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Chiral Polymethine Dyes. Part 6 [1] [1])

Synthesis, Absolute Configuration, UV/Vis Spectroscopic, and Chiroptical Properties of Chiral Tri- and Pentamethinium Cyanine Dyes with 1,2,3,4-Tetrahydro-3,6-dimethylquinolyl End Groups

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Abstract. Starting with monochiral 1,2,3,4-tetrahydro-3,6-dimethyl quinoline **14a,b** (Schemes 1 and 2), we have synthesized the new chiral, symmetrical and unsymmetrical, tri- and pentamethinium streptocyanine dyes **2a** (Scheme 8), **4a** (Scheme 5), and **5a,b** (Scheme 4), resp. **9a** (Scheme 6), **10a,b** (Scheme 4), and **11a** (Scheme 7) with one or two stereogenic centers in the two heterocyclic end groups. The absolute configuration of **14a,b**, and thus the absolute configuration of all monochiral polymethinium dyes derived from **14a,b** has been determined by a single-crystal X-ray analysis of its 4-bromobenzenesulfonyl derivative **17a** (Scheme 1 and Fig. 1). The UV/Vis spectroscopic and chiroptical properties of the new polymethinium dyes have been studied for the first time and compared with that of similar streptocyanine dyes synthesized earlier (Tables 1 and 2) in order to find possible correlations between chiroptical properties and molecular structure.

In addition to aromatic and polyenic π-systems, polymethine dyes constitute a third independent type of π-systems with their own intrinsic electronic properties [4, 5]. Whereas chiral aromatics (*e.g.* helicenes) and chiral polyenes (*e.g.* carotinoids) are well known, chiral polymethines have been studied only scarcely up to now [6], although, as functional dyes [7], they should exhibit interesting new chiroptical properties, as, for example, different sensitivity for circularly polarized light when used as sensitizers for silver halide emulsions applied in photography.

Some natural dyes (*e.g.* Musca-aurine I and Betanine) are known to be chiral pentamethinium cyanines with end groups stemming from L-α-amino acids [6]. The first synthetic chiral polymethinium dyes have been prepared by König and Langbein [8] in 1928 and by Götze [9] in 1938. However, both reports are only rather short communications, in the first case without any experimental details [8, 9]. Because of its historical importance [6], the insufficient elaboration of the synthetic details, the mostly unknown enantiomeric purity and absolute configuration of the stereogenic centers of these polymethine dyes, as well as in continuation of our work on chiral dyes [1, 10, 11], we have repeated and significantly improved some of the work of König [12, 13] und Götze [14]. Further work on intrinsically chiral polymethine dyes has been done recently by Wolf *et al.* [15] and Buß *et al.* [16]. Dähne *et al.* have found that achiral trimethinium cyanine dyes with long *N*-alkyl groups form in solution spontaneously chiral *J*-aggregates which exhibit optical activity [17].

In this paper, we describe for the first time syntheses and chiroptical properties of monochiral [18, 19] trimethinium (**4**, **5**) and pentamethinium cyanine dyes (**9**–**11**) with 1,2,3,4-tetrahydro-3,6-dimethylquinolyl end groups and one or two stereogenic centers at the C-3/3' atoms, together with their achiral non-3,3'-methylsubstituted parent dyes **1** and **6** (Table 1). The syntheses of the corresponding C-2/2' methylsubstituted trimethinium (**3**) and pentamethinium cyanine dyes (**7**, **8**) (Table 1), first synthesized by König and Langbein [8], have been already described in a preceding paper [12]. Some of the UV/Vis spectroscopic and chiroptical properties of the new cyanine dyes **1**, **2**, **4**–**6**, and

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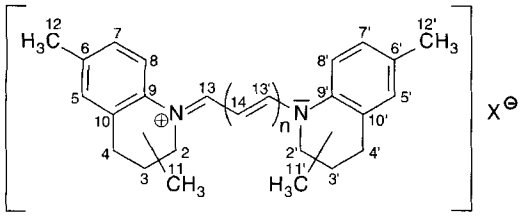
Table 1 Molecular structure of tri- (**1–5**) and pentamethinium cyanine dyes (**6–11**) with 1,2,3,4-tetrahydro-(2 or 3),6-dimethylquinolyl end groups (numbering for the assignment of the NMR signals)



n = 1,2 and X = ClO_4, Br

Methyl substition in position	n = 1	n = 2
–	**1**	**6**
2	**2**	**7**
2,2'	**3**	**8**
3	**4**	**9**
3,3'	**5**	**10**
2,3'	–	**11**

9–11 have already been given and discussed in ref. [13], in comparison with the corresponding data of the known cyanine dyes **3**, **7** and **8** [8, 12]. In the new cyanine dyes **4**, **5**, and **9–11**, the stereogenic centers at C-3/3' are away from the vinylogous amidinium chromophore by one more carbon atom, as compared to cyanine dyes **2**, **3**, **7**, and **8** with the stereogenic centers at C-2/2'. It is of interest to find out to what extent the position of the stereogenic centers in the end groups control the chiroptical properties of the cyanine chromophore in dyes **2–5** and **7–11**.

3,6-Dimethylquinoline (**13**) was prepared from 4-methylaniline and 2-methylprop-2-en-1,1-diol bisacetate (**12**) (instead of 2-methylprop-2-en-1-al) according to Doebner and v. Miller's [20, 21] variation of Skraup's quinoline synthesis [22], however, using the modification of Utermohlen [23]. This modification uses a solution of in situ prepared 3-nitrobenzene-sulfonic acid in sulfuric acid (called "sulfomix") as oxidizing agent [23] (Scheme 1).

The reduction of **13** to isochiral **14c** [18, 19] was carried out with $NaBH_4/NiCl_2$ in methanol [24]. Flash-chromatographic separation of **14c** from unreacted **13** was necessary in order to obtain pure **14c**. The separation of isochiral **14c** into its enantiomers **14a** and **14b** [19] was carried out according to a method first described by Pope *et al.* [25], later also used by König and Langbein [8], by means of the nowadays commercially available ammonium (+)-(1*R*)- and (–)-(1*S*)-3-*endo*-bromocamphor-8-sulfonate as resolving agent. In order to get a water-soluble starting material, **14c** was first converted into its isochiral hydrochloride **15c**. After addition of the (+)-(1*R*)-ammonium sulfonate to an aqueous solution of **15c**, the diastereomeric salt **16a** precipitated and was further purified by threefold recrystallization from acetone until a constant optical rotation was observed, and until the ^1H NMR spectrum of a diastereomeric camphanoyl derivative of **14a** (prepared from **16a**) exhibited the absence of the other enantiomer **14b** (see later; in particular Scheme 3). Addition of aqueous ammonia to an aqueous solution of **16a** eventually afforded the monochiral quinoline **14a** as colorless crystals with high enantiomeric purity (*e.e.* > 98%; see later). The absolute configuration at C-3 of (–)-**14a** was, however, not known. Therefore, **14a** was first converted into its crystalline perchlorate **18a**. Unfortunately, the fine colorless needles of **18a** were not suitable for a crystal structure determination. After various attempts to get crystalline derivatives of **14a** which are suitable for a X-ray analysis, the 4-bromobenzene-sulfonyl derivative **17a** proved to be appropriate [2] (see later).

