyl sulfoxides.[37,38]

[‡] Chiral Polymethine Dyes, VIII. − Part VII: Ref.[1]

[‡‡] See Ref.[2]

[‡‡‡] X-ray crystal structure analyses

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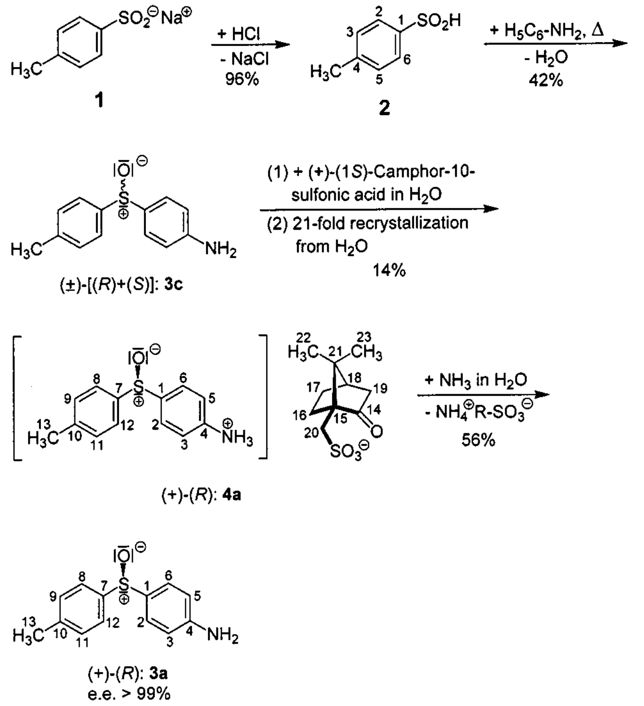
Results and Discussion

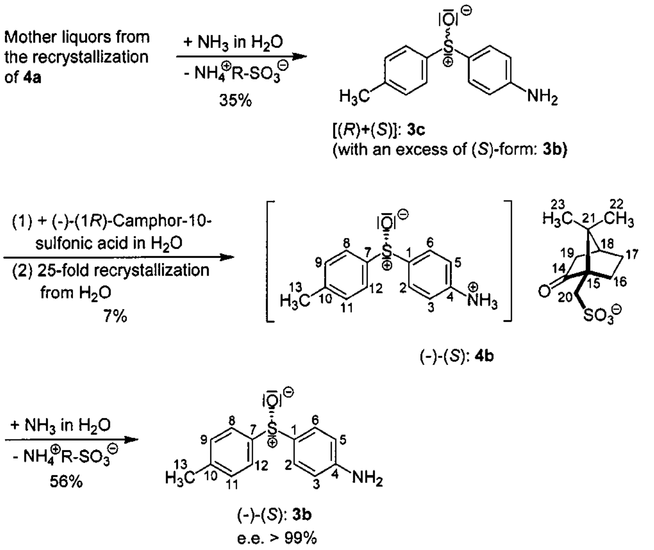
1. Syntheses and Molecular Structures

Isochiral[14] 4-aminophenyl 4-methylphenyl sulfoxide (**3c**)[39] was prepared from 4-toluenesulfinic acid (**2**)[40] and aniline according to Harrison et al.[37] and Oae et al.[38] (Scheme 1). Through the use of a procedure first reported by Harrison et al.,[37] and later adapted by Liewald,[10c] isochiral **3c** was separated into its enantiomers **3a** and **3b**[39] by means of a laborious recrystallization of the diastereomeric salts obtained with (+)-(1*S*)- and with (−)-(1*R*)-camphor-10-sulfonic acid[41] (Schemes 1 and 2). Attempts to replace this acid by other chiral acids such as tartaric acid, *O*,*O'*-dibenzoyltartaric acid, mandelic acid, or 3-bromocamphor-8-sulfonic acid were unsuccessful, because the corresponding diastereomeric salts did not crystallize.[2] Eventually, after 21 recrystallizations of (+)-(1*S*)-camphor-10-sulfonate **4a** (Scheme 1) from water containing an excess of (+)-(1*S*)-camphor-10-sulfonic acid (c = 4 cg/g) and deprotonation with aqueous ammonia, enantiomerically pure, dextrorotatory **3a** was obtained in an overall yield of 8%, relative to the amount of starting material **3c**. The progress of enantiomeric enrichment after each recrystallization step was monitored by the molar optical rotation obtained for the free amine **3a**, a small test sample of which was prepared with ammonia after each step. It was not possible to monitor the enantiomeric enrichment by measuring the optical rotation of the diastereomeric salt itself, as these values were very variable.



Scheme 1. Preparation of monochiral (+)-(*R*)-4-aminophenyl 4-methylphenyl sulfoxide **3a** (atom numbering as in Figure 1)

The combined mother liquors from the recrystallization of sulfonate **4a** were used to obtain the other enantiomer **3b** (Scheme 2). Deprotonation with aqueous ammonia provided the anisochiral[14] sulfoxide **3c**, already containing an excess of **3b**. Its corresponding (−)-(1*R*)-camphor-10-sulfonate **4b** was recrystallized 25 times from water containing an excess of (−)-(1*R*)-camphor-10-sulfonic acid[41] (c = 4 cg/g), to give, after deprotonation with ammonia, the monochiral, levorotatory sulfoxide **3b** in an overall yield of 5%, relative to the amount of starting material **3c**. The enantiomeric enrichment was againe monitored by measuring the molar optical rotation of a small test sample of the free amine **3b**, prepared after each recrystallization step.



Scheme 2. Preparation of monochiral (−)-(*S*)-4-aminophenyl 4-methylphenyl sulfoxide **3b** (atom numbering as in Figure 1)

In the cases both of **3a** and of **3b**, recrystallization was continued until a constant molar optical rotation was observed. The optical rotations given in the literature[10c,37] were not very helpful, since they differ considerably from our values (see Exp. Sect.). Additionally, the enantiomeric purities of **3a** and **3b** were determined by HPLC chromatography on a chiral stationary phase (Chiralcel® OD) with achiral solvents (*n*-heptane/2-propanol, 80:20, cL/L) as eluants. Whereas the HPLC chromatogram of isochiral **3a** consisted of two peaks of equal intensity, the corresponding chromatograms for monochiral **3a** and **3b** each showed *one peak* only. This corresponded in both cases to an *ee* value of ≥ 99%.

The absolute configurations of sulfoxides **3a** and **3b** seem to be unreported.[42] The absolute configuration of levorotatory **3b** was therefore determined by X-ray structure analysis of a single crystal of **3b**, crystallized from acetone/petroleum ether (b.p. 40−60 °C). Figure 1 clearly shows that levorotatory **3b** has the (*S*) configuration at the stereogenic S1 center.[43]

The refined Flack parameter of only 0.02(3) (close to zero!) found for the anomalous X-ray scattering of **3b** substantiates this assignment of the absolute configuration at *S*1 (see Exp. Sect.).

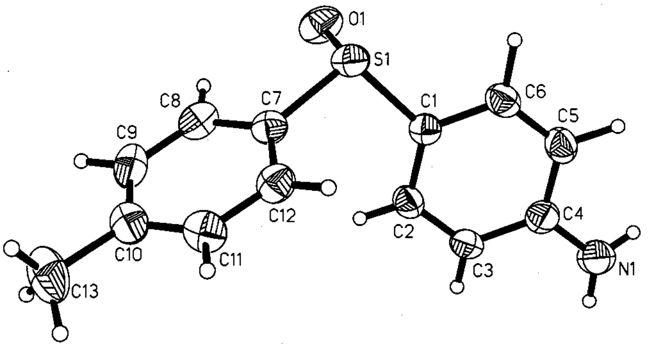


Figure 1. ORTEP drawing of the molecular structure of monochiral (−)-(*S*)-sulfoxide **3b** in the crystal (thermal ellipsoids 50% probability); selected bond lengths [pm]: S(1)−O(1) 150.8(3), S(1)−C(1) 176.7(3), S(1)−C(7) 178.8(3); selected bond angles [°]: O(1)−S(1)−C(1) 108.14(15), O(1)−S(1)−C(7) 104.74(17), C(1)−S(1)−C(7) 101.17(15); selected torsion angles [°]: O(1)−S(1)−C(1)−C(6) 95.0(3), O(1)−S(1)−C(1)−C(2) −77.5(3), O(1)−S(1)−C(7)−C(8) −10.8(3), O(1)−S(1)−C(7)−C(12) 175.0(3); for further details see Exp. Sect. and ref.[43]

To simplify matters, the atom numbering used in this paper follows the numbering used by crystallographers, as shown in the ORTEP drawings in Figures 1, 2 and 4, which does not always correspond to the numbering usually applied in IUPAC nomenclature.

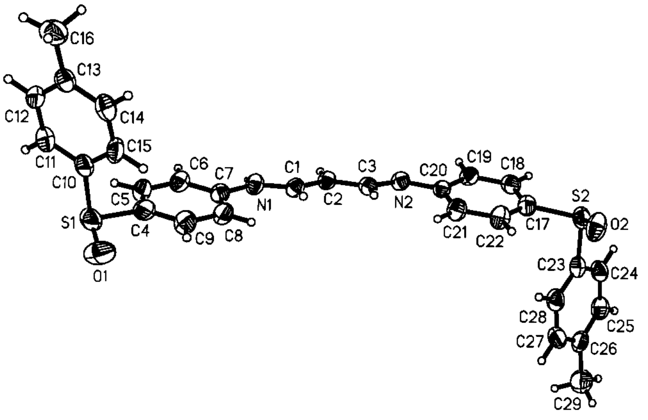


Figure 2. ORTEP drawing of the molecular structure of monochiral (−)-(*S*,*S*)-trimethinium dye **5b** in the crystal, without bromide ion (thermal ellipsoids with 50% probability); selected bond lengths [pm]: S(1)−O(1) 149.8(5), S(2)−O(2) 148.4(4), N(1)−C(1) 131.9(7), N(2)−C(3) 131.5(6), C(1)−C(2) 137.2(7), C(2)−C(3) 136.3(7); selected bond angles [°]: C(4)−S(1)−C(10) 99.2(2), C(17)−S(2)−C(23) 99.0(2), C(4)−S(1)−O(1) 106.3(3), C(17)−S(2)−O(2) 107.5(2), C(7)−N(1)−C(1) 126.8(5), N(1)−C(1)−C(2) 124.9(5), C(1)−C(2)−C(3) 118.5(6), C(2)−C(3)−N(2) 125.6(5), C(3)−N(2)−C(20) 128.3(5); selected torsion angles [°]: C(7)−N(1)−C(1)−C(2) 177.2(5), N(1)−C(1)−C(2)−C(3) −178.0(5), C(20)−N(2)−C(3)−C(2) −175.9(5), C(1)−C(2)−C(3)−N(2) 179.2(5), O(1)−S(1)−C(4)−C(9) −13.8(6), O(1)−S(1)−C(4)−C(5) 165.6(5), C(10)−S(1)−C(4)−C(9) 94.3(5); for further details see Exp. Sect. and ref.[43]

Through the use of well-established methods for the preparation of streptocyanines,[6,10,18] treatment of the monochiral amino sulfoxides **3a** and **3b** with 3,3-diethoxy-1-propyne and aqueous HBr in ethanol afforded the monochiral trimethinium bromides **5a** and **5b** as hydrates in satisfactory yields as yellow crystals (Scheme 3). According to their ^{1}H and ^{13}C NMR spectra in DMSO solution, the streptocyanines **5a** and **5b** were C_2-symmetrical with all-(*E*) configurations along the methine chains. The ^{1}H NMR signals of 2-H and 1/3-H were triplets, with $^{3}J_{\mathrm{H,H}}$ = 11.4 and 11.8 Hz for the vicinal coupling between 2-H and 1/3-H and between 1/3-H and NH, typical for their mutual *trans* relationships.[6b,44]

The all-(*E*) configurations of the trimethinium chains are maintained in the solids, as shown by an X-ray analysis of a single crystal of **5b** (Figure 2), which also demonstrates that the (*S*) configuration of the sulfinyl center in the starting compound **3b** has been retained in the two stereogenic sulfinyl centers of **5b** during its synthesis. That means that no racemization had taken place under the applied reaction conditions.

Within the usual limits of experimental error, the bond lengths and bond angles of **5b** are in reasonable agreement with those of other corresponding polymethine dyes.[15,45−47] As expected, the trimethinium chain of **5b** is practically planar and has the all-(*E*) configuration with averaged C−C bond lengths of $l \approx 137$ pm. The two *N*-phenyl endgroups are arranged nearly in the same plane as the trimethinium chain; the torsion angles C(8)−C(7)−N(1)−C(1) and C(3)−N(2)−C(20)−C(21), at −9.4° and +8.4°, respectively, are very small. In contrast to this, the two terminal phenyl groups are arranged out of this plane at opposite sites of the trimethine chain. In the crystal, this gives rise to a kind of helical structure, with up to four dye cations lying on the top of each other, as illustrated in Figure 3. In the crystal lattice, the bromide counterions are located in the middle of the conjugated trimethinium chains.

Knowledge of the spatial arrangement of the vinylogous amidinium cations of trimethinium streptocyanine dye **5b** in the unit cell is valuable for discussion of the aggregation behavior of streptocyanine dyes in the crystal and, particularly, in solution (see, for example, ref.[48]). It is well known that, under certain experimental conditions, polymethine dyes in solution form higher aggregates, mostly Scheibe or J-aggregates,[49,50] with peculiar UV/Vis spectroscopic properties.[51−53]

Suitable single crystals of **5b** were obtained by a special technique: a layer of petroleum ether (b.p. 40−60 °C) was added to a concentrated solution of **5b** in ethanol. After this had stood unperturbed for some weeks at room temp. in the dark, yellow plates of **5b**, sufficiently large for the X-ray analysis, had formed at the boundary between the two solvent layers.