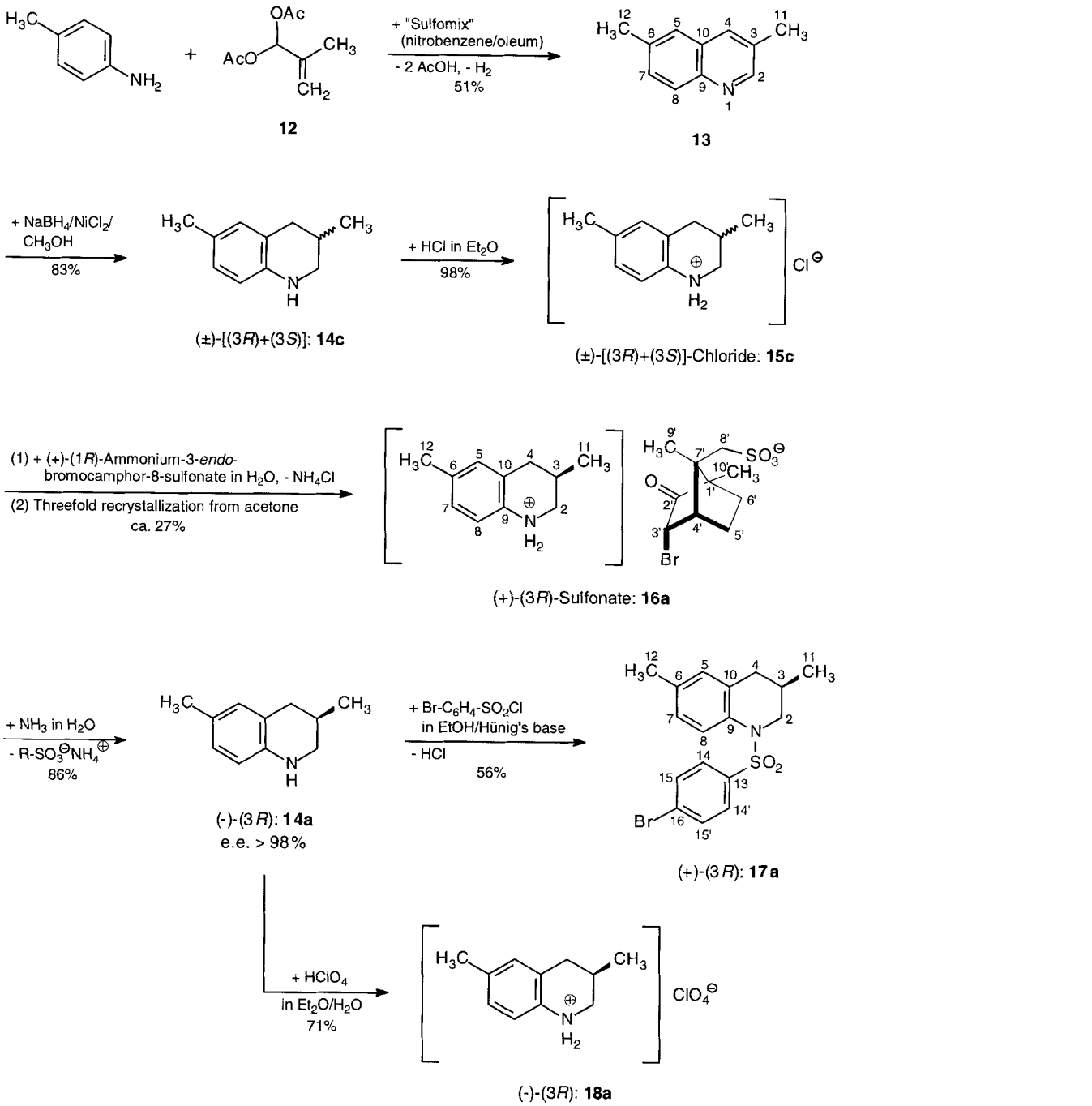
The mother liquor from the crystallization of **16a** was treated first with aqueous ammonia and then the ethereal extract with dry gaseous HCl to give the crude hydrochloride **15c**, which now contained more of the other enantiomeric quinoline derivative (Scheme 2). Addition of ammonium (–)-(1*S*)-3-*endo*-bromocamphor-8-sulfonate to an aqueous solution of crude **15c** led to precipitation of the diastereomeric salt **16b**. After threefold recrystallisation from acetone and treatment of an aqueous solution of **16b** with aqueous ammonia, the crystalline (+)-enantiomer **14b** could be isolated with high enantiomeric purity (*e.e.* > 98%).

For the determination of the enantiomeric purity, the enantiomers **14a,b** as well as isochiral **14c** were converted into the amides **19a–c** by means of (–)-(1*S*)-camphanoyl chloride according to a method described by Bolm *et al.* [26] (Scheme 3). From the relative intensity of the ^1H NMR signals of the diastereotopic 2-H atoms in **19a–c** an enantiomeric purity of *e.e.* > 98% for **19a,b** and hence **14a,b** was found [3].

The absolute configuration at C-3 of **14a,b** was determined by means of a crystal structure analysis with a single crystal of the 4-bromobenzene-sulfonyl derivative (+)-**17a** of (–)-**14a** (Fig. 1; for details see Experimental Part and refs. [2, 27]).

Fig. 1 shows, that (+)-**17a** has an (*R*)-configuration at the stereogenic center C-3. With this result, not only the absolute configuration of (–)-(3*R*)-**14a** and consequently (+)-(3*S*)-**14b** is established, but also the absolute configuration of all polymethine dyes derived from **14a** and **14b**, *i.e.* **4**, **5**, and **9–11** [3]. This result is of particular importance because an assignment of the absolute configuration of the stereogenic centers in dyes **4** and **5** as well as **9** and **10** on the basis of their CD spectra was not unequivocally possible, as has been shown in a preceding paper [13].

The syntheses of symmetrical (**5a,b** and **10a,b**; Scheme 4) and nonsymmetrical (**4a**, **9a**, and **11a**;