For comparison of chiroptical properties, the monochiral neutral streptocyanines **6a** and **6b** were prepared from the trimethinium bromides **5a** and **5b** (Scheme 3). Addition of aqueous NaOH to suspensions of **5a** and **5b** in ethanol yielded orange-colored homogeneous solutions, from which the neutrocyanines **6a** and **6b** were precipitated in good yields on addition of water, as yellow microcrystalline solids. Their ^{1}H and ^{13}C NMR spectra, measured in $CDCl_3$, were again in agreement with a C_2-symmetrical molecular structure. However, the ^{1}H NMR signals of the three me-

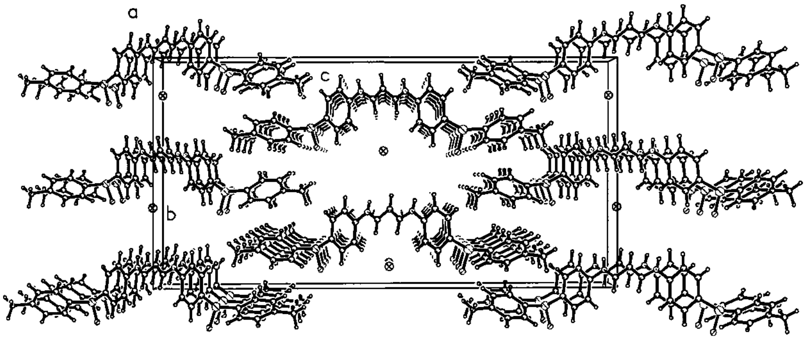


Figure 3. Crystal structure (unit cell) of the monochiral (−)-(*S*,*S*) trimethinium bromide **5b** (water of crystallization not shown), viewed along the *c* axis; for further details see Exp. Sect. and ref.[43]

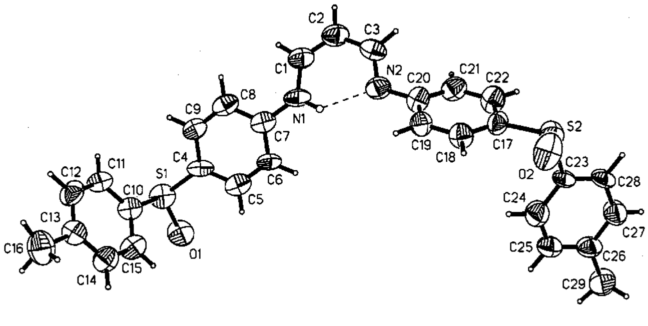
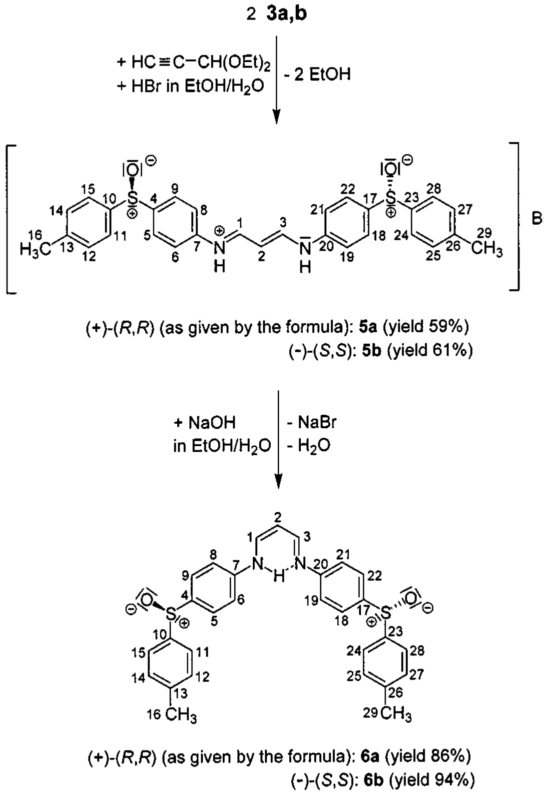


Figure 4. ORTEP drawing of the molecular structure of the monochiral neutral (−)-(*S*,*S*)-trimethine dye **6b** in the crystal (thermal ellipsoids with 50% probability); selected bond lengths [pm]: S(1)−O(1) 149.2(5), S(2)−O(2) 151.6(5), N(1)−C(1) 132.8(9), N(1)−H 84.6(10), N(2)−C(3) 129.4(8), C(1)−C(2) 135.7(9), C(2)−C(3) 142.2(10); selected bond angles [°]: C(4)−S(1)−C(10) 99.8(3), C(17)−S(2)−C(23) 100.5(3), C(4)−S(1)−O(1) 106.5(3), C(17)−S(2)−O(2) 106.6(3), C(7)−N(1)−C(1) 125.3(7), N(1)−C(1)−C(2) 125.3(8), C(1)−C(2)−C(3) 125.3(8), C(2)−C(3)−N(2) 123.1(7), C(3)−N(2)−C(20) 117.6(7); selected torsion angles [°]: C(7)−N(1)−C(1)−C(2) −172.9(7), N(1)−C(1)−C(2)−C(3) −1.9(14), C(20)−N(2)−C(3)−C(2) −179.2(7), C(1)−C(2)−C(3)−N(2) −0.1(13), O(1)−S(1)−C(4)−C(9) 168.8(6), O(1)−S(1)−C(4)−C(5) −6.0(6), C(10)−S(1)−C(4)−C(9) −79.9(6); for further details see Exp. Sect. and ref.[43]



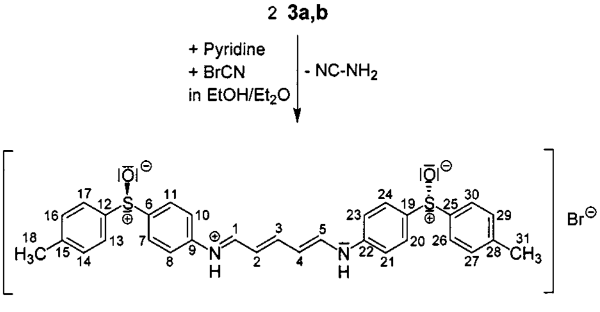
Scheme 3. Synthesis of the monochiral trimethinium dyes **5a** and **5b** and the corresponding neutral trimethines **6a** and **6b** (atom numbering as in Figures 2 and 4)

thine H atoms now consisted of a triplet and a doublet with $J_{H,H}$ = 6.2 Hz for the vicinal coupling between 2-H and 1/3-H, typical of a *cis* arrangement.[6b,44] Therefore, the neutrocyanines **6a** and **6b**, in contrast to **5a** and **5b**, adopt all-(*Z*) configurations along the trimethine chains in $CDCl_3$ solution, obviously supported by intramolecular N−H···N hydrogen bonds. The existence of strong intramolecular hydrogen bonds in **6a** and **6b** in $CDCl_3$ was substantiated by the large downfield shifts of the N−H signals to δ = 12.1! The methine 1/3-H NMR signals in **6a** and **6b** both experienced highfield shifts of Δδ ≈ 1.4 ppm relative to the corresponding signals in **5a** and **5b**, as a result of the missing positive charge.

Yellow, rod-like crystals of monochiral **6b** were obtained analogously to those of **5b**, with a two-phase acetone/petroleum ether (b.p. 40−60 °C) solvent system, and analyzed by X-ray diffraction. As Figure 4 shows, the all-(*Z*) configuration is maintained in solid **6b**, with a planar, intramolecularly H-bonded neutral trimethine chain, with N(1)−C(1)−C(2)−C(3) and C(1)−C(2)−C(3)−N(2) torsion angles of only −1.9° and −0.1°, respectively. The flexible endgroups are severely twisted both relative to one another and to the planar trimethine chain, with C(8)−C(7)−N(1)−C(1) and C(3)−N(2)−C(20)−C(19) torsion angles of −29.4° and +133.4°, respectively (Figure 4). This and the two stereogenic sulfinyl centers give rise to a helical structure in the overall molecule.

Whereas dye **5b** possesses nearly equalized C−C bond lengths (*l* ≈ 137 pm) along the trimethinium chain (Figure 2), as expected for typical conjugated polymethine π-systems,[3,4] the neutrocyanine **6b** exhibits pronounced C−C bond length alternation [*l* ≈ 136 and 142 pm for C(1)−C(2) and C(2)−C(3), respectively; Figure 4]. That means that neutrocyanines such as **6a** and **6b** are *polyenic* rather than *polymethinic* conjugated π-systems.[3,4] In comparison to that in the crystal structure of the trimethinium bromide **5b** (cf. its unit cell in Figure 3), the packing of the molecules of neutrocyanine **6b** in the unit cell is much looser and less dense,[2,43] obviously due to the absence of planarity between the intramolecularly H-bonded trimethine chain and the phenyl endgroups with stereogenic sulfinyl centers.

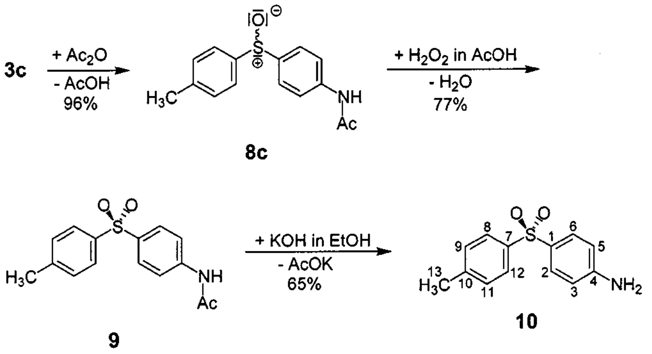
Treatment of the monochiral amino sulfoxides **3a** and **3b** with cyanogen bromide and pyridine in ethanol/diethyl ether according to a method first described by König[10,54] afforded the monochiral pentamethinium streptocyanines **7a** and **7b** as hydrates in satisfactory yield as felted red crystals (Scheme 4). The ^1H and ^{13}C NMR spectra of **7a** and **7b**, measured in DMSO, were in agreement with the C_2-symmetrical, all-(*E*)-configurated molecular structure shown in Scheme 4. The ^1H NMR signals of 3-H and 2/4-H were both triplets, with $^3J_{H,H} = 13.1$ and 12.2 Hz for the vicinal coupling of 3-H with 2/4-H and of 2/4-H with 3-H and 1/5-H, respectively. The 1/5-H signals are doublets with $^3J_{H,H} = 12.0$ Hz. All these vicinal coupling constants are characteristic of a *trans* configuration of the methine H-atoms in **7a** and 7**b**.[6b,44] Attempts to obtain crystals suitable for X-ray analysis were unsuccessful.



(+)-(*R*,*R*) (as given by the formula): **7a** (yield 73%)
(-)-(*S*,*S*): **7b** (yield 76%)

Scheme 4. Synthesis of the monochiral pentamethinium dyes **7a** and **7b** (atom numbering analogous to formula **5a** and **5b** in Scheme 3)

Replacement of the two stereogenic sulfinyl groups in the monochiral streptocyanines **5a** and **5b** (Scheme 3) and in **7a** and **7b** (Scheme 4) by nonstereogenic sulfonyl groups should provide the corresponding achiral but otherwise practically identical tri- and pentamethinium streptocyanines **11** and **13** (Scheme 6), of interest for comparison of their respective UV/Vis and possibly CD spectra. For this reason, we prepared the achiral 4-aminophenyl 4-methylphenyl sulfone (**10**) from isochiral[14] sulfoxide **3c** by the reaction sequence shown in Scheme 5: protection of the amino group by acetylation to give **8c**, its oxidation with H_2O_2/AcOH to the sulfone **9**, and deprotection to afford the sulfone **10**, as straw-colored crystals and in satisfactory yield.



Scheme 5. Synthesis of the achiral 4-aminophenyl 4-methylphenyl sulfone (**10**) (atom numbering analogous to **3a** in Scheme 1)

Treatment of the amino sulfone **10** either with 3,3-diethoxy-1-propyne and aqueous HBr[6,10,18] or with cyanogen bromide and pyridine[10,54] provided the desired streptocyanines **11** and **13**, with three and five methine groups, respectively, in satisfactory yields as yellow (**11**) and red (**13**) crystals, solutions of which now had optical rotation values of zero (Scheme 6). Deprotonation of the trimethinium bromide **11** afforded the achiral, neutral streptocyanine **12** as a light yellow, microcrystalline solid in satisfactory yield (Scheme 6).

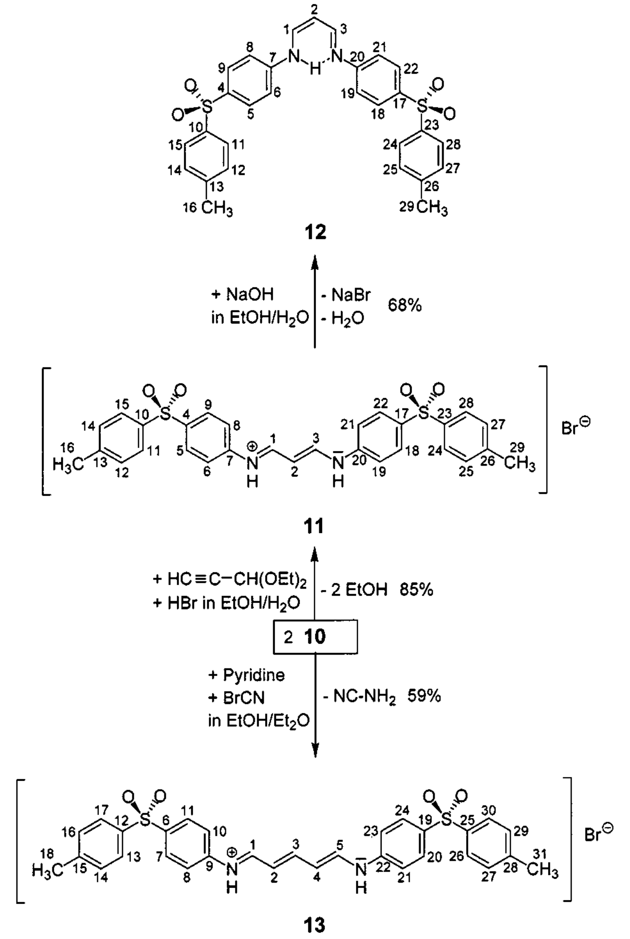
The ^1H NMR chemical shifts of the methine H-atoms of the corresponding polymethinium dyes **5a**, **5b** (Scheme 3) and **11** and of **7a**, **7b** (Scheme 4) and **13** were nearly equal (see Exp. Sect.). That is, replacement of the sulfinyl moieties by the more electron-withdrawing sulfonyl groups had practically no influence on the electron density along the tri- and pentamethinium chain of **11** and **13**, respectively. The vicinal coupling constants along the methine chains of **11** and **13** ($^3J_{H,H} \approx 11-12$ Hz) were compatible with the all-(*E*) configurations shown in Scheme 6, whereas the corresponding vicinal couplings for the neutral streptocyanine **12** ($^3J_{H,H} \approx 6$ Hz) corresponded to the given all-(*Z*) configuration in $CDCl_3$ solution. The large downfield shift (δ = 12.1!) found for the N−H signal of **12** in $CDCl_3$ solution, attested to the existence of a strong intramolecular N-H···N hydrogen bond (see Exp. Sect.).