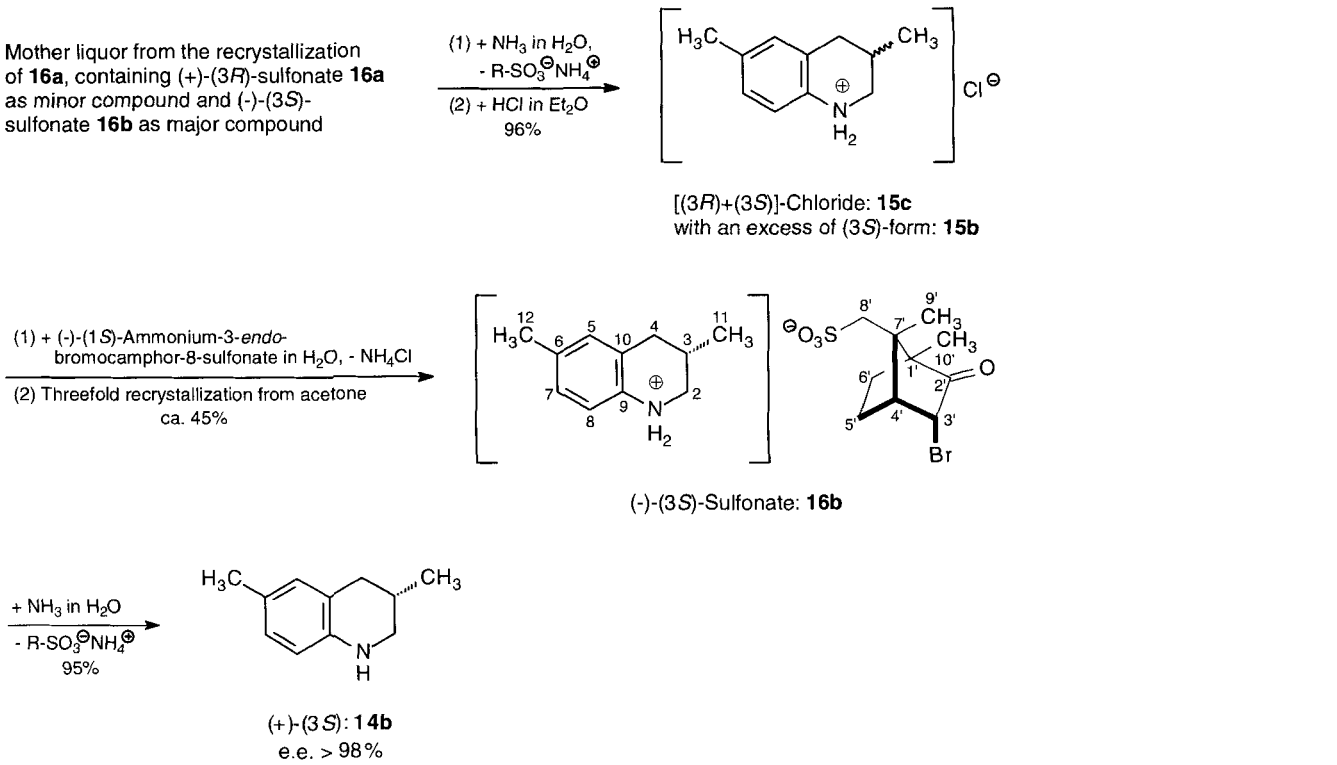


Scheme 1 Synthesis, separation into enantiomers, and derivatization of 1,2,3,4-tetrahydro-3,6-dimethylquinoline **14**

Schemes 5–7) monochiral tri- and pentamethinium cyanine dyes followed the known methods for the preparation of streptocyanines [5, 8, 12] (Scheme 4).

Reaction of the monochiral secondary amines **14a,b** with 1,1,3,3-tetramethoxypropane in ethanol/perchloric acid afforded the trimethinium dyes **5a,b** as yellow crystals in less satisfactory yields. Reaction of monochiral **14a,b** with cyanogen bromide and pyridine in ethanol yielded the pentamethinium dyes **10a,b** as red needles in rather low yields, following a method first described by König, without isolation of the intermediate 1-cyanopyridinium bromide [8, 28].

In order to test whether the overall molecular optical rotation of monochiral cyanine dyes such as **5a,b** and **10a,b** (Scheme 4) could be calculated simply by addition of individual contributions stemming from the two, supposingly independent, end groups with one stereogenic center each, the monochiral tri- and pentamethinium dyes **4a** (Scheme 5) and **9a** (Scheme 6) with altogether only one stereogenic center at C-3 have been



Scheme 2 Isolation of the (+)-(3*S*) enantiomer **14b** of 1,2,3,4-tetrahydro-3,6-dimethylquinoline **14**

synthesized. The pretended additivity, observed by König *et al.* [8] in calculating the overall molecular optical rotation for the monochiral 2,2'-dimethylsubstituted tri- and pentamethinium dyes **3a,b** and **8a,b** (in comparison to **2** resp. **7**), let him conclude that (i) the cations of these cyanine dyes have a symmetrical π-electronic structure, and (ii) the two heterocyclic end groups are chemically equivalent. At that time (1928), this conclusion was a landmark in the development of a theory for the description of the electronic ground state of polymethine dyes. Unfortunately, this work was only published as a short report of a lecture given by König on June 1, 1928, in Dresden/Germany [8a], and it was largely overlooked by his contemporaries and also not appreciated later. Nevertheless, the so-called 'chromostate' theory of König was an important predecessor in the description of electron-delocalized π-systems by means of mesomeric or resonance structures [6, 12, 29].

The nonsymmetrical monochiral trimethinium dye **4a** was obtained by a four-step synthesis (Scheme 5): Reduction of 6-methylquinoline with hydrogen developed with a Raney aluminium/nickel alloy in KOH/H_2O/CH_3OH [30] yielded 1,2,3,4-tetrahydro-6-methylquin-

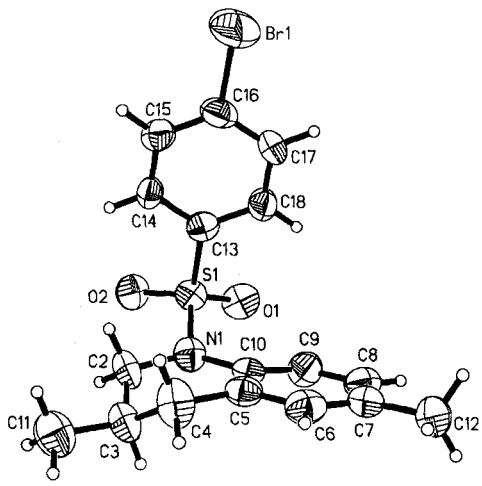
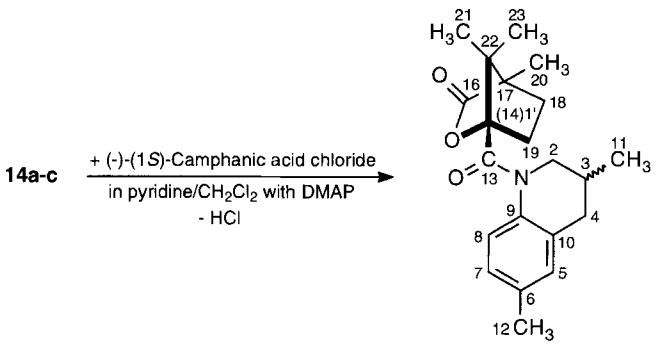


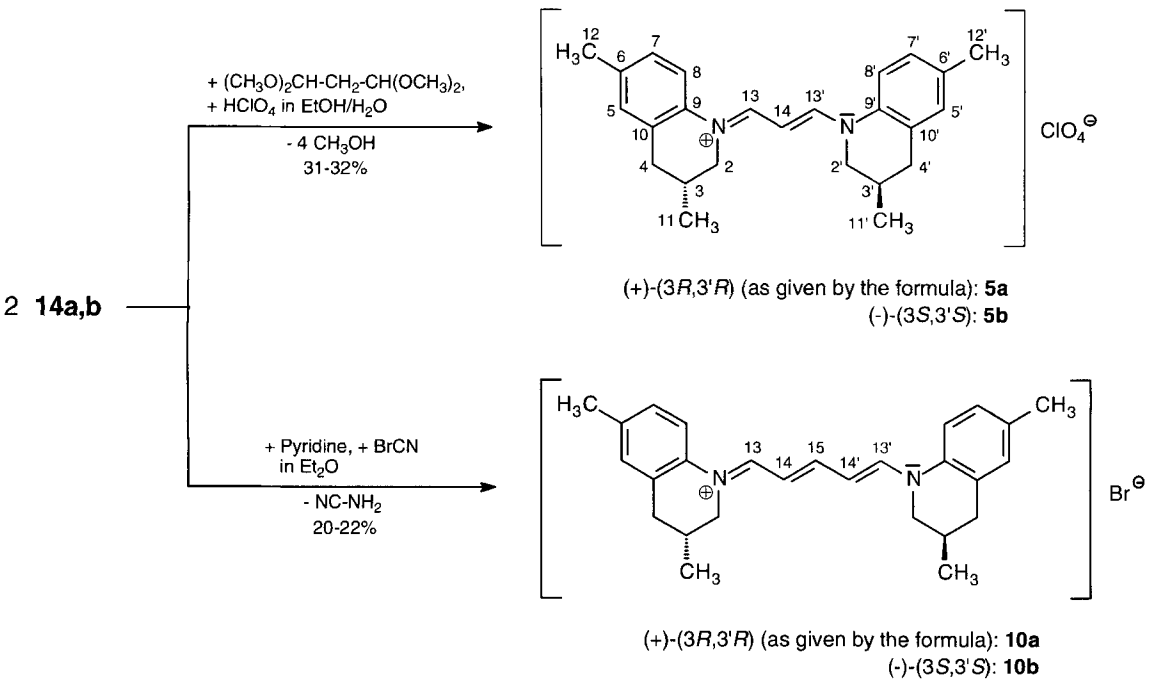
Fig. 1 ORTEP drawing of the molecular structure of the (+)-(3*R*)-4-bromobenzenesulfonyl derivative **17a** (of **14a**) in the crystal (thermal ellipsoids with 50% probability). Selected bond lengths [pm]: C(10)–N(1) 148.4(9), N(1)–C(2) 148.4(9), C(2)–C(3) 146.4(10), C(3)–C(11) 150.7(10), C(3)–C(4) 153.2(10), C(4)–C(5) 146.4(11), N(1)–S(1) 164.1(6), S(1)–C(13) 176.3(7), S(1)–O(1) 141.3(6), S(1)–O(2) 142.9(6); selected bond angles [°]: C(10)–N(1)–C(2) 117.4(6). N(1)–C(2)–C(3) 115.7(7), C(2)–C(3)–C(4) 107.2(6), C(3)–C(4)–C(5) 112.2(7), C(2)–C(3)–C(11) 111.4(7), C(4)–C(3)–C(11) 113.4(6), N(1)–S(1)–C(13) 106.8(3), N(1)–S(1)–O(1) 109.8(3), N(1)–S(1)–O(2) 105.7(3), O(1)–S(1)–O(2) 118.8(4); selected torsion angles [°]: C(10)–N(1)–C(2)–C(3) –22.7(9), N(1)–C(2)–C(3)–C(11) 178.8(6), N(1)–C(2)–C(3)–C(4) 54.3(9), C(2)–C(3)–C(4)–C(5) – 55.7(10), C(11)–C(3)–C(4)–C(5) –179.0(7), C(3)–C(4)–C(5)–C(10) 26.5(11). For further details see Experimental Part and ref. [27].



Scheme 3 Derivatization of **14a–c** with (–)-(1*S*)-camphanic acid chloride for the determination of *e.e.*-values

methinium dye **9a** was prepared (Scheme 6): Reaction of **20** with cyanogen bromide and pyridine in ethanol/diethyl ether [8, 28] afforded the achiral symmetrical pentamethinium dye **6** as red needles in low yield. Partial hydrolysis of **6** with H_2O/MgO in a steam distillation apparatus led to the 5-(dialkylamino)pentadienal **22** in satisfactory yield, which, on condensation with the monochiral (–)-(3*R*)-perchlorate **18a** in ethanol, gave the nonsymmetrical monochiral pentamethinium dye **9a** as red needles in excellent yield.

With the monochiral (–)-(3*R*)-perchlorate **18a** (cf. Scheme 1), it was also possible to obtain the nonsymmetrical monochiral pentamethinium dye **11a** with two different stereogenic centres at each side, one at C-2 and the other at C-3' (Scheme 7): Condensation of **18a** with the monochiral (+)-(2*S*)-pentadienal **23a**, the synthesis of which is described in ref. [12], yielded **11a** as red needles in good yield.

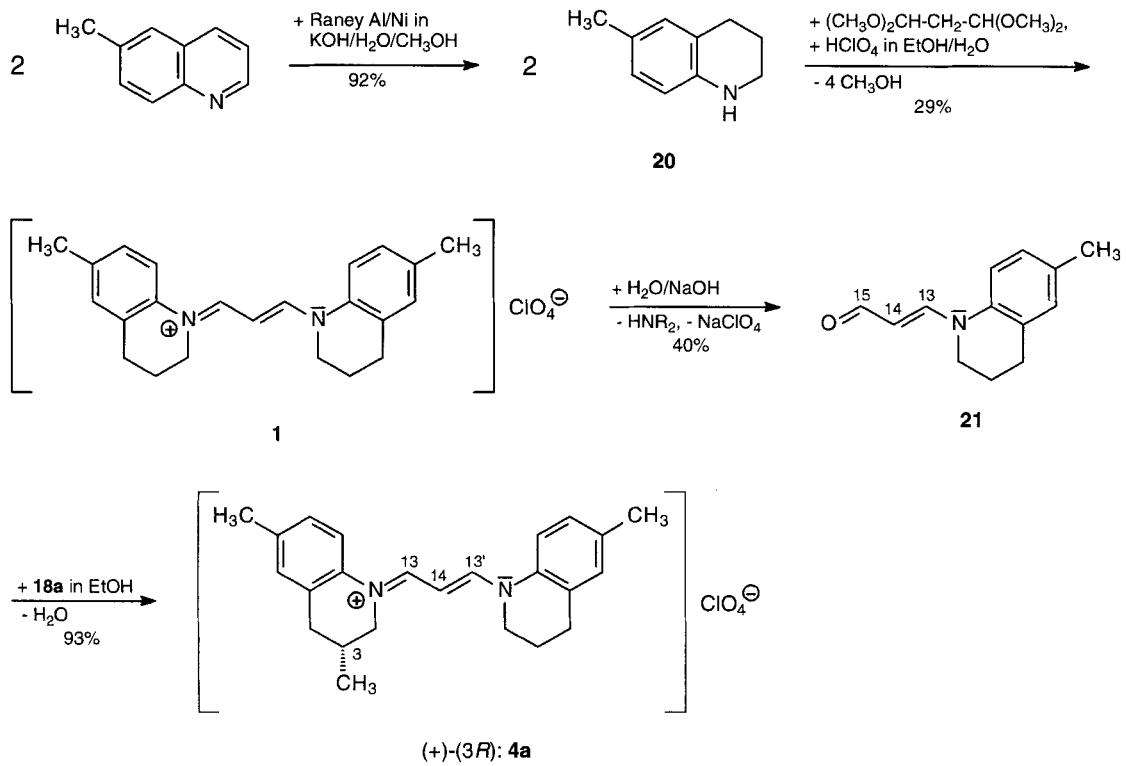


Scheme 4 Syntheses of the symmetrical chiral tri- and pentamethinium dyes **5a,b** and **10a,b** with two stereogenic centers at C-3 and C-3'