The molecular structure of all new compounds was confirmed by elemental analysis, UV/Vis, IR, ^1H and ^{13}C NMR spectroscopy and mass spectrometry (see Exp. Sect.).

Attempts to synthesize analogous tri- and pentamethinium streptocyanines with *2-amino*phenyl 4-methylphenyl sulfoxide endgroups were unsuccessful, as the isochiral *2-amino*phenyl 4-methylphenyl sulfoxide could not be separated into its enantiomers; its diastereomeric salts with a variety of monochiral acids did not crystallize.[2] Further attempts to prepare chiral sulfoxides suitable for polymethine syntheses by *S*-oxidation of sulfur heterocycles such as 2-methylbenzothiazole and 3-ethyl-2-methylbenzothiazolium tetrafluoroborate were also unsuccessful.[2]

2. Optical Rotations and UV/Vis and CD Spectra

The maxima of the intense long-wavelength π−π* UV/Vis absorption bands and the chiroptical properties of the



Scheme 6. Synthesis of the achiral trimethinium dye **11** (as well as its corresponding neutral trimethine **12**) and the achiral pentamethinium dye **13** (atom numbering analogous to Schemes 3 and 4)

Table 1. Long-wavelength UV/Vis π−π* absorption maxima, λ_{max} (ε), specific, $[\alpha]_D$, and molar optical rotations, $[\Phi]_D$, of the sulfoxides **3a** and **3b** as well as the streptocyanines **5a** and **5b**, **7a** and **7b**, and **11−13**, measured at room temperature

Formula number	Absolute configuration	λ_{max} [nm] (ε [L·mol^{-1}·cm^{-1}])	$[\alpha]_D$ [a] (T [°C])	$[\Phi]_D$ [b]
3a	(*R*)	276 (17400)[c]	+101.6 (20)	+235
3b	(*S*)	276 (17000)[c]	−102.1 (22)	−236
5a	(*R*,*R*)	403 (54900)[d]	+29.3 (21)	+170
5b	(*S*,*S*)	402 (53700)[d]	−30.6 (22)	−177
6a	(*R*,*R*)	394 (26300)[e]	+63.7 (21)	+318
6b	(*S*,*S*)	394 (27500)[e]	−62.9 (21)	−314
7a	(*R*,*R*)	497 (69200)[f]	+194.3 (21)[g]	+1177
7b	(*S*,*S*)	498 (70800)[f]	−193.0 (21)[g]	−1169
11	−	380 (60300)[c] 405 (−)[e]	0	0
12	−	381 (49000)[c] 397 (−)[e]	0	0
13	−	513 (81300)[c] 495 (−)[e]	0	0

[a] Measured in EtOH; unit: 10^{-1}·deg·cm^2·g^{-1}. [b] $[\Phi]_D = ([\alpha]_D \cdot M_r)/100$, with M_r = relative molar mass. [c] In MeOH. [d] In MeOH/EtOH (1:4). [e] In CH_2Cl_2. [f] In $CHCl_3$. [g] In EtOH + a drop of aqueous HBr (48 cg/g) in order to avoid solvolysis.

new streptocyanines are compiled in Table 1. The UV/Vis spectra of the chiral tri- and pentamethinium dyes **5a**, **5b**, **7a**, and **7b** exhibited long-wavelength Vis absorption bands with vinylene shifts of $\Delta\lambda$ = 94−96 nm, as to be expected for symmetrical polymethine dyes on lengthening of the conjugated methine chain by one double bond.[5,6] An analogous vinylene shift of $\Delta\lambda$ = 90 nm (measured in CH_2Cl_2) was found for the achiral tri- and pentamethinium dyes **11** and **13**. Deprotonation of **5a** and **5b** (to give **6a** and **6b**; Scheme 3) and **11** (to give **12**; Scheme 6) resulted in small hypsochromic band shifts of up to $\Delta\lambda \approx 9$ nm.

Replacement of the two stereogenic sulfinyl endgroups by the more electronegative sulfonyl groups[55] gave rise only to small band shifts of $\Delta\lambda = \pm 2$ nm (measured in CH_2Cl_2) for the trimethinium dyes **5a**/**5b** → **11** and the pentamethinium dyes **7a**/**7b** → **13**. The more strongly electron-withdrawing natures of the sulfonyl endgroups[55] practically did not influence the corresponding UV/Vis spectra.

The Vis absorption maxima of the new chiral streptocyanine dyes **5a**, **5b**, **7a**, and **7b** were, with λ_{max} = 402−403 (**5**) and 497−498 (**7**) nm, nearly in the same absorption range as recently observed for other chiral tri- and pentamethinium streptocyanine dyes with two 1,2,3,4-tetrahydro-2,6(or 3,6)-dimethylquinolyl endgroups (tri: λ_{max} = 388−398 nm; penta: λ_{max} = 492−501 nm[18,20]) and pentamethinium streptocyanine dyes with two 1′,2′,3′,4′,10,11-hexahydroquinin-1′-yl endgroups (penta: λ_{max} = 506−511 nm[1]).

The long-wavelength Vis absorption maxima of the chiral streptocyanine dyes **5a**, **5b**, **7a**, and **7b** seemed to be sufficiently hypsochromically separated from the sodium D line emission at 589 nm to permit polarimetric measurements of their specific optical rotations (Table 1). The molar optical rotations of the new chiral streptocyanines **5a**, **5b**, **7a**, and **7b** were, with $\Phi \approx 173$ (**5**) and 1173 (**7**), rather high, lying at the same order of magnitude as observed for other chiral streptocyanines with stereogenic centers more remote from the polymethine chain;[20] however, they were considerably smaller than those observed for streptocyanines with stereogenic centers closer to the methine chromophore.[18] The main optical activity of **5a**, **5b**, **7a**, and **7b** is obviously caused by the two stereogenic centers in the sulfoxide endgroups as part of the whole conjugated polymethinic chromophore, but there seem to be additional contributions to the overall optical activity, either from dye aggregation in solution or from helical twisting of the planar methine π-system, as found in other cases; see refs.[1,18,20,21] for a more detailed discussion. It should also be noted that on going from **5a**/**5b** ($\lambda_{max} \approx 403$ nm) to **7a**/**7b** ($\lambda_{max} \approx 498$ nm), an increasing dispersion enhancement of the optical rotation could take place as the Vis absorption maxima come closer to the sodium D line, making a correlation between molecular structure and observed optical rotation more difficult.

The CD spectrum of the monochiral trimethinium streptocyanine dye **5b** is shown in Figure 5; the corresponding CD spectrum of the enantiomeric monochiral dye **5a** is identical but mirror-inverted.[2] Coincident with the Vis absorption maximum of **5b** at 403 nm there is a broad CD band, with an increasing negative amplitude ($\Delta\varepsilon < 0$) on going to lower temperatures, accompanied by new bands at these lower temperatures. The strong temperature dependence of the CD spectrum of **5b** (as well as that of **7b**[2]) points to the existence of a dynamic equilibrium in solution, either between monomers and higher aggregates (possibly J-aggregates;[49−53] see also Figure 3) or between different conformers with varying helical twisting. The complete absence of optical activity in solutions of the achiral tri- and pentamethinium streptocyanine dyes **11** and **13**, which differ from **5a** and **5b** and from **7a** and **7b** only by two additional oxygen atoms at the stereogenic S centers, rules out the preferential spontaneous formation of helically twisted conformations of **11** and **13**, as has been found in other cases.[31−34] However, with the experimental results available at present, no definite answer to the question of the conformational and aggregational behavior of the new chiral streptocyanine dyes in solution is yet possible. For a detailed discussion of the CD spectra of corresponding chiral tri- and pentamethinium streptocyanine dyes with other endgroups possessing stereogenic centers see ref.[21].

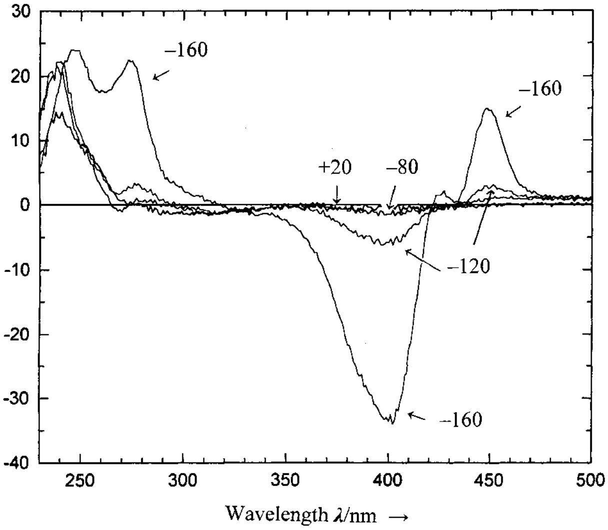


Figure 5. Temperature-dependent CD spectra of the monochiral (−)-(*S*,*S*)-trimethinium bromide **5b**, measured in MeOH/EtOH (1:4) at +20, −80, −120, and −160 °C with a dye concentration of $c = 2.5\cdot10^{-4}$ mol/L

Conclusion

Chiral polymethine dyes combine the features of polymethinic π-electronic structures with chirality and allow the study of their mutual interplay. As a new endgroup for chiral tri- and pentamethinium streptocyanine dyes, 4-aminophenyl 4-methylphenyl sulfoxide (**3c**) has been synthesized and separated into its enantiomers **3a** and **3b**, the absolute configurations of which have been determined by X-ray analysis. From the monochiral sulfoxides **3a** and **3b**, new chiral cationic (**5a**, **5b**, **7a**, and **7b**) and neutral (**6a**, **6b**) tri- and pentamethine streptocyanine dyes have been prepared, together with their achiral sulfonyl analogues **11**−**13**. Relationships between their UV/Vis and chiroptical properties and their molecular structure have been discussed, continuing the efforts of König, who was first to reach conclusions about polymethine structure and optical activity.[9,10] As functional dyes, chiral polymethine dyes should be of interest as sensitizers for silver halide emulsions applied in photography; because of their peculiar chiroptical properties, they should have different sensitivities for right- and left-handed circularly polarized light.

Experimental Section

General Methods: Melting points (not corrected): Kofler Mikroheiztisch (Reichert). Elemental analyses: CHN-Automat Rapid (Heraeus) at the Analytik-Servicelabor of the Department of Chemistry, Marburg. UV/Vis spectra: Double-beam UV/Vis/NIR U-3410 spectrophotometer (Hitachi) with 1.00-cm Suprasil (Hellma) quartz cells. IR spectra: IFS 88 spectrophotometer (Bruker) with KBr discs. ^{1}H and ^{13}C NMR spectra: AC 300 and AMX 500 spectrometers (Bruker), with tetramethylsilane as internal standard. Assignments of the signals according to the atom numbering given in the reaction schemes. Mass spectra: MAT CH-7A (Varian) with electron impact (EI, 70 eV) and HP 5989-B (Hewlett−Packard) with atmospheric pressure chemical ionization (APCI) technique. Optical rotation: Polarimeter 241 (Perkin−Elmer) with 10-cm quartz cell at $\lambda = 589$ nm (sodium D line) at ambient temperature; concentration *c* expressed in g of substance in 100 mL of solution. CD spectra: AVIV 62A DS spectrometer, equipped for thermostatted low-temperature measurements (Cryostate DN 714, Oxford Instruments) and automated data collection. The CD spectra were measured at the University of Duisburg/Germany, Chair of Theoretical Chemistry, with the permission of Prof. Dr. V. Buß and the help of his co-worker R. Knierim. Analytical TLC: 60F-245 microcards with silica gel and fluorescence indicator on aluminium foil (Merck). Flash chromatography: 60 silica gel (Merck−Schuchardt), particle size 0.040−0.063 mm, carried out according to Still et al.[56] HPLC: Apparatus Gynkotek-HPLC with Diode-Array-Detector (DAD) ($\lambda = 210-280$ nm), automatic sampling (Model Gina 50), and HPLC pump (Model M 480), with a Chiralcel OD column (Daicel) as chiral stationary phase. Solvents: solvents for synthetic work were purified according to usual standard methods.[57] Solvents for UV/Vis, CD, and polarimetric spectroscopic measurements were used in the highest quality commercially available (analytical or spectroscopic grade). Crystal structure determination: X-ray Servicelabor of the Department of Chemistry, Marburg, with automated Enraf-Nonius four-circle diffractometer CAD 4 or Stoe IPDS image-plate system with graphite-monochromated Mo-K_α [$\lambda = 71.073$ pm at 193(2) K] (for **5b** and **6b**) or Cu-K_α radiation [$\lambda = 154.178$ pm at 213(2) K] (for **3b**), and with software for data collection (CAD4-Express or Stoe Expose), cell refinement (CAD4-Expess or Stoe Cell), and data reduction (XCAD4 or Stoe Integrate). As the UV/Vis, IR, NMR, and MS data for the monochiral compound pairs **a** and **b**[39] are practically identical, spectroscopic data for only one of the enantiomers are given in each case.