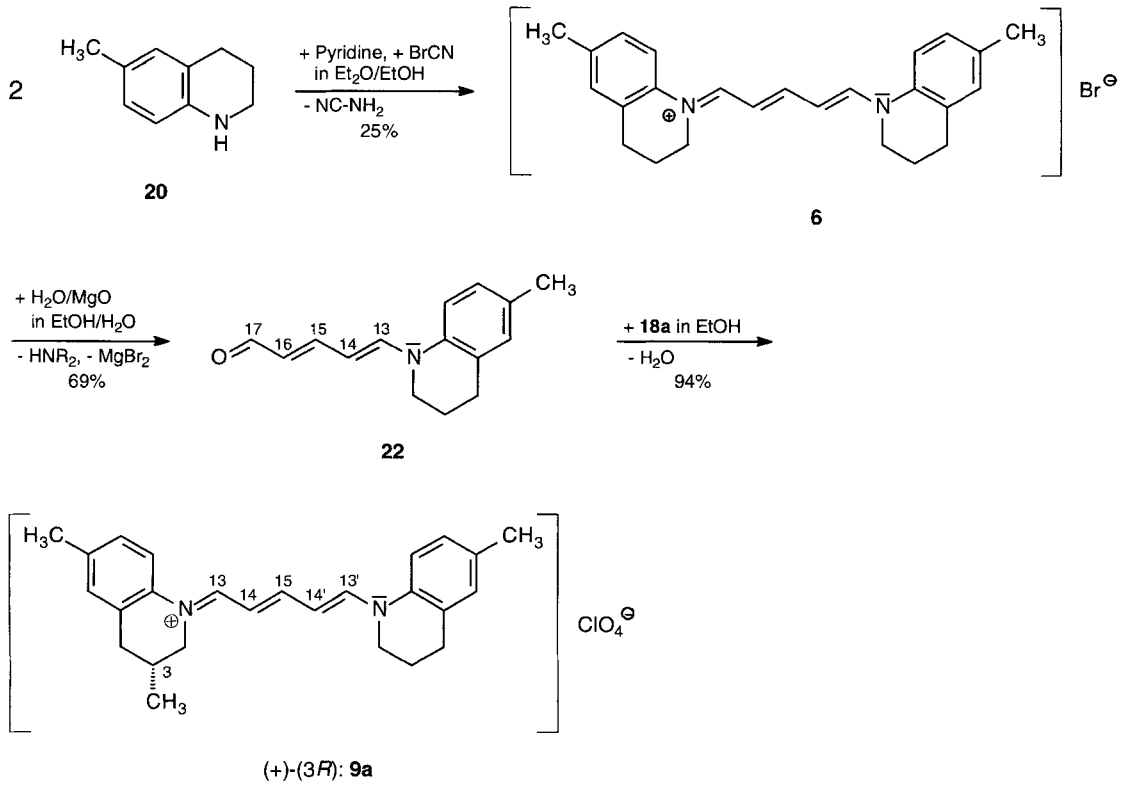
Eventually, for reasons of comparison, the nonsymmetrical monochiral trimethinium dye **2a** has been synthesized by condensation of the propenal **21** (cf. Scheme 5) with the (–)-(2*S*)-perchlorate **24a** [12] in ethanol, to give **2a** as yellow needles in moderate yield (Scheme 8). According to its ^1H NMR spectrum, **2a** exists in $CDCl_3$ solution as a mixture of (*E,E,E,E*) and (*E,E,Z,E*) isomers [3].

oline (**20**) [31], which on reaction with 1,1,3,3-tetramethoxypropane in ethanol/perchloric acid afforded the symmetrical achiral trimethinium dye **1** as yellow needles in moderate yield. Partial hydrolysis of **1** under the condition of a steam distillation led to the 3-(dialkylamino)propenal **21**, which was then condensated with the monochiral (–)-(3*R*)-perchlorate **18a** (cf. Scheme 1) to give the monochiral unsymmetrical trimethinium dye **4a** as yellow crystals in good yield.

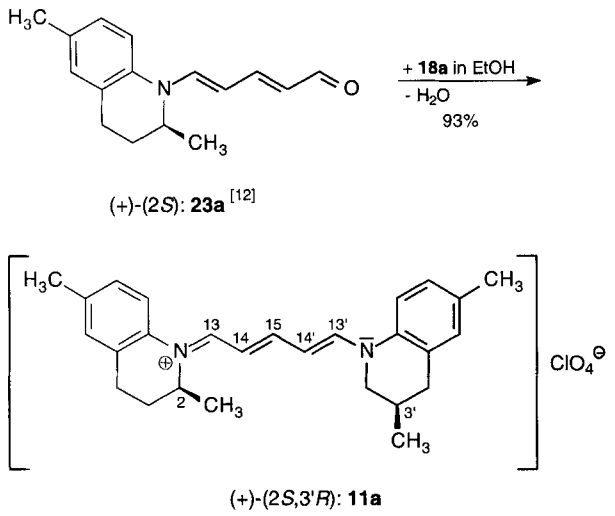
Analogously, the monochiral unsymmetrical penta-



Scheme 5 Synthesis of the nonsymmetrical chiral trimethinium dye **4a** with one stereogenic center at C-3



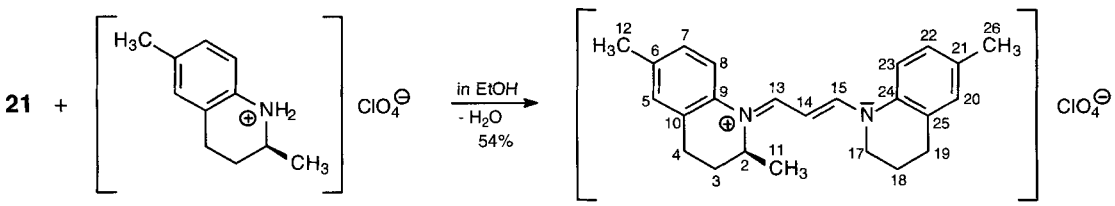
Scheme 6 Synthesis of the nonsymmetrical chiral pentamethinium dye **9a** with one stereogenic center at C-3



Scheme 7 Synthesis of the nonsymmetrical chiral pentamethinium dye **11a** with two stereogenic centers at C-2 and C-3'

2, for reasons of comparison together with the corresponding values of the chiral dyes **3a,b**, **7a**, and **8a,b** already described in ref. [12] (Table 2).

Introduction of one or two methyl groups in the C-2 and C-3 positions of the two heterocyclic end groups has only a minor influence on the absorption maxima of the basic chromophores **1** (λ_{max} = 396 nm) and **6** (λ_{max} = 500 nm), measured in ethanol: Introduction of two methyl groups in the C-2/2' positions of **1** resp. **6** leads in both cases to a small hypsochromic band shift of $\Delta\lambda$ = 8 nm, whereas the introduction of only one methyl group at C-2 or C-3, or both methyl groups at C-3/3', results in a negligible band shift ($\Delta\lambda$ = 1–3 nm). The hypsochromic shifts obtained for the C-2/2' dimethyl-substituted dyes **3a,b** and **8a,b** is obviously due to some steric interaction between the C-2/2' methyl groups and the neighbouring H-atoms of the methine chain, which does not exist in dyes **5a,b** and **10a,b** with methyl groups in the more remote C-3/3' positions. This sterical hindrance should lead to a helically twisted cy-



Scheme 8 Synthesis of the nonsymmetrical chiral trimethinium dye **2a** with one stereogenic center at C-2

The structure of all new compounds has been proven by elemental analysis, UV/Vis, IR, mass, ^{1}H and ^{13}C NMR spectra (see Experimental Part). All monochiral compounds are characterized by their specific and molecular rotation; some of the UV/Vis and CD spectra of the monochiral cyanine dyes given in this paper and in ref. [12] have been already described and discussed in part in ref. [13].

According to the vicinal ^{1}H-NMR coupling constants of the methine H-atoms (^3J ca. 11–12 Hz), the tri- and pentamethinium dyes described in this paper take on the all-(*E*) configuration along the methine chain (with the exception of **2a**) in $CDCl_3$ solution. The single-crystal X-ray analysis of the pentamethinium bromide **8a**, already described in a preceding paper [12], shows a nearly planar pentamethinium chain with the expected all-(*E*) configuration, an averaged C–C bond length of ca. 138 pm, and the typical C–C–C bond angle alternation along the methine chain [32].