Preparation of Monochiral Sulfoxides 3a and 3b (Schemes 1 and 2)

4-Toluenesulfinic Acid (2): An aqueous solution of HCl ($c = 16$ cg/g; 250 mL, 1.275 mol) was added dropwise to a vigorously stirred solution of dried sodium 4-toluenesulfinate (**1**, 200.1 g, 1.123 mol; Sigma−Aldrich) in water (1500 mL) at room temp. Stirring was then continued for 2 h at ca. 0 °C. The colorless precipitate formed was filtered off, washed three times with ice-cold water, and dried in vacuo in a desiccator with P_4O_{10}, fixed on a carrier (Sicapent®; Merck). For purification, *n*-hexane (300 mL) was added dropwise to a stirred solution of the crude product in diethyl ether (300 mL). The precipitate formed was filtered off and dried in vacuo to give **2** (168.4 g, 96%) as colorless solid with m.p. 86 °C (ref.[40] 85 °C). ^{1}H NMR (CD_3SOCD_3): $\delta = 2.35$ (s, 3 H, CH_3), 7.35 (d, $^3J = 8.2$ Hz, 2 H, 2/6-H), 7.54 (d, $^3J = 8.2$ Hz, 2 H, 3/5-H), ca. 10.5 (broad s, SO_2 H). ^{13}C NMR (CD_3SOCD_3): $\delta = 21.1$ (CH_3), 124.7 (C-2/6), 129.6 (C-3/5), 141.5 (C-1), 146.2 (C-4). MS (EI): *m*/*z* (%) = 156 (2) [M^+], 155 (23) [$M^+ - H$], 139 (69) [$M^+ - OH$], 123 (100) [$M^+ - O_2H$], 91 (91) [$M^+ - O_2H - S$], 77 (24) [$C_6H_5^+$]. $C_7H_8O_2S$ (156.2): calcd. C 53.83, H 5.16; found C 53.60, H. 5.24.

(±)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3c): A stirred mixture of sulfinic acid **2** (168.4 g, 1.078 mol) and freshly distilled aniline (673.0 g, 7.227 mol) was heated at 110−115 °C for 30 h in a 1-L three-necked, round-bottomed flask, equipped with stirrer, reflux condenser, and interior thermometer, during which the mixture turned violet. After the mixture had cooled to room temp. overnight, a suspension of a violet, crystalline precipitate in a violet solution was obtained. The excess aniline was removed from this suspension by steam distillation, collecting ca. 5 L of aqueous distillate altogether. After the remaining suspension had cooled to room temp. with stirring, been allowed to stand for ca. 12 h, and the aqueous phase decanted, a solid contaminated with a highly viscous, violet oil was obtained. The oil was removed by filtration under vacuum, the solid was recrystallized twice from ethanol (ca. 250 mL), washed with ethanol, and dried with P_4O_{10} (Sicapent®) in vacuo to afford isochiral **3c** (105.3 g, 42%) as colorless needles with m.p. 169 °C (ref.[38] 169.5−170.5 °C). HPLC: chromatogram with Chiralcel® OD as chiral stationary phase and *n*-heptane/2-propanol (80:20, cL/L) as eluant gave two peaks of equal intensity, with retention times of $t = 37.6$ and 47.2 min, one for each enantiomer. IR (KBr): $\tilde{\nu} = 3427$, 3341, and 3236 cm^{-1} (NH_2), 1022 (S=O). ^{1}H NMR (CD_3SOCD_3): $\delta = 2.29$ (s, 3 H, CH_3), 5.80 (s, 2 H, NH_2), 6.65 (d, $^3J = 8.6$ Hz, 2 H, 3/5-H), 7.28 (d, $^3J = 7.4$ Hz, 2 H, 2/6-H or 9/11-H), 7.30 (d, $^3J = 8.3$ Hz, 2 H, 9/11-H or 2/6-H), 7.46 (d, $^3J = 8.1$ Hz, 2 H, 8/12-H). ^{13}C NMR (CD_3SOCD_3): $\delta = 20.9$ (CH_3), 113.9 (C-3/5), 124.2 (C-2/6), 127.3 (C-9/11), 129.8 (C-8/12), 130.7 (C-1), 140.3 (C-10), 143.8 (C-7), 152.1 (C-4). MS (EI): *m*/*z* (%) = 233 (1) [$M^+ + 2$ H], 232 (5) [$M^+ + H$], 231 (38) [M^+], 215 (21) [$M^+ - O$], 183 (100) [$M^+ - O - NH_2 - CH_3$], 140 (56) [$M^+ - C_7H_7$], 124 (28) [$M^+ - O - C_7H_7$], 108 (47) [$M^+ - O - C_7H_7 - NH_2$], 91 (8) [$C_7H_7^+$], 65 (14) [$C_5H_5^+$]. $C_{13}H_{13}NOS$ (231.3): calcd. C 67.50, H 5.66, N 6.06; found C 67.30, H 5.63, N 5.98.

Monochiral (+)-(*R*)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3a)[14]

(a) (*R*)-4-Ammoniophenyl 4-Methylphenyl Sulfoxide (1*S*)-Camphor-10-sulfonate (4a): Isochiral[14] **3c** (123.4 g, 533 mmol) was added with stirring to a solution of (+)-(1*S*)-camphor-10-sulfonic acid (135.3 g, 582 mmol; Fluka: purity 99 cg/g, *ee* = 99%) in water (300 mL) at 80 °C. Stirring at 80 °C was continued until a clear solution was formed and the solution was then allowed to cool slowly to room temp. The first crystals appeared after 3 h, and after 2 d the precipitate formed was filtered off, washed with ice-cold water, and dried with P_4O_{10} (Sicapent®) in vacuo to yield the crude diastereomeric sulfonate **4a** (147.1 g, 60%) as large, colorless needles with m.p. 134 °C. Because the sulfonate obtained was not yet diastereomerically pure, recrystallization from an aqueous (+)-(1*S*)-camphor-10-sulfonic acid solution (c = 4 cg/g) was repeated 21 times. Since the optical rotations of the diastereomeric sulfonate obtained after each recrystallization step varied considerably, the progress of enantiomeric enrichment was monitored by releasing small amounts of the crude amino sulfoxide **3a** and measuring the optical activities as follows.

(b) Anisochiral (+)-(*R*)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3a) for Purification Monitoring:[14] Aqueous ammonia (c = 25 cg/g; 0.1 mL, 5.7 mmol) was added with stirring to a solution of diastereomerically enriched camphor-10-sulfonate **4a** (200 mg, 0.43 mmol) in water (2 mL) at 70 °C. The colorless precipitate formed was filtered off, washed with a small amount of water, and dried with P_4O_{10} (Sicapent®) in vacuo to give enantiomerically enriched anisochiral amino sulfoxide **3a** as colorless crystals with $[\alpha]_D^{22} = +22.3$ (c = 0.321 in ethanol). This procedure was repeated analogously after each of the following 21 recrystallization steps, until a constant specific optical rotation was reached for **3a**.

(c) First Recrystallization of Diastereomerically Enriched Sulfonate 4a: Enriched **4a** (145.0 g, 312 mmol), obtained according to Procedure (a), was dissolved with stirring in an aqueous solution of (+)-(1*S*)-camphor-10-sulfonic acid (c = 4 cg/g; 180 mL) at 80 °C. Stirring at 80 °C was continued until a clear solution was formed. The solution was allowed to cool slowly to room temp. After the mixture had been allowed to stand for 24 h, the precipitate formed was filtered off, washed with water (20 mL), and dried with P_4O_{10} (Sicapent®) in vacuo to give diastereomerically further enriched sulfonate **4a** (107.8 g, 44%, relative to the isochiral starting compound **3c**) as colorless needles with m.p. 134 °C. The specific optical rotation measured for the corresponding enantiomerically enriched anisochiral amino sulfoxide **3a**, obtained from this sulfonate according to Procedure (b), was $[\alpha]_D^{21} = +33.5$ (c = 0.319 in ethanol).

(d) Second Recrystallization of Diastereomerically Enriched Sulfonate 4a: Enriched **4a** (107.0 g, 230 mmol), obtained according to Procedure (c), was dissolved with stirring in an aqueous solution of (+)-(1*S*)-camphor-10-sulfonic acid (c = 4 cg/g; 130 mL) at 80 °C. Stirring at 80 °C was continued until a clear solution was formed, and the hot solution was filtered. The filtrate was allowed to cool slowly to room temp. After the mixture had been allowed to stand for 24 h, the precipitate formed was filtered off, washed with water (20 mL), and dried with P_4O_{10} (Sicapent®) in vacuo to afford diastereomerically further enriched sulfonate **4a** (100.5 g, 41%, relative to the isochiral starting compound **3c**) with m.p. 134 °C. The specific optical rotation measured for the corresponding amino sulfoxide **3a**, obtained from this sulfonate according to Procedure (b), was $[\alpha]_D^{22} = +41.7$ (c = 0.318 in ethanol).

(e) Recrystallization Steps 3−20 for Diastereomerically Enriched Sulfonate 4a: The recrystallization Procedure (d) was repeated analogously 20 times, with gradual, step-by-step ($\Delta V = -5$ mL) reduction of the volume of the aqueous solution of (+)-(1*S*)-camphor-10-sulfonic acid (c = 4 cg/g) from 130 mL (step 2) to 40 mL (step 20). The specific optical rotation of the corresponding enantiomerically enriched anisochiral amino sulfoxides **3a**, prepared from the respective sulfonates according to Procedure (b), increased from $[\alpha]_D^{22} = +41.7$ (step 2) to $[\alpha]_D^{21} = +101.3$ (c = 0.320 in ethanol) (step 20).

(f) Diastereomerically Pure Sulfonate 4a after the Final Recrystallization (Step 21): The enriched **4a** (34.4 g, 74.0 mmol) obtained after recrystallization step 20 was dissolved with stirring in an aqueous solution of (+)-(1*S*)-camphor-10-sulfonic acid (c = 4 cg/g; 40 mL) at 80 °C. Stirring at 80 °C was continued until a clear solution was formed, and the hot solution was filtered. The filtrate was allowed to cool slowly to room temp. After the mixture had been allowed to stand for 24 h, the precipitate formed was filtered off, washed with water, and dried with P_4O_{10} (Sicapent®) in vacuo to give diastereomerically pure sulfonate **4a** (34.0 g, 14%, relative to the isochiral starting compound **3c**) as colorless needles with m.p. 131 °C (ref.[10c] 131 °C) and $[\alpha]_D^{22} = +18.1$ ($c = 0.356$ in ethanol). The specific optical rotation measured for the now enantiomerically pure monochiral amino sulfoxide **3a**, obtained from this sulfonate according to Procedure (b), was a practically constant value of $[\alpha]_D^{23} = +101.7$ ($c = 0.319$ in ethanol) {ref.[10c] $[\alpha]_D^{20} = +96.0$ ($c = 0.319$ in ethanol)}. The analytical data for the diastereomerically pure sulfonate **4a** are as follows. IR (KBr): $\tilde{\nu} = 3409$ cm^{-1} (NH_3), 1739 (C=O), 1028 (S=O). ^1H NMR (CD_3SOCD_3): $\delta = 0.55$ (s, 3 H, 22-H), 0.73−0.78 (m, 1 H), 0.82 (s, 3 H, 23-H), 1.03−1.19 (m, 2 H), 1.59−1.68 (m, 2 H), 1.74−1.77 (m, 1 H), 2.02−2.11 (m, 1 H), 2.13 (s, 3 H, 13-H), 2.30 (d, $^2J = 14.7$ Hz, 1 H, 20-H_a), 2.39 (m, 1 H), 2.78 (d, $^2J = 14.7$ Hz, 1 H, 20-H_b), 7.01 (d, $^3J = 8.5$ Hz, 2 H, 3/5-H), 7.15 (d, $^3J = 8.1$ Hz, 2 H, 9/11-H), 7.37 (d, $^3J = 8.2$ Hz, 2 H, 8/12-H), 7.43 (d, $^3J = 8.6$ Hz, 2 H, 2/6-H). A complete assignment of all signals was not possible. ^{13}C NMR (CD_3SOCD_3): $\delta = 19.7$ and 20.1 (C-22 and C-23), 21.0 (C-13), 24.3, 26.5, 42.3, 42.4, and 47.1 (C-16, C-17, C-18, C-20, and C-21), 47.3 (C-19), 58.3 (C-15), 120.4 (C-3/5), 124.4 (C-2/6), 126.3 (C-9/11), 130.1 (C-8/12), 140.1 (C-1), 141.2 (C-10), 141.4 (C-7), 143.1 (C-4), 216.1 (C-14). A complete assignment of all signals was not possible. MS (EI): m/z (%) = 232 (6) [M^+ + H − camphorsulfonic acid], 231 (31) [M^+ − camphorsulfonic acid], 215 (51) [M^+ − O − camphorsulfonic acid], 199 (12) [M^+ − 2O − camphorsulfonic acid], 183 (100) [M^+ − SO − camphorsulfonic acid], 151 (26) [camphorsulfonic acid$^+$ − SO_3], 140 (73) [M^+ − C_7H_7 − camphorsulfonic acid], 124 (42) [M^+ − O − C_7H_7 − camphorsulfonic acid], 123 (44) [M^+ − O − C_7H_7 − H − camphorsulfonic acid], 108 (79) [M^+ − O − C_7H_7 − NH_2 − camphorsulfonic acid], 91 (46) [$C_7H_7^+$], 81 (37) [HSO_3^+], 65 (51) [$C_5H_5^+$]. $C_{23}H_{29}NO_5S_2\cdot 0.5H_2O$ (463.6 + 9.0 = 472.6): calcd. C 58.45, H 6.40, N 2.96; found C 58.41, H 6.33, N 2.96.

(g) Monochiral (+)-(*R*)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3a): Diastereomerically pure sulfonate **4a** (33.2 g, 71.0 mmol), obtained according to Procedure (f), was dissolved with stirring in water (ca. 40 mL) at 80 °C. The solution was filtered hot, and aqueous ammonia (c = 25 cg/g; 10 mL, 568 mmol) was added dropwise to the hot filtrate with stirring. The precipitate formed was filtered off, washed with water, dried with P_4O_{10} (Sicapent®), and recrystallized from water-free ethanol (ca. 50 mL) to give the monochiral amino sulfoxide **3a** (9.3 g, 8%, relative to the isochiral starting compound **3c**) as colorless crystals with m.p. 151 °C (ref.[10c] 151 °C). $[\alpha]_D^{20} = +101.6$ ($c = 0.316$ in ethanol) {ref. [10c] $[\alpha]_D^{20} = +96.0$ ($c = 0.319$ in ethanol)}. HPLC: chromatogram with Chiralcel® OD as chiral stationary phase and *n*-heptane/2-propanol (80:20 cL/L) as eluant to give only *one* peak with retention time $t = 37.5$ min. UV/Vis (methanol): λ_{max} (lg ε) = 276 nm (4.24). The ^1H and ^{13}C NMR, IR, and MS data were identical to those obtained for isochiral **3c**. $C_{13}H_{13}NOS$ (231.3): calcd. C 67.50, H 5.66, N 6.06; found C 67.32, H 5.56, N 5.90.

Monochiral (−)-(*S*)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3b)[14]

(h) (*S*)-4-Ammoniophenyl 4-Methylphenyl Sulfoxide (1*R*)-Camphor-10-sulfonate (4b): Aqueous ammonia (c = 25 cg/g; 30 mL, 1.70 mol) was added dropwise with stirring at room temp to the collected mother liquors (i.e., filtrates) from the preceding Procedures (a) and (c) for the isolation of **4a**. The precipitate formed was filtered off, washed with water, and dried with P_4O_{10} (Sicapent®) in vacuo to afford enantiomerically enriched anisochiral[14] amino sulfoxide **3b** (42.8 g, 35%, relative to the isochiral starting compound **3c**) as colorless crystals with $[\alpha]_D^{21} = -55.6$ ($c = 0.314$ in ethanol). This anisochiral amino sulfoxide **3b** (42.8 g, 185 mmol) was added with stirring to a solution of (−)-(1*R*)-camphor-10-sulfonic acid (46.9 g, 202 mmol; Fluka: purity 99 cg/g, *ee* = 99%) in water (100 mL) at 80 °C. The clear solution was allowed to cool slowly to room temp. After this solution had been allowed to stand for 24 h, the precipitate formed was filtered off, washed with a small amount of ice-cold water, and dried with P_4O_{10} (Sicapent®) in vacuo to afford crude diastereomerically enriched sulfonate **4b** (85.2 g, 34%, relative to the isochiral starting compound **3c**) as colorless needles.

(i) Recrystallization Steps 1−25 for Diastereomerically Enriched Sulfonate 4b: In order to obtain diastereomerically pure sulfonate **4b**, its recrystallization from aqueous solutions of (−)-(1*R*)-camphor-10-sulfonic acid (c = 4 cg/g) was repeated 25 times, analogously to the preceding Procedures (d) and (e). The progress of purification was monitored by releasing small amounts of the corresponding amino sulfoxide **3b** with aqueous ammonia after each recrystallization step and measuring their optical activities, analogously to the preceding Procedure (b).

(j) Diastereomerically Pure Sulfonate 4b after the Final Recrystallization (Step 25): After the 25th recrystallization, diastereomerically pure sulfonate **4b** (17.3 g, 7%, relative to the isochiral starting compound **3c**) was obtained as colorless crystals with m.p. 131−132 °C (ref.[37] 133−134 °C) and $[\alpha]_D^{20} = -17.9$ ($c = 0.347$ in ethanol). IR (KBr): $\tilde{\nu} = 3413$ cm^{-1} (NH_3), 1740 (C=O), 1029 (S=O). ^1H NMR (CD_3SOCD_3): $\delta = 0.65$ (s, 3 H, 22-H), 0.83−0.88 (m, 1 H), 0.93 (s, 3 H, 23-H), 1.13−1.30 (m, 2 H), 1.69−1.79 (m, 2 H), 1.85−1.87 (m, 1 H), 2.12−2.21 (m, 1 H), 2.23 (s, 3 H, 13-H), 2.41 (d, $^2J = 14.7$ Hz, 1 H, 20-H_a), 2.47−2.56 (m, 1 H), 2.90 (d, $^2J = 14.7$ Hz, 1 H, 20-H_b), 7.13 (d, $^3J = 8.5$ Hz, 2 H, 3/5-H), 7.25 (d, $^3J = 8.1$ Hz, 2 H, 9/11-H), 7.47 (d, $^3J = 8.1$ Hz, 2 H, 8/12-H), 7.54 (d, $^3J = 8.5$ Hz, 2 H, 2/6-H). A complete assignment of all signals was not possible. ^{13}C NMR (CD_3SOCD_3): $\delta = 19.6$ and 20.1 (C-22 and C-23), 21.0 (C-13), 24.3, 26.5, 42.3, 42.4, and 47.1 (C-16, C-17, C-18, C-20, and C-21), 47.3 (C-19), 58.2 (C-15), 120.4 (C-3/5), 124.3 (C-2/6), 126.3 (C-9/11), 130.1 (C-8/12), 140.1 (C-1), 141.1 (C-10), 141.4 (C-7), 143.1 (C-4), 216.0 (C-14). A complete assignment of all signals was not possible. MS (EI): practically identical with that of **4a** [see Procedure (f)]. $C_{23}H_{29}NO_5S_2$ (463.6): calcd. C 59.59, H 6.30, N 3.02; found C 59.40, H 6.31, N 2.92.

(k) Monochiral (−)-(*S*)-4-Aminophenyl 4-Methylphenyl Sulfoxide (3b):[14] Analogously to the preparation of **3a** [see Procedure (g)], diastereomerically pure sulfonate **4b** (16.9 g, 36.0 mmol), obtained according to Procedure (j), was dissolved with stirring in water (ca. 20 mL) at 80 °C. The solution was filtered hot, and aqueous ammonia (c = 25 cg/g; 10 mL, 568 mmol) was added dropwise to the hot filtrate with stirring. The precipitate formed was filtered off, washed with water, dried with P_4O_{10} (Sicapent®) in vacuo, and recrystallized from water-free ethanol (12 mL) to yield monochiral **3b** (6.52 g, 5%, relative to the isochiral starting compound **3c**) as colorless crystals with m.p. 151 °C (ref.[37] 151 °C). $[\alpha]_D^{22} = -102.1$ ($c = 0.327$ in ethanol) {ref.[37] $[\alpha]_D^{25} = -97.0$ ($c = 1.211$)}. HPLC: Chromatogram with Chiralcel® OD as chiral stationary phase and *n*-heptane/2-propanol (80:20 cL/L) as eluant to give only *one* peak with retention time $t = 47.0$ min. UV/Vis (methanol): λ_{max} (lg ε) = 276 nm (4.23). The ^1H and ^{13}C NMR, IR, and MS data were identical to those obtained for isochiral **3c**. $C_{13}H_{13}NOS$ (231.3): calcd. C 67.50, H 5.66, N 6.06; found C 67.56, H 5.63, N 6.00. X-ray analysis: see Figure 1 and ref.[43]

Preparation of Monochiral Trimethine Streptocyanine Dyes 5 and 6 (Scheme 3)

(+)-(*R,R*)-1,3-Bis[4-(4-methylphenylsulfinyl)phenylamino]trimethinium Bromide (5a): 3,3-Diethoxy-1-propyne (1.11 g, 8.66 mmol) and then aqueous hydrobromic acid (*c* = 48 cg/g; 2.92 g, 17.5 mmol) were added dropwise with stirring to a solution of monochiral **3a** (4.00 g, 17.3 mmol) in ethanol (20 mL) at 60 °C. The reaction mixture turned brownish and after ca. 15 min a lemon-yellow precipitate was formed. Stirring and heating at 60 °C was continued for 1 h. After the mixture had cooled to room temp. and been allowed to stand for ca. 12 h, the precipitate formed was filtered off, washed with small amounts of ice-cold ethanol and acetone, dried with P_4O_{10} (Sicapent®) in vacuo, and recrystallized from water-free ethanol to yield **5a** (2.95 g, 59%) as yellow needles with m.p. 215−216 °C (ref.[10c] 215 °C). $[\alpha]_D^{21} = +29.3$ (*c* = 0.113 in ethanol) {ref.[10c] $[\alpha]_D^{20} = +69$ (*c* = 0.101 in ethanol)}. IR (KBr): $\tilde{\nu} = 3388\ \text{cm}^{-1}$ (NH), 1030 (S=O). UV/Vis (methanol/ethanol, 1:4): λ_{max} (lg ε) = 403 nm (4.74), 338 (4.29), 199 (4.96). ^{1}H NMR (CD_3SOCD_3): δ = 2.28 (s, 6 H, 16/29-H), 6.43 (t, ^3J = 11.4 Hz, 1 H, 2-H), 7.32 (d, ^3J = 7.4 Hz, 4 H, 8/21-H and 6/19-H), 7.54 (d, ^3J = 8.8 Hz, 4 H, 15/28-H and 11/24-H or 14/27-H and 12/25-H), 7.57 (d, ^3J = 8.2 Hz, 4 H, 14/27-H and 12/25-H or 15/28-H and 11/24-H), 7.77 (d, ^3J = 7.9 Hz, 4 H, 9/22-H and 5/18-H), 9.02 (t, ^3J = 11.8 Hz, 2 H, 1/3-H), 12.5 (d, ^3J = 11.3 Hz, 2 H, NH). ^{13}C NMR (CD_3SOCD_3): δ = 21.0 (C-16/29), 99.9 (C-2), 118.6 (C-8/21 and C-6/19), 124.4 (C-9/22 and C-5/18), 126.2 (C-14/27 and C-12/25), 130.2 (C-15/28 and C-11/24), 140.7 (C-4/17), 141.5 (C-13/26), 142.7 (C-10/23), 143.3 (C-7/20), 159.5 (C-1/3). MS (electrospray, positive): *m/z* = 499 $[M^+ - Br]$. $C_{29}H_{27}BrN_2O_2S_2 \cdot 2H_2O$ (579.6 + 36.0 = 615.6): calcd. C 56.58, H 5.08, N 4.55; found C 56.60, H 4.97, N 4.39.

(−)-(*S,S*)-1,3-Bis[4-(4-methylphenylsulfinyl)phenylamino]trimethinium Bromide (5b): According to the procedure described for **5a**, 3,3-diethoxy-1-propyne (1.04 g, 8.11 mmol), aqueous hydrobromic acid (*c* = 48 cg/g; 2.75 g, 16.5 mmol), and a solution of monochiral **3b** (3.77 g, 16.3 mmol) in water-free ethanol (15 mL) were transformed at 60 °C into **5b** (2.89 g, 61%), obtained as yellow needles with m.p. 215−216 °C. $[\alpha]_D^{22} = -30.6$ (*c* = 0.110 in ethanol). UV/Vis (methanol/ethanol 1:4): λ_{max} (lg ε) = 402 nm (4.73), 339 (4.28), 199 (4.94). The ^{1}H and ^{13}C NMR, IR, and MS data were identical to those obtained for **5a**. $C_{29}H_{27}BrN_2O_2S_2 \cdot 3H_2O$ (579.6 + 54.0 = 633.6): calcd. C 54.97, H 5.25, N 4.42; found C 54.87, H 5.07, N 4.29. X-ray analysis: see Figures 2 and 3 and ref.[43]

(+)-(*R,R*)-3-[4-(4-Methylphenylsulfinyl)phenylamino]propenal 4-(4-Methylphenylsulfinyl)phenylimine (6a): An aqueous NaOH solution (*c* = 37 cg/g: 1.50 mL, 13.9 mmol) was added with stirring to a suspension of the bromide **5a** (0.50 g, 0.86 mmol) in ethanol (50 mL) at room temp. After further stirring for 30 min, the orange-colored solution was filtered and the filtrate was added dropwise to water (250 mL) with vigorous stirring. The precipitate formed was filtered off, washed with diethyl ether, and dried with P_4O_{10} (Sicapent®) in vacuo. For purification, a solution of the product in acetone (10 mL) was added dropwise to diethyl ether (200 mL) with stirring. The precipitate formed was filtered off and dried to afford **6a** (0.37 g, 86%) as a yellow, microcrystalline solid with m.p. 95 °C (ref.[10c] 93−94 °C). $[\alpha]_D^{21} = +63.7$ (*c* = 0.520 in ethanol) {ref.[10c] $[\alpha]_D^{20} = +90$ (*c* = 0.195 in ethanol)}. IR (KBr): $\tilde{\nu} = 3431\ \text{cm}^{-1}$ (NH), 1027 (S=O). UV/Vis (dichloromethane): λ_{max} (lg ε) = 394 nm (4.42), 218 (4.39). ^{1}H NMR ($CDCl_3$): δ = 2.29 (s, 6 H, 16/29-H), 5.10 (t, ^3J = 6.2 Hz, 1 H, 2-H), 7.02 (d, ^3J = 8.5 Hz, 4 H, 8/21-H and 6/19-H), 7.18 (d, ^3J = 8.0 Hz, 4 H, 14/27-H and 12/25-H), 7.44 (d, ^3J = 8.1 Hz, 4 H, 15/28-H and 11/24-H), 7.50 (d, ^3J = 8.5 Hz, 4 H, 9/22-H and 5/18-H), 7.58 (d, ^3J = 6.2 Hz, 2 H, 1/3-H), 12.1 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ = 21.5 (C-16/29), 96.9 (C-2), 119.0 (C-8/21 and C-6/19), 125.0 (C-9/22 and C-5/18), 126.8 (C-14/27 and C-12/25), 130.2 (C-15/28 and C-11/24), 140.4 (C-4/17), 141.6 (C-13/26), 142.8 (C-10/23), 149.0 (C-7/20), 149.1 (C-1/3). MS (APCI, positive): *m/z* = 499 $[M^+ + H]$. $C_{29}H_{26}N_2O_2S_2 \cdot 3.5\ H_2O$ (498.7 + 63.0 = 561.7): calcd. C 62.00, H 5.92, N 4.99; found C 61.66, H 5.64, N 4.83.