The maxima of the long-wavelength intense π-π^* absorption bands and the chiroptical properties of the new polymethine cyanine dyes are compiled in Table

anine chromophore in the dyes **3a,b** and **8a,b** as compared to **5a,b** and **10a,b**. This is indeed the case as shown by the X-ray structure of **8a** [12] and the CD spectra of **3a,b** and **8a,b**, reported in ref. [13]. According to the CD spectra (and corresponding semiempirical calculations), (*S*)-configurated C-2/2' methylsubstituted stereogenic centers give rise to a twisted cyanine chromophore with (*M*)-helicity [13]. Such slightly twisted cyanine dyes can be considered as new inherently chiral chromophores, in spite of the fact that, because of the shortness of the molecular helix, the screw sense is insufficiently developed.

The CD spectra of C-2/2' methylsubstituted cyanine dyes are nearly temperature-invariant with respect to their long-wavelength absorption bands. However, the CD spectra of C-3/3' methylsubstituted cyanine dyes exhibit a pronounced temperature dependence (t = +20 to –160 °C in methanol/ethanol 1:4) [13]. This is probably due to the greater conformational flexibility of the C-3/3' methylsubstituted cyanine dyes which are obviously less sterically hindered. This is also in agreement with the finding, that the asymmetric unit of **17a**

Table 2 Long-wavelength UV/Vis $\pi-\pi^*$ absorption maxima, λ_{max}, specific, $[\alpha]_D$, and molar optical rotations, $[\Phi]_D$, of the polymethinium cyanine dyes **1–11**, measured in ethanol at room temperature

Formula number (X)		Absolute Configuration	λ_{max}/nm	$[\alpha]_D$ [a] (°C)	$[\Phi]_D$ [b]	Average value of $[\Phi]_D$
1	(ClO_4) [c,d]	–	396	–	–	–
2a	(ClO_4) [c,d]	(2*S*)	394	+ 245 (19)	+1090	–
3a	(ClO_4) [e,d]	(2*S*,2'*S*)	389	+780 (19)	+3580	3578
3b	(ClO_4) [e,d]	(2*R*,2'*R*)	388	–779 (19)	–3576	
4a	(ClO_4) [c,d]	(3*R*)	397	+48 (28)	+214	–
5a	(ClO_4) [c,d]	(3*R*,3'*R*)	398	+78 (22)	+358	358
5b	(ClO_4) [c,d]	(3*S*,3'*S*)	398	–78 (22)	–358	
6	(Br) [c,d]	–	500	–	–	–
7a	(ClO_4) [e,d]	(2*S*)	497	+1268 (17)	+6200	–
8a	(Br) [e,d]	(2*S*,2'*S*)	492	+2549 (20)	+11866	11870
8b	(Br) [e,d]	(2*R*,2'*R*)	492	–2551 (19)	–11875	
9a	(ClO_4) [c,d]	(3*R*)	501	+153 (28)	+748	–
10a	(Br) [c,d]	(3*R*,3'*R*)	501	+322 (18)	+1615	1620
10b	(Br) [c,d]	(3*S*,3'*S*)	502	–324 (23)	–1625	
11a	(ClO_4) [c]	(2*S*,3'*R*)	497	+1458 (18)	+7071	

[a]) Dimension: 10^{-1}·deg·cm^2·g^{-1}; [b]) $[\Phi]_D = ([\alpha]_D \cdot M_r)/100$, with M_r = relative molar mass; [c]) This work; [d]) See ref. [13] for the corresponding CD spectra; [e]) See ref. [12]

(cf. Fig. 1) contains two molecules with a different conformation of the tetrahydropyran ring, but with the same (*R*)-configuration [27].

The long-wavelength UV/Vis absorption maxima of the monochiral cyanine dyes in Table 2 are sufficiently hypsochromically separated from the sodium D line emission at 589 nm, permitting a polarimetric measurement of their specifical optical rotations, which are with values up to $[\alpha]_D \approx 2550$ rather large (Table 2). The optical activity is certainly caused by the stereogenic centers in the heterocyclic end groups of the cyanine dyes, but there seem to exist additional contributions to their optical activity stemming from the twisting of the planar π-system due to the steric interactions between the end groups and the methine H-atoms of the polymethine chain, at least for the C-2/2' methyl-substituted dyes [12, 13]. For the further discussion, the molar optical activity, $[\Phi]_D$, will be used because it compensates for unequal molar masses of the compounds being compared.

First, it can be noticed that the molar rotation decreases considerably (by a factor of 5 to 10) on going from **2a** to **4a**, **7a** to **9a**, **3a,b** to **5a,b**, and **8a,b** to **10a,b**, that is on moving the stereogenic centers from the C-2/2' to the C-3/3' position of the corresponding chiral dyes. This is obviously due to the larger distance between the C-3/3' stereogenic centers and the cyanine chromophor as well as to the incidentally reduced steric hindrance. Therefore, the contribution of a helically twisting of the polymethine chain to the overall optical rotation should be negligible for the C-3/3' methylsubstituted tri- (**4a** and **5a,b**) and pentamethinium dyes (**9a** and **10a,b**). Surprisingly enough, the molar rotation of the unsymmetrical chiral pentamethinium dye **11a**, with one stereogenic center at C-2 and the other at C-3', is rather large in comparison to **8a,b** and **10a,b**!

Secondly, provided that each stereogenic center of the two heterocyclic end groups contributes equally to the overall molar optical rotation, then the molar rotation of the dimethyl-substituted tri- (**3a,b** and **5a,b**) and pentamethinium dyes (**8a,b** and **10a,b**) should be twice as large as the molar rotation of the corresponding monomethyl-substituted tri- (**2a** and **4a**) and pentamethinium dyes (**7a** and **9a**), as has been postulated by König in 1928 [8]. This group additivity of the molar rotation has been found by König for the C-2/2' methyl-substituted pentamethinium dyes **7a** and **8a,b** and was one reason for his general conclusion that polymethine cyanine dyes are symmetrical compounds with two chemically equivalent heterocyclic end groups and an overall symmetrical electronic structure [6, 8].

A closer inspection of the newly determined molar rotations of Table 2 exhibits that the averaged molar rotation of the pentamethinium dyes **8a,b** is with $[\Phi]_D$ = 11870 indeed nearly twice as large as the molar rotation of **7a** with $[\Phi]_D$ = 6200. The difference between the calculated and experimental molar rotation [(6200 × 2) – 11870 = 530] is only 4.5% of the experimental value. However, this is obviously a happy accident. If one compares the molar rotation of the trimethinium dyes **2a** and **3a,b**, the difference between calculated and experimental values amounts up to 39%! Obviously, the helical twist of the cyanine chromophore induced by steric interactions between the C-2/2' methyl groups and the methine H-atoms contributes significantly to the molar rotation observed experimentally.

In case of the C-3/3' methyl-substituted polymethinium dyes, the deviations from the group additivity of the molar rotation are much smaller: the difference between calculated and experimental values is for the pentamethinium dyes **9a** and **10a,b** equal to 7%, and for the trimethinium dyes **4a** and **5a,b** equal to 20%. As for

the C-2/2' methyl-substituted pentamethinium dyes (deviation only 4.5%), the group additivity rule is also accidentally valid for the C-3/3' methyl-substituted pentamethinium dyes (deviation only 7%).

An interesting case is given by the C-2/3' dimethyl-substituted pentamethinium dye **11a**. Its rather high molar rotation of $[\Phi]_D = 7071$ can be calculated by taking one half of the molar rotation of **8a,b** (11870:2 = 5935) and one half of that of **10a, b** (1620:2 = 810). The addition of both values gives for **11a** a calculated molar rotation of $[\Phi]_D = 6745$, which deviates from the experimental value by only 5%. The chiroptical behaviour of **11a** is a striking example for the group additivity of molar optical rotations obtained for cyanine dyes with longer methine chains and, therefore, with less sterical hindrance between the substituted end groups and the methine H-atoms.

In conclusion, the group additivity of the molar optical rotation, found by König in 1928 for certain chiral pentamethinium dyes [8], is limited to sterically less hindered cyanine dyes. In general, the overall molar rotation of a chiral polymethinium dye is not only determined by the stereogenic centers in the two heterocyclic end groups, but also by the length and the helical twist of the chromophoric polymethine chain [12, 13]. Therefore, König's conclusions [8] about the symmetrical structure of chiral and achiral polymethine cyanine dyes with two equal end groups were quite correct, but have been drawn for the somewhat wrong reason.

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Experimental

Melting points (not corrected): Kofler-Mikroheiztisch (Reichert, Wien). – Elemental analyses: Analytik-Servicelabor Marburg, Vario EL (Elementar, Hanau). – UV/Vis: Spectrometer U-3410 (Hitachi, Tokyo) with 1.00-cm quartz cells at 25 °C. – IR: Interferometer IFS 88 (Bruker, Rheinstetten), films between NaCl plates for liquids and KBr discs for solids. – ^{1}H and ^{13}C NMR: AC-200, AC-300, and AM-400 (Bruker, Rheinstetten), with TMS as internal standard. Assignment of the signals according to the formula numbering given in Table 1. – MS: Spectrometer MAT CH-7 with electron impact (EI) or MAT 711 with field desorption technique (FD) (Varian, Darmstadt). – Optical rotation: Polarimeter 241 (Perkin-Elmer, Überlingen), with 10-cm quartz cell at $\lambda = 589$ nm (sodium D-line) at room temperature, with concentration c in g of substance in 100 mL of solution . – Crystal structure determination: Stoe IPDS image-plate system with Mo-K_α radiation ($\lambda = 71.073$ pm) at 190(2) K (Stoe, Darmstadt), with software for data collection 'Stoe expose', cell refinement 'Stoe Cell', and data reduction 'Stoe Integrate'. – Analytical TLC: Micro cards 60F-245, with silica gel and fluorescene indicator on aluminium foil (Merck, Darmstadt). – Flash chromatography: Silica gel (Merck, Darmstadt), particle size 0.040–0.063 mm, mixtures of petroleum ether (*b.p.* 40–60 °C (PE) and diethyl ether (DE) as eluent; carried out according to Still *et al.* [33]. – The UV/Vis, IR, NMR, and Mass spectra are identical for the respective two monochiral compounds and the one isochiral compound; only one of the three spectra is given in each case.

3,6-Dimethylquinoline [22, 23] **(13)** (Scheme 1)

a) Preparation of the Oxidizing Agent ("Sulfomix") [23]

18.47 g (0.15 mol) of nitrobenzene was sulfonated by running it dropwise with stirring into 82.50 g of oleum (concentration of SO_3 20 cg/g) at 25–30 °C. This temperature range must be regulated by the rate of addition. Then the yellowish-brown mixture was slowly heated with stirring to 65 °C during 3h. It was maintained at this temperature for another 6–8 h (or overnight), until a sample was completely soluble in water, to give finally 101.00 g of "sulfomix".

b) Ring Closure and Oxidation to **13** [23]

In a distillation apparatus, consisting of a 500 mL round-bottom three-necked flask, KPG stirrer, dropping funnel, inside thermometer, and Claisen still-head with water-cooled condenser and receiving flask, 101.00 g of "sulfomix" was slowly poured into 25 mL of water with stirring, and 26.79 g (0.25 mol) of 4-methylaniline was added. With stirring, the mixture was heated to 125 °C, and 43.05 g (0.25 mol) of 2-methyl-2-propen-1,1-diol-diacetate (**12**) (Aldrich; purity 98%) was added over a period of 3 h. During the addition, the reaction temperature was slowly raised to 175 °C. After the addition, about 25 mL of an acetic acid/water mixture has been distilled off. The black viscous reaction mixture was cooled to 60 °C and poured onto ca. 200 g of ice, and then a concentrated aqueous sodium hydroxide solution was added until an alkaline reaction with litmus paper was observed (pH ca. 9). The crude product was removed from the mixture by steam distillation, collecting ca. 4 L of distillate. The aqueous distillate was extracted several times with altogether 2 L of diethyl ether. The combined ether extracts were dried with $MgSO_4$, the desiccant was filtered off, and the ether was removed by distillation in a rotary evaporator to afford a yellow oil. This oil was then subjected to a fractional distillation *in vacuo* (*b.p.* 68 °C/0.002 Torr; ref. [23] 270.0–271.5 °C) to give 20.01 g (51%) of a slightly yellow oil, which crystallized on standing at room temp. to yield colorless plates with *m.p.* 57 °C (ref. [23] 56.6 °C). – IR (KBr): ν/cm^{-1} = 3069 and 3028 (aromatic C–H), 2972 and 2916 (aliphatic C–H), 2000–1600 (aromatic C–H), 1568 and 1499 (aromatic C=C), 823. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.42 (s, 3H, 12-H), 2.45 (s, 3H, 11-H), 7.45–7.48 (m, 2H, 5- and 7-H), 7.81 (s, 1H, 2-H), 7.94 (m, 1H, 8-H), 8.69 (m, 1H, 4-H). – ^{13}C NMR ($CDCl_3$): δ/ppm=18.6 (C-12), 21.5 (C-11), 125.9 (C-5), 128.1 and 128.8 (C-8 and C-10), 130.3 and 130.6 (C-3 and C-7), 133.9 (C-4), 136.2 (C-6), 145.1 (C-9), 151.4 (C-2). – MS (EI, 70 eV): *m/z* (%) = 158 (12) [M^+ + H], 157 (100) [M^+], 156 (34) [M^+–H], 142 (13) [M^+–CH_3].

$C_{11}H_{11}N$ calcd.: C 84.04 H 7.05 N 8.91
(157.2) found: C 83.90 H 7.39 N 8.95.