(−)-(*S,S*)-3-[4-(4-Methylphenylsulfinyl)phenylamino]propenal [4-(4-Methylphenylsulfinyl)phenylimine] (6b): According to the procedure described for **6a**, the monochiral bromide **5b** (1.00 g, 1.72 mmol), suspended in ethanol (100 mL), was transformed with aqueous NaOH (*c* = 37 cg/g; 3.00 mL, 27.8 mmol) into an orange solution of **6b**, which was precipitated by pouring this solution slowly into water (500 mL) with stirring. Analogous workup and purification by addition of a solution of the product in acetone (20 mL) to diethyl ether (400 mL) yielded **6b** (0.81 g, 94%) as a yellow, microcrystalline solid with m.p. 95 °C. $[\alpha]_D^{21} = -62.9$ (*c* = 0.522 in ethanol). UV/Vis (dichloromethane): λ_{max} (lg ε) = 394 nm (4.44), 219 (4.40). The ^{1}H and ^{13}C NMR, IR, and MS data were identical to those of **6a**. $C_{29}H_{26}N_2O_2S_2 \cdot 0.5H_2O$ (498.7 + 9.0 = 507.7): calcd. C 68.61, H 5.36, N 5.52; found C 68.34, H 5.29, N 5.62. X-ray analysis: see Figure 4 and ref.[43].

Preparation of Monochiral Pentamethinium Streptocyanine Dyes 7a and 7b (Scheme 4)

(+)-(*R,R*)-1,5-Bis[4-(4-methylphenylsulfinyl)phenylamino]pentamethinium Bromide (7a): Dry pyridine (0.34 g, 4.32 mmol) and a solution of cyanogen bromide (0.46 g, 4.32 mmol) in dry diethyl ether (5 mL) were added dropwise with stirring at 60 °C to a solution of monochiral amino sulfoxide **3a** (2.00 g, 8.65 mmol) in water-free ethanol (12 mL). The reaction mixture turned from yellow to reddish-brown, and a brown precipitate was slowly formed. Stirring and heating at 60 °C was continued for 30 min. After the mixture had cooled to room temp. and been allowed to stand for 24 h, the precipitate formed was filtered off, washed with a small amount of water-free, ice-cold ethanol, dried with P_4O_{10} (Sicapent®) in vacuo, and recrystallized from methanol to yield **7a** (1.91 g, 73%) as felted red crystals with m.p. 131−133 °C (dec.) (ref.[10c] 130−132 °C). $[\alpha]_D^{21} = +194.3$ (*c* = 0.386 in ethanol + one drop aqueous HBr) {ref.[10c] $[\alpha]_D^{21} = +283$ (*c* = 0.035 in ethanol + HBr)}. IR (KBr): $\tilde{\nu} = 3432\ \text{cm}^{-1}$ (NH), 1027 (S=O). UV/Vis (chloroform): λ_{max} (lg ε) = 497 nm (4.84), 277 (3.83). ^{1}H NMR (CD_3SOCD_3): δ = 2.31 (s, 6 H, 18/31-H), 6.39 (t, ^3J = 12.2 Hz, 2 H, 2/4-H), 7.27 (d, ^3J = 8.7 Hz, 4 H, 10/23-H and 8/21-H), 7.51 (d, ^3J = 8.0 Hz, 4 H, 16/29-H and 14/27-H), 7.53 (d, ^3J = 7.7 Hz, 4 H, 17/30-H and 13/26-H), 7.74 (d, ^3J = 8.6 Hz, 4 H, 11/24-H and 7/20-H), 7.86 (t, ^3J = 13.1 Hz, 1 H, 3-H), 8.65 (d, ^3J = 12.0 Hz, 2 H, 1/5-H), 12.0 (broad s, 2 H, NH). ^{13}C NMR (CD_3SOCD_3): δ = 21.0 (C-18/31), 111.0 (C-2/4), 118.6 (C-10/23 and C-8/21), 124.4 (C-11/24 and C-7/20), 126.1 (C-16/29 and C-14/27), 130.2 (C-17/30 and C-13/26), 141.0 (C-6/19), 141.4 (C-15/28), 142.4 (C-12/25), 142.9 (C-9/22), 156.3 (C-1/5), 165.0 (C-3). MS (electrospray, positive): *m/z* = 525 $[M^+ - Br]$. $C_{31}H_{29}BrN_2O_2S_2 \cdot 2.5\ H_2O$ (605.6 + 45.0 = 650.6): calcd. C 57.23, H 5.27, N 4.31; found C 57.09, H 5.30, N 4.16.

(−)-(*S,S*)-1,5-Bis[4-(4-methylphenylsulfinyl)phenylamino]pentamethinium Bromide (7b): According to the procedure described for **7a**, monochiral amino sulfoxide **3b** (1.50 g, 6.49 mmol) dissolved in dry ethanol (10 mL), dry pyridine (0.26 g, 3.24 mmol), and cyanogen bromide (0.34 g, 3.24 mmol) in dry diethyl ether

(5 mL), was transformed analogously into the bromide **7b** (1.49 g, 76%), obtained as felted red crystals with m.p. 131−133 °C (dec.). $[\alpha]_D^{21} = -193.0$ ($c = 0.367$ in ethanol + HBr). UV/Vis (chloroform): λ_{max} (lg ε) = 498 nm (4.85), 277 (3.84). The ^1H and ^{13}C NMR, IR, and MS data were identical to those of **7a**. $C_{31}H_{29}BrN_2O_2S_2\cdot1.5H_2O$ (605.6 + 27.0 = 632.6): calcd. C 58.86, H 5.10, H 4.43; found C 58.56, H 5.09, N 4.46.

Preparation of the Corresponding Achiral Sulfonyl Derivatives 10−13 (Schemes 5−6)

(±)-4-(Acetylamino)phenyl 4-Methylphenyl Sulfoxide (8c): A mixture of isochiral[14] amino sulfoxide **3c** (24.0 g, 0.10 mol) and acetic anhydride (102.0 g, 1.00 mol) was heated at 70 °C for 1 h. After the mixture had been cooled with an ice-bath, the precipitate formed was filtered off, washed twice with water (2 × 200 mL), and dried with P_4O_{10} (Sicapent®) in vacuo to give isochiral **8c** (26.2 g, 96%), as colorless crystals with m.p. 182 °C. TLC: R_f = 0.3 (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3312 and 3271 cm^{-1} (NH), 1695 (C=O), 1034 (S=O). ^1H NMR ($CDCl_3$): δ = 2.07 (s, 3 H, H_3C-CO), 2.33 (s, 3 H, 13-H), 7.21 (d, ^3J = 8.0 Hz, 2 H, 9/11-H), 7.44 (d, ^3J = 8.2 Hz, 2 H, 8/12-H), 7.45 (d, ^3J = 8.7 Hz, 2 H, 3/5-H), 7.63 (d, ^3J = 8.7 Hz, 2 H, 2/6-H), 9.1 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ = 21.3 (C-13), 24.3 (H_3C-CO), 120.2 (C-3/5), 124.8 (C-2/6), 126.0 (C-9/11), 130.0 (C-8/12), 139.2 (C-4), 141.5 (C-10), 141.7 (C-1 and C-7), 169.3 (C=O). MS (EI): m/z (%) = 275 (3) (M^+ + 2 H], 274 (7) [M^+ + H), 273 (37) [M^+], 257 (11) [M^+ − O], 226 (18) [M^+ − SO + H], 225 (77) [M^+ − SO], 215 (20) [M^+ − O − CH_3CO + H], 214 (14) [M^+ − O − CH_3CO], 200 (5) [M^+ − O − CH_3CO − CH_3 + 2 H], 199 (6) [M^+ − O − CH_3CO − CH_3 + H], 184 (24) [M^+ − O − CH_3CO − CH_3 − NH_2 + H], 183 (100) [M^+ − O − CH_3CO − CH_3 − NH_2], 182 (38) [M^+ − O − CH_3CO − CH_3 − NH_2 − H], 167 (8) [M^+ − O − C_7H_7 + H], 166 (17) [M^+ − O − C_7H_7], 150 (34) [M^+ − O − C_7H_7 − NH_2], 141 (11) [M^+ − C_7H_7 − CH_3CO + 2 H], 140 (65) [M^+ − C_7H_7 − CH_3CO + H], 139 (12) [M^+ − C_7H_7 − CH_3CO], 125 (11) [M^+ − O − C_7H_7 − CH_3CO + 2 H], 124 (70) [M^+ − O − C_7H_7 − CH_3CO + H], 123 (17) [M^+ − O − C_7H_7 − CH_3CO], 109 (10) [M^+ − O − C_7H_7 − CH_3CO − NH + H], 108 (84) [M^+ − O − C_7H_7 − CH_3CO− NH], 91 (27) [$C_7H_7^+$], 65 (29) [$C_5H_5^+$]. $C_{15}H_{15}NO_2S$ (273.4): calcd. C 65.91, H 5.53, N 5.12; found C 65.69, H 5.30, N 5.03.

4-(Acetylamino)phenyl 4-Methylphenyl Sulfone (9): Aqueous hydrogen peroxide (c = 30 cg/g; 14.0 mL, 137 mmol) was added dropwise with stirring to a solution of sulfoxide **8c** (20.1 g, 74.0 mmol) in glacial acetic acid (320 mL) at room temp. With TLC monitoring, the mixture was heated at 65 °C for ca. 18 h, until starting material **8c** was no longer detectable (TLC solvent: ethyl acetate). After the mixture had cooled to room temp., water (150 mL) was added and the reaction mixture was neutralized with aqueous NaOH (c = 25 cg/g). The aqueous mixture was extracted three times with dichloromethane (3 × 200 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was distilled off in a rotary evaporator to give crude **9** as brownish solid. This solid was purified by digesting it with ethyl acetate at room temp. After drying with P_4O_{10} (Sicapent®) in vacuo, sulfone **9** (16.5 g, 77%) was obtained as colorless crystals with m.p. 196 °C. TLC: R_f = 0.5 (ethyl acetate). IR (KBr): $\tilde{\nu}$ = 3340 and 3299 cm-1 (NH), 1311 and 1146 (SO_2). ^1H NMR (CD_3SOCD_3): δ = 2.06 (s, 3 H, H_3C-CO), 2.31 (s, 3 H, 13-H), 7.36 (d, ^3J = 8.0 Hz, 2 H, 9/11-H), 7.78 (d, ^3J = 8.3 Hz, 4 H, 3/5-H and 8/12-H), 7.86 (d, ^3J = 8.9 Hz, 2 H, 2/6-H), 10.4 (broad s, 1 H, NH). ^{13}C NMR (CD_3SOCD_3): δ = 21.1 (C-13), 24.2 (H_3C-CO), 119.1 (C-3/5), 127.2 (C-8/12), 128.6 (C-9/11), 130.2 (C-2/6), 134.9 (C-4), 139.1 (C-1), 143.9 (C-10), 144.0 (C-7), 169.2 (C=O). MS (EI): m/z (%) = 290 (13) [M^+ + H], 289 (88) [M^+], 248 (15) [M^+ − CH_3CO + 2 H], 247 (100) [M^+ − CH_3CO + H], 183 (7) [M^+ − 2 O − CH_3CO − CH_3 − NH_2], 141 (9) [M^+ −C_7H_7 − CH_3CO − NH_2 + 2 H], 140 (24) [M^+ − C_7H_7 − CH_3CO − NH_2 + H], 139 (10) [M^+ −C_7H_7 − CH_3CO − NH_2], 108 (66) [M^+ − 2 O − C_7H_7 − CH_3CO − NH], 92 (16) [$C_7H_8^+$], 91 (19) [$C_7H_7^+$], 65 (13) [$C_5H_5^+$]. $C_{15}H_{15}NO_3S$ (289.4): calcd. C 62.27, H 5.22, N 4.84; found C 61.65, H 4.96, N 4.63.

4-Aminophenyl 4-Methylphenyl Sulfone (10): A solution of sulfone **9** (15.1 g, 61.0 mmol) in aqueous/ethanolic (80:20) KOH (c = 20 cg/g; 200 mL, ca. 700 mmol) was heated at 90 °C for ca. 4 h, until starting material **9** was no longer detectable by TLC (solvent: ethyl acetate). After cooling to room temp., the reaction mixture was poured into water (100 mL). The aqueous mixture was extracted three times with dichloromethane (3 × 100 mL). The combined organic phases were dried with $MgSO_4$ and the solvent was distilled off in a rotary evaporator. The yellowish solid residue was dried with P_4O_{10} (Sicapent®) in vacuo and recrystallized from ethanol to afford the achiral amino sulfone **10** (9.8 g, 65%) as large, straw-colored crystals with m.p. 181 °C. IR (KBr): $\tilde{\nu}$ = 3476 and 3383 cm^{-1} (NH_2), 1304 and 1148 (SO_2). ^1H NMR (CD_3SOCD_3): δ = 2.30 (s, 3 H, 13-H), 6.14 (s, 2 H, NH_2), 6.62 (d, ^3J = 8.8 Hz, 2 H, 3/5-H), 7.32 (d, ^3J = 8.1 Hz, 2 H, 9/11-H), 7.54 (d, ^3J = 8.8 Hz, 2 H, 2/6-H), 7.71 (d, ^3J = 8.3 Hz, 2 H, 8/12-H). ^{13}C NMR (CD_3SOCD_3): δ = 21.0 (C-13), 113.2 (C-3/5), 126.0 (C-1), 126.6 (C-8/12), 129.4 (C-9/11), 129.9 (C-2/6), 140.7 (C-7), 143.1 (C-10), 153.6 (C-4). MS (EI): m/z (%) = 249 (9) [M^+ + 2 H], 248 (23) [M^+ + H], 247 (100) [M^+], 183 (12) [M^+ − 2 O − CH_3 − NH_2 − H], 141 (6) [M^+ − C_7H_7 − NH_2 + H], 140 (54) [M^+ − C_7H_7 − NH_2], 139 (12) [M^+ − C_7H_7 − NH_2 − H], 108 (96) [M^+ − 2 O − C_7H_7 − NH_2], 92 (30) [$C_7H_8^+$], 91 (19) [$C_7H_7^+$], 65 (38) [$C_5H_5^+$]. $C_{13}H_{13}NO_2S$ (247.3): calcd. C 63.13, H 5.30, N 5.66; found C 62.75, H 5.18, N 5.61.

1,3-Bis[4-(4-methylphenylsulfonyl)phenylamino]trimethinium Bromide (11): 3,3-Diethoxy-1-propyne (0.64 g, 5.0 mmol) and then aqueous hydrobromic acid (c = 48 cg/g; 0.91 g, 5.5 mmol) were added dropwise with stirring to a solution of amino sulfone **10** (2.50 g, 10.1 mmol) in ethanol (ca. 20 mL) at 70 °C. The reaction mixture turned brownish and after ca. 15 min a voluminous yellow precipitate was formed. Stirring and heating at 70 °C was continued for 1 h. After the mixture had cooled to room temp. and been allowed to stand for ca. 12 h, the precipitate formed was filtered off, washed twice with a small of ethanol, and dried with P_4O_{10} (Sicapent®) in vacuo to yield the bromide **11** (2.63 g, 85%) as yellow needles with m.p. 253−254 °C. IR (KBr): $\tilde{\nu}$ = 3478 cm^{-1} (NH), 1313 and 1150 (SO_2). UV/Vis (methanol): λ_{max} (lg ε) = 380 (4.78), 337 (4.24), 292 (4.32); (dichloromethane): λ_{max} = 405 nm. ^1H NMR (CD_3SOCD_3): δ = 2.34 (s, 6 H, 16/29-H), 6.47 (t, ^3J = 11.4 Hz, 1 H, 2-H), 7.41 (d, ^3J = 8.1 Hz, 4 H, 6/19-H and 8/21-H), 7.58 (d. ^3J = 8.8 Hz, 4 H, 12/25-H and 14/27-H), 7.83 (d, ^3J = 8.4 Hz, 4 H, 5/18-H and 9/22-H), 8.04 (d, ^3J = 8.8 Hz, 4 H, 11/24-H and 15/28-H), 9.04 (t, ^3J = 11.0 Hz, 2 H, 1/3-H), 12.6 (d, ^3J = 11.0 Hz, 2 H, NH). ^{13}C NMR (CD_3SOCD_3): δ = 21.1 (C-16/29), 100.8 (C-2), 118.6 (C-6/19 and C-8/21), 127.5 (C-11/24 and C-15/28), 129.4 (C-4/17), 129.6 (C-12/25 and C-14/27), 130.3 (C-5/18 and C-9/22), 138.4 (C-10/23), 142.4 (C-13/26), 144.5 (C-7/20), 160.3 (C-1/3). MS (APCI, positive): m/z = 531 [M^+ − Br]. $C_{29}H_{27}BrN_2O_4S_2\cdot1.5H_2O$ (611.9 + 27.0 = 638.9): calcd. C 54.54, H 4.73, N 4.39; found C 54.64, H 4.48, N 4.29.

3-[4-(4-Methylphenylsulfonyl)phenylamino]propenal [4-(4-Methylphenylsulfonyl)phenylimine] (12): An aqueous NaOH solution (c = 37 cg/g; 2.0 mL, 18.5 mmol) was added with stirring to a suspension of bromide **11** (1.20 g, 1.96 mmol) in ethanol (60 mL) at room temp. After further stirring for 1 h, the orange-colored solution was filtered and the filtrate was slowly added to water (250 mL) with vigorous stirring. The precipitate formed was filtered off, washed with diethyl ether, and dried with P_4O_{10} (Sicapent®) in vacuo. For purification, a solution of the product in acetone (15 mL) was added dropwise to diethyl ether (250 mL) with stirring. The precipitate formed was filtered off and dried to give **12** (0.71 g, 68%) as a light-yellow, microcrystalline solid with m.p. 222−223 °C. IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (NH), 1316 and 1149 (SO_2); (methanol): λ_{max} (lg ε) = 381 nm (4.69), 289 (4.51); UV/Vis (CH_2Cl_2): λ_{max} = 397 nm. ^{1}H NMR ($CDCl_3$): δ = 2.37 (s, 6 H, 16/29-H), 5.23 (t, ^3J = 6.2 Hz, 1 H, 2-H), 7.08 (d, ^3J = 8.7 Hz, 4 H, 6/19-H and 8/21-H), 7.27 (d, ^3J = 8.2 Hz, 4 H, 12/25-H and 14/27-H), 7.64 (d, ^3J = 6.2 Hz, 2 H, 1/3-H), 7.79 (d, ^3J = 8.3 Hz, 4 H, 11/24-H and 15/28-H), 7.86 (d, ^3J = 8.7 Hz, 4 H, 5/18-H and 9/22-H), 12.1 (broad s, 1 H, NH). ^{13}C NMR ($CDCl_3$): δ = 21.5 (C-16/29), 97.5 (C-2), 118.4 (C-6/19 and C-8/21), 127.4 (C-5/18 and C-9/22), 129.3 (C-12/25 and C-14/27), 129.9 (C-11/24 and C-15/28), 136.4 (C-4/17), 139.1 (C-13/26), 143.9 (C-10/23), 149.2 (C-7/20), 150.2 (C-1/3). MS (APCI, positive): *m/z* = 531 (M$^+$ + 1]. $C_{29}H_{26}N_2O_4S_2 \cdot 0.5H_2O$ (530.7 + 9.0 = 539.7): calcd. C 64.54, H 5.60, N 5.19; found C 64.88, H 5.17, N 5.11.

1,5-Bis[4-(4-methylphenylsulfonyl)phenylamino]pentamethinium Bromide (13): Dry pyridine (0.37 g, 4.73 mmol) and a solution of cyanogen bromide (0.50 g, 4.73 mmol) in dry diethyl ether (10 mL) were added dropwise with stirring at 60 °C to a solution of amino sulfone **10** (2.34 g, 9.46 mmol) in water-free ethanol (50 mL). The reaction mixture turned from yellow to reddish-brown and a voluminous reddish-brown precipitate was slowly formed. Stirring and heating at 60 °C was continued for 30 min. After the mixture had cooled to room temp. and been allowed to stand for 24 h, the precipitate formed was filtered off, washed with a small amount of ice-cold, water-free ethanol, dried with P_4O_{10} (Sicapent®) in vacuo, and recrystallized from methanol to afford the bromide **13** (1.79 g, 59%) as felted red crystals with m.p. 154−155 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3447 cm^{-1} (NH), 1311 and 1149 (SO_2). UV/Vis (methanol): λ_{max} (lg ε) = 513 (4.91), 295 (3.19). UV/Vis (CH_2Cl_2): λ_{max} = 495 nm. ^{1}H NMR (CD_3SOCD_3): δ = 2.35 (s, 6 H, 18/31-H), 6.46 (t, ^3J = 12.2 Hz, 2 H, 2/4-H), 7.41 (d, ^3J = 8.1 Hz, 4 H, 8/21-H and 10/23-H), 7.62 (d, ^3J = 8.8 Hz, 4 H, 14/27-H and 16/29-H), 7.83 (d, ^3J = 8.3 Hz, 4 H, 7/20-H and 11/24-H), 7.94 (t, ^3J = 12.8 Hz, 1 H, 3-H), 7.99 (d, ^3J = 8.8 Hz, 4 H, 13/26-H and 17/30-H), 8.74 (d, ^3J = 11.3 Hz, 2 H, 1/5-H), 12.2 (broad s, 2 H, NH). ^{13}C NMR (CD_3SOCD_3): δ = 21.1 (C-18/31), 113.2 (C-2/4), 118.6 (C-8/21 and C-10/23), 127.4 (C-7/20 and C-11/24), 129.3 (C-14/27 and C-16/29), 130.3 (C-13/26 and C-17/30), 137.7 (C-6/19), 138.5 (C-15/28), 142.8 (C-12/25), 144.4 (C-9/22), 157.0 (C-1/5), 166.1 (C-3). MS (electrospray, positive): *m/z* = 557 [M$^+$ − Br]. $C_{31}H_{29}BrN_2O_4S_2$ (637.6): calcd. C 58.40, H 4.58, N 4.39; found C 58.30, H 4.77, N 4.53.

X-ray Crystallographic Analyses of 3b, 5b, and 6b (Figures 1−4 and Ref.[43]): Suitable single crystals were obtained for **3b** (colorless plates) by recrystallization from acetone/petroleum ether (b.p. 40−60 °C), and for **5b** (small yellow plates) and **6b** (thin yellow plates) by careful addition of a layer of petroleum ether (b.p. 40−60 °C) to a concentrated solution of **5b/6b** in ethanol. After the two-phase system had been allowed to stand unperturbed for some weeks in the dark, suitable crystals had formed at the boundary between the two solvent layers.

X-ray Crystal Structure of 3b (Scheme 2): $C_{13}H_{13}NOS$ with M_r = 231.3 g/mol; crystal size: 0.33 × 0.21 × 0.05 mm; orthorhombic crystal system with space group $P2_12_12_1$ and Z = 4, a = 575.3(1), b = 829.7(1), and c = 2509.8(2) pm; V = 1198.0(3)·10^{-30} m^3; $\rho_{calcd.}$ = 1.282 Mg/m^3; F(000) = 488; linear absorption coefficient μ = 2.212 mm^{-1}; type of diffractometer: Enraf−Nonius CAD 4; Cu-K_α radiation; scan type: ω-scans; θ range 3.52−70.05°; index ranges $-7 \le h \le 6$, $-4 \le k \le 10$, $-30 \le l \le 15$; reflections collected 2619, independent reflections 2167 (R_{int} = 0.0368), observed reflections 1797 [$I > 2\sigma(I)$], reflections used for refinement 2167, extinction coefficient X = 0.0039(8); "Flack parameter" (absolute structure) = 0.02(3). Program system used: SHELXS-97, SHELXL-97, and SHELXTL. Empirical absorption correction, direct methods, full-matrix refinement at F^2 with all independent reflections, weighting scheme SHELXL, goodness-of-fit parameter (based on F^2) S = 1.054; residual densities $\Delta\rho_{max}$ and $\Delta\rho_{min}$ = 0.246·10^{30} and −0.194·10^{30} e/m^{-3}. Hydrogen atoms: localized, isotropic refinement; non-hydrogen atoms were refined anisotropically. R index (all data): wR_2 (based on F^2) = 0.1166; R index conventional [$I > 2\sigma(I)$]: R_1 (based on F) = 0.0479.

X-ray Crystal Structure of 5b (Scheme 3): $C_{58}H_{66}Br_2N_4O_{10}S_4$ with M_r = 1267.2 g/mol (the X-ray analysis is based on two identical dye molecules; there are four water molecules in the asymmetric unit); crystal size: 0.60 × 0.16 × 0.08 mm; monoclinic crystal system with space group $P2_1$ and Z = 2, a = 540.2(1), b = 1648.2(1), and c = 3313.0(18) pm, β = 91.40(2)°, V = 2949.1(16)·10^{-30} m^3; $\rho_{calcd.}$ = 1.427 Mg/m^3; F(000) = 1312; linear absorption coefficient μ = 1.576 mm^{-1}; type of diffractometer: Enraf−Nonius CAD 4; Mo-K_α radiation; scan type: ω-scans; θ range 2.22−25.00°; index ranges $-6 \le h \le 6$, $-18 \le k \le 19$, $-39 \le l \le 39$; reflections collected 14939, independent reflections 9952 [R_{int} = 0.0400], observed reflections 7113 [$I > 2\sigma(I)$], reflections used for refinement 9952; "Flack parameter" (absolute structure) = −0.003(7). Program system used: same as for **3b.** Empirical absorption correction, direct methods, full-matrix refinement at F^2 with all independent reflections, weighting scheme $w = [\sigma^2 (F_o^2) + (0.0517\ P)^2 + 1.7238\ P]^{-1}$, with $P = (F_o^2 + 2\ F_c^2)/3$. Goodness-of-fit parameter (based on F^2) S = 1.031; residual densities $\Delta\rho_{max}$ and $\Delta\rho_{min}$ = 0.319·10^{30} and −0.392·10^{30} e/m^{-3}. Hydrogen atoms: C−H calculated, N−H and O−H localized; non-hydrogen atoms were refined anisotropically. R index (all data): wR_2 (based on F^2) = 0.1221; R index (conventional) [$I > 2\sigma(I)$]: R_1 (based on F) = 0.0478.

X-ray Crystal Structure of 6b (Scheme 3): $C_{29}H_{26}N_2O_2S_2$ with M_r = 498.6 g/mol; crystal size: 0.51 × 0.22 × 0.02 mm; monoclinic crystal system with space group $P2_1$ and Z = 2, a = 794.3(2), b = 726.0(1), and c = 2192.1(5) pm, β = 92.11(3)°, V = 1263.3(4)·10^{-30} m^3; $\rho_{calcd.}$ = 1.311 Mg/m^3; F(000) = 524; linear absorption coefficient μ = 0.240 mm^{-1}; type of diffractometer: Stoe IPDS; θ range 2.57−26.21°; index ranges $-9 \le h \le 9$, $-8 \le k \le 8$, $-27 \le l \le 26$; reflections collected 12291, independent reflections 4346 (R_{int} = 0.1387), observed reflections 1629 [$I > 2\sigma(I)$], reflections used for refinement 4346; absorption correction: Gaussian (Platon); formula for extinction correction: $F_c{}^* = F_c \cdot k \cdot [(1 + 0.001 \cdot X \cdot F_c^2 \cdot \lambda^3)/\sin 2\theta]^{-1/4}$; "Flack parameter" (absolute structure) = 0.02(15). Program system used: same as for **3b** and Stoe IPDS software. Direct methods, full-matrix refinement at F^2 with all independent reflections, weighting scheme $w = [\sigma^2 (F_o^2) + (0.0482\ P)^2 + 0.0000\ P]^{-1}$ with $P = (F_o^2 + 2\ F_c^2)/3$. Goodness-of-fit parameter (based an F^2) S = 0.818; residual densities $\Delta\rho_{max}$ and $\Delta\rho_{min}$ = 0.296·10^{30} and −0.294·10^{30} e/m^{-3}. Hydrogen atoms: C−H calculated, N−H isotropically refined; non-hydrogen atoms were refined anisotropically. R index (all data): wR_2 (based on F^2) = 0.1434; R index (conventional) [$I > 2\sigma(I)$]: R_1 (based on F) = 0.0567.

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[1] C. Reichardt, J. Stein, *Eur. J. Org. Chem.* **1999**, 2899–2908.

[2] H.-P. Erfurt, Ph.D. Thesis, Philipps-University, Marburg, Germany, **1999**.

[3] [3a] H. Kuhn, *Angew. Chem.* **1959**, *71*, 93–101.[3b] H. Kuhn, *Fortschr. Chem. Org. Naturst.* **1958**, *16*, 169–205; **1959**, *17*, 404–451.

[4] [4a] S. Dähne, *Z. Chem.* **1965**, *5*, 444–451. [4b] S. Dähne, D. Leupold, *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 618–625. [4c] S. Dähne, *Chimia* **1991**, *45*, 19–27.

[5] J. Fabian, H. Hartmann, *Light Absorption of Organic Colorants*, Springer, Berlin, **1980**.

[6] [6a] D. Lloyd, H. McNab, *Angew. Chem.* **1976**, *88*, 496–504; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 459–468. [6b] A. D. Kachkovski, *Stroenie i Tsvet Polimetinovych Krasitelei* ("Structure and Color of Polymethine Dyes"), Naukova Dumka, Kiev/Ukraine, **1989**; *Chem. Abstr.* **1990**, *112*, 200590k. [6c] N. Tyutyulkov, J. Fabian, A. Mehlhorn, F. Dietz, A. Tadjer, *Polymethine, Dyes – Structure and Properties*, St. Kliment Ohridski University Press, Sofia, Bulgaria, **1991**. [6d] A. A. Ishchenko, *Stroenie i Spektral'no– Ljuminescentnye Svojstva Polimethinovych Krasitelei* ("Constitution and Spectral – Luminescent Properties of Polymethine Dyes"). Naukova Dumka, Kiev, Ukraine, **1994**. [6e] G. Bach, S. Dähne, "Cyanine Dyes and Related Compounds" in *Rodd's Chemistry of Carbon Compounds*, 2nd ed., 2nd suppl., Elsevier, Amsterdam, **1997**. [6f] A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra, G. B. Behera, *Chem. Rev.* **2000**, *100*, 1973–2011.

[7] Recent reviews on functional dyes: [7a] Z. Yoshida, T. Kitao, *Chemistry of Functional Dyes*, Mita Press, Tokyo, **1989**. [7b] J. Griffiths, *Chem. Unserer Zeit* **1993**, *27*, 21–31.

[8] H. Kampfer, *Spectral Sensitization*, in *Ullmann's Encyclopedia of Industrial Chemistry.* 5th ed., VCH, Weinheim, **1992**, vol. A 20, chapter "Photography", section 2.2, pp. 10–17.

[9] Recent review on chiral polymethine dyes: C. Reichardt, *J. Phys. Org. Chem.* **1995**, *8*, 761–773.

[10] [10a] W. König, *Optisch aktive Polymethinfarbstoffe und deren Bedeutung für das allgemeine Problem der Farbstoffnatur* ("Optically Active Polymethine Dyes and their Importance for the General Problem of the Nature of Dyes"), *Z. Angew. Chem.* **1928**, *41*, 615–616. [10b] G. Langbein, PhD Thesis, Technical University, Dresden, Germany, **1927**. [10c]F. Liewald, PhD Thesis, Technical University, Dresden, Germany, **1935**.

[11] J. Götze, *Ber. Dtsch. Chem. Ges.* **1938**, *71*, 2289–2291.

[12] Reviews on Musca-aurines and related dyes: [12a] H. Musso, *Tetrahedron* **1979**, *35*, 2843–2853. [12b] H. Musso, *Naturwissenschaften* **1982**, *69*, 326–331.

[13] Reviews on betalain dyes: [13a] H. Wyler, *Chem. Unserer Zeit* **1969**, *3*, 111–115, 146–151. [13b] T. J. Mabry, Betalains, *Red-Violet and Yellow Alkaloids of the Centrospermae* in *Chemistry of Alkaloids* (Ed.: S. W. Pelletier), Van Nostrand Reinhold, New York, **1970**, pp. 367–384.

[14] We prefer the designations *monochiral* (one-handed), *isochiral* (equal-handed), and *anisochiral* (unequal-handed) in place of the ambiguous terms *homochiral*, *racemic*, and *scalemic*, respectively, as recently recommended by: J. W. Cornforth, *Aust. J. Chem.* **1993**, *46*, 157–170; *Aldrichimica Acta* **1994**, *27*(3), 71–77 (footnote 21).

[15] C. Reichardt, H.-D. Engel, R. Allmann, D. Kucharczyk, M. Krestel, *Chem. Ber.* **1990**, *123*, 565–581 (Part I).

[16] C. Reichardt, U. Budnik, *Chem. Ber.* **1990**, *123*, 2023–2030 (Part II).

[17] C. Reichardt, U. Budnik, *Liebigs Ann. Chem.* **1994**, 927–930 (Part III).

[18] C. Reichardt, K. Harms, M. Kinzel, G. Schäfer, J. Stein, S. Wocadlo, *Liebigs Ann.* **1995**, 317–327 (Part IV).

[19] C. Reichardt, U. Budnik, K. Harms, G. Schäfer, J. Stein, *Liebigs Ann.* **1995**, 329–340 (Part V).

[20] C. Reichardt, W. Amann, K. Harms, G. Schäfer, J. Stein, *J. Prakt. Chem.* **1998**, *340*, 513–529 (Part VI).

[21] V. Buß, D. Ulbrich, C. Reichardt, *Liebigs Ann.* **1996**, 1823–1831.

[22] P. G. Jones, W. Grahn, B. Scheibel, *Z. Kristallogr.* **1994**, *209*, 461–463; *Chem. Abstr.* **1995**, *122*, 238929x.

[23] C. Payrastre, N. Obaya, Y. Madaule, J.-G. Wolf, *Tetrahedron Lett.* **1994**, *35*, 3059–3062.

[24] L. Eggers, V. Buß, G. Henckel, *Angew. Chem.* **1996**, *108*, 973–975; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 870–872.

[25] L. Eggers, V. Buß, *Liebigs Ann.* **1996**, 979–983.

[26] V. Buß, L. Eggers, *Tetrahedron: Asymmetry* **1997**, *8*, 1531–1533.

[27] L. Eggers, K. Kolster, V. Buß, *Chirality* **1997**, *9*, 243–249; *Chem. Abstr.* **1997**, *126*, 331619p.

[28] V. Buß, F. Terstegen, S. Falzewski, *Chem. Phys.* **1999**, *243*, 179–188.

[29] V. Buß, S. Falzewski, K. Kolster, *J. Org. Chem.* **1999**, *64*, 1071–1073 (and references cited therein).

[30] G. Nuding, E. Zimmermann, V. Buß, *Tetrahedron Lett.* **2001**, *42*, 2649–2651.

[31] U. de Rossi, S. Dähne, S. C. J. Meskers, H. P. J. M. Dekkers, *Angew. Chem.* **1996**, *108*, 827–830; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 760–763.

[32] A. Pawlik, S. Kirstein, U. de Rossi, S. Dähne, *J. Phys. Chem. B* **1997**, *101*, 5646–5651.

[33] H. von Berlepsch, C. Böttcher, A. Quart, C. Burger, S. Dähne, S. Kirstein, *J. Phys. Chem. B* **2000**, *104*, 5255–5262.

[34] S. Kirstein, H. von Berlepsch, C. Böttcher, C. Burger, A. Quart, G. Reck, S. Dähne, *ChemPhysChem* **2000**, 146–150.

[35] S. Hauptmann, G. Mann, *Stereochemie*, Spektrum Akademischer Verlag, Heidelberg, **1996**, p. 63.

[36] For leading references on chiral sulfoxides see: [36a] H. B. Kagan, "Asymmetric Oxidation of Sulfides" in *Catalytic Asymmetric Synthesis* (Ed.: I. Ojima), VCH, Weinheim, **1993**, pp. 203–226. [36b] J. Drabowicz, P. Kielbasinski, M. Mikolajczyk, "Synthesis of Sulfoxides" in *The Synthesis of Sulfones, Sulfoxides and Cyclic Sulfides* (Eds.: S. Patai, Z. Rappoport), Wiley-Interscience, Chichester, **1994**, pp. 109–388. [36c] M. Mikolajczyk, J. Drabowicz, P. Kielbasinski, *Chiral Sulfur Reagents*, CRC Press, London, **1997**. [36d] P. Page (Ed.), *Organosulfur Chemistry*, Academic Press, San Diego, USA, **1998**, vol. 2 ("Synthetic and Stereochemical Aspects").

[37] P. W. B. Harrison, J. Kenyon, H. Phillips, *J. Chem. Soc.* **1926**, 2079–2090.

[38] S. Oae, T. Kitao, Y. Kitaoka, *Bull. Chem. Soc. Jpn.* **1965**, *38*, 543–546.

[39] In accordance with previous papers in this series,[1] the formula numbers of all monochiral ("homochiral") compounds are accompanied by letters **a** and **b**, all isochiral ("racemic") compounds by the letter **c**, and *meso* compounds by the letter **d**.

[40] [40a] F. C. Whitmore, F. H. Hamilton, *Org. Synth.* **1922**, *2*, 89–91; *Org. Synth., Coll. Vol. I* **1932**, 492–494. [40b] G. S. Hamilton, *p*-Toluenesulfinic Acid, in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), **1995**, vol. 7, p. 4939–4940. [40c] S. Budavari (Ed.), *The Merck Index – An Encyclopedia of Chemicals, Drugs, and Biologicals.* 12th ed., Merck and Co., Inc., Whitehouse Station, N. J., USA, **1996**, pp. 1626–1627.

[41] R. Herrmann, *Methoden Org. Chem. (Houben-Weyl)*. 4th ed., Thieme, Stuttgart, **1996**, vol. E 21f ("Stereoselective Synthesis:

Survey of Chiral Auxiliaries, Solvents, Reagents, and Catalysts"), p. 5866 ("10-Camphorsulfonic Acid").

[42] W. Klyne, J. Buckingham, *Atlas of Stereochemistry. Absolute Configurations of Organic Molecules*, Chapman and Hall, London; "Chirality at Sulfur": 1st ed., **1974**, pp. 237−238; 2nd ed., **1978**, vol. 1, pp. 235−236; vol. 2, pp. 123−127.

[43] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-168039 (**3b**), -168040 (**5b**), and -168041 (**6b**) Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[44] For a review on the conformations of polymethine dyes see: A. M. Kolesnikov, F. A. Mikhailenko, *Usp. Khim.* **1987**, *56*, 466−488; *Chem. Abstr.* **1987**, *106*, 197818j.

[45] R. Allmann, T. Debaerdemaker, *Cryst. Struct. Commun.* **1976**, *5*, 211−214.

[46] S. Dähne, S. Kulpe, "Structural Principles of Unsaturated Compounds − With Reference to X-Ray Analyses of Coloured Substances" in *Abh. Akad. Wiss. DDR, Abt. Math., Naturwiss., Techn.*, Akademie-Verlag, Berlin, **1977**, vol. 8 N, pp. 1−128; *Chem. Abstr.* **1978**, *88*, 189321m.

[47] K. Nakatsu, H. Yoshioka, S. Nishigaki, *Nippon Shashin Gakkaishi* (*J. Soc. Photogr. Sci. Technol. Japan*) **1983**, *46*, 89−98; *Chem. Abstr.* **1984**, *100*, 42885f.

[48] L. Dähne, *J. Am. Chem. Soc.* **1995**, *117*, 12855−12860.

[49] [49a] G. Scheibe, *Angew. Chem.* **1937**, *50*, 212−219. [49b] G. Scheibe, L. Kandler, H. Ecker, *Naturwissenschaften* **1937**, *25*, 75. [49c]G. Scheibe, in *Optische Anregung Organischer Systeme* (Ed.: W. Foerst), Verlag Chemie, Weinheim, **1966**, pp. 109−159.

[50] [50a] E. E. Jelley, *Nature* **1936**, *138*, 1009−1010. [50b] E. E. Jelley, *Nature* **1937**, *139*, 631−632.

[51] See also ref.[6b], pp. 107−123: "Polymethine Dye Aggregate Structures".

[52] D. Möbius, *Adv. Mater.* **1995**, *7*, 437−444.

[53] S. Dähne, U. de Rossi, J. Moll, *Nippon Shashin Gakkaishi* (*J. Soc. Photogr. Sci. Technol. Japan*) **1996**, *59*, 250−259; *Chem. Abstr.* **1996**, *124*, 355923t.

[54] W. König, *J. Prakt. Chem.* [2] **1904**, *69*, 105−137 (particularly p. 134); cf. also: T. Zincke, W. Würker, *Justus Liebigs Ann. Chem.* **1905**, *338*, 107−141 (particularly p. 121).

[55] For comparison, the Hammett substituent constants for $-SOCH_3$ and $-SO_2CH_3$ are $\sigma_p = 0.49$ and 0.73, respectively; see O. Exner, *Correlation Analysis of Chemical Data*, Plenum, New York, and SNTL, Prague, **1988**, pp. 61−62.

[56] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923−2925.

[57] [57a]C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., VCH, Weinheim, **1988**; chapter A.2, pp. 407−416. [57b]D. D. Perrin, W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, Oxford, **1988**.

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