(±)-[(3R)+(3S)]-1,2,3,4-Tetrahydro-3,6-dimethylquinoline [24] (**14c**)

To a cooled (3 to 5 °C) and stirred solution of 13.05 g (83.00 mmol) of **13** and 3.09 g (13.00 mmol) of $NiCl_2 \cdot 6H_2O$ in 300 mL of dry methanol 11.99 g (317.00 mmol) of $NaBH_4$ was added in small portions. The solution foamed up and turned black. After the addition, the reaction mixture was stirred for 1 h at room temp. The methanol was then distilled off, affording a black solid residue, which was dissolved in 4 L of aqueous hydrochloric acid (conc. 10 cg/g). This solution was made alkaline (pH = 9) by adding an aqueous ammonia solution (conc. 25 cg/g), then extracted three times with 500 mL each of diethyl ether. The combined ether extracts were dried with $MgSO_4$. The ether was distilled off in a rotary evaporator affording a crude reddish oil, which contained product **14c** and unreacted **13**. **13** and **14c** were separated by flash chromatography on silica gel (column diameter 6 cm) with DE/PE (*b.p.* 40–60 °C) (1:1) as eluant (**13**: R_f ca. 0.29; **14c**: R_f ca. 0.75, determined by TLC on silica gel), using portions of 4.00 g of the crude product dissolved in 5 mL each of diethyl ether. The product-containing fractions were combined, and the solvent was distilled off in a rotary evaporator, to give a light yellow oil, which crystallizes on standing at room temp. Yield 11.11 g (83%) of **14c** as colorless crystals with *m.p.* 50 °C. – $[\alpha]_D^{21} = 0.00$ (c = 0.140 in benzene). – IR (KBr): ν/cm^{-1} = 3370 and 3316 (N-H), 3049 and 3005 (aromatic C–H), 2955, 2910, and 2829 (aliphatic C–H), 2000–1600 (aromatic C–H), 1512 (aromatic C=C), 1466, 1287, 1261, 811. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.10 (d, ^3J = 4.5 Hz, 3 H, 11-H), 2.27 (s, 3H, 12-H), ABCMNX signal-system with δ_X = 2.11 (m, 1H, 3-H_X), δ_A = 2.42–2.50 (m, 1H, 4-H_A), δ_B = 2.88–2.96 (m, 1H, 4-H_B), δ_M = 2.78–2.83 (m, 1H, 2-H_M), δ_N = 3.28–3.31 (m, 1H, 2-H_N), δ_C = 3.69 (m, 1H, 1-H_C); 6.46–6.49 (m, 1H, 8-H), 6.83 (broad s, 2H, 5- and 7-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 19.1 (C-11), 20.4 (C-12), 27.5 (C-3), 35.5 (C-4), 49.1 (C-2), 114.2 (C-8), 121.3 (C-10), 125.2 (C-6), 127.3 (C-7), 130.1 (C-5), 141.9 (C-9). – MS (EI, 70 eV): *m/z* (%) = 162 (11) [M^+ + H], 161 (100) [M^+], 160 (48) [M^+ –H], 146 (21) [M^+–CH_3], 131 (10) [M^+–CH_4N].
$C_{11}H_{15}N$ calcd.: C 81.94 H 9.38 N 8.69
(161.2) found: C 82.56 H 9.66 N 8.52.

(±)-[(3R)+(3S)]-1,2,3,4-Tetrahydro-3,6-dimethylquinolinium Hydrochloride (**15c**)

Dry gaseous hydrogen chloride was passed into a cooled solution of 8.00 g (49.61 mmol) of **14c** in 400 mL of dry diethyl ether for ca. 2 h with stirring, affording a microcrystalline precipitate, which was washed with 100 mL of dry diethyl ether, and dried *in vacuo* to give 9.66 g (98%) of **15c** as hygroscopic, colorless needles with *m.p.* 188 °C. – ν/cm^{-1} = 2962 and 2924 (aliphatic C–H), 2635, 2520, 2469, 2363 (N-H), 1609, 1561, 1510 (aromatic C=C), 836. – ^{1}H NMR (CD_3OD): δ/ppm = 1.14 (d, ^3J = 6.7, 3H, 11-H), ABMNX signal-system with δ_X = 2.17–2.27 (m, 1H, 3-H_X), δ_M = 2.47–2.56 (m, 1H, 4-H_M), δ_A and δ_N = 2.91–3.05 (m, 2H, 2-H_A and 4-H_N), δ_B = 3.45–3.53 (m, 1H, 2-H_B); 2.30 (s, 3H, 12-H), 4.84 (broad s, 2H, 1-H), 7.14 (broad s, 3H, 5-, 7-, and 8-H). – ^{13}C NMR (CD_3OD): δ/ppm = 17.8 (C-11), 20.3 (C-3), 26.7 (C-12), 48.6 (C-2), 123.0 (C-8), 127.4, 128.8, 128.9, and 131.7 (C-5, C-6, C-7, and C-10), 140.3 (C-9). – MS (FD): *m/z* (%) = 162 (10) [M^+ –Cl^-], 161 (100) [M^+ –HCl], 146 (31) [M^+ – HCl–CH_3], 132 (11) [M^+ –HCl–CH_4N].
$C_{11}H_{16}NCl$ calcd.: C 66.83 H 8.16 N 7.08
(197.7) found: C 66.89 H 8.25 N 7.06.

(+)-(3R)-1,2,3,4-Tetrahydro-3,6-dimethylquinolinium (1R)-endo-3-Bromocamphor-anti-8-sulfonate [8, 25] (**16a**)

To a warm (ca. 60 °C) solution of 9.50 g (48.05 mmol) of **15c** in 200 mL of water was added with stirring a warm (ca. 40 °C) solution of 7.88 g (24.00 mmol) of (+)-(1*R*)-ammonium *endo*-3-bromo-camphor-*anti*-8-sulfonate {Aldrich; purity 97%; $[\alpha]_D^{25}$ = 84.5 (c = 4 in water)} in 100 mL of water. A cloudy precipitate was formed, which sometimes disappeared after a while. Then, ca. 100 mL of water was removed in a rotary evaporator. With stirring, the cloudy suspension was slowly cooled to room temp., stirred for 1 h at 0 °C, and then allowed to stand for 24 h at 5 °C. The precipitate formed was filtered off, washed with a small amount of water, and dried *in vacuo*, affording 8.77 g (77%) of diastereomerically enriched **16a** as colorless needles with *m.p.* 189 °C. – $[\alpha]_D^{19}$ = +83 (c = 0.040 in methanol). – In order to get diastereomerically pure **16a**, the product was three times recrystallized from acetone.

First recrystallization: 8.60 g (18.20 mmol) of enriched **16a** was recrystallized from 200 mL of acetone. The hot solution was filtrated, slowly cooled to room temp., and then allowed to stand for 24 h at –17 °C. The precipitate was filtered off, washed with acetone, and dried in vacuo to give 4.12 g of further enriched **16a** as colorless crystals with *m.p.* 190 °C. – $[\alpha]_D^{19}$ = +61 (c = 0.093 in methanol).

Second recrystallization: Analogously, 4.00 g (8.47 mmol) of enriched **16a** from the first recrystallization was again recrystallized from 250 mL of acetone to give 2.83 g of further enriched **16a** as colorless needles with *m.p.* 198 °C. – $[\alpha]_D^{19}$ = +48 (c = 0.137 in methanol).

Third recrystallization: Analogously, 2.60 g (5.50 mmol) of enriched **16a** from the second recrystallization was again recrystallized from 400 mL of acetone to give 2.31 g (ca. 27%) of diastereomerically pure **16a** as colorless needles with *m.p.* 201 °C. – $[\alpha]_D^{19}$ = +47 (c = 0.059 in methanol). – IR (KBr): ν/cm^{-1} = 2972 and 2934 (aliphatic C-H), 2759, 2695, 2565 (N-H), 1754 (C=O), 1225, 1137, 1036. – ^{1}H NMR ($CDCl_3$): δ/ppm = 0.86 (s, 3 H, 9'-H), 0.99 (s, 3 H, 10'-H), 1.17 (d, ^3J = 6.4 Hz, 3H, 11-H), 1.31–1.40 (m, 1H, *endo*-5'-H), 1.40–1.47 (m, 1H, *endo*-6'-H), 1.91–1.96 (m, 2H, *exo*-5'-H and *exo*-6'-H), 2.35 (s, 3H, 12-H), AB signal-system with δ_B = 2.45–3.06 (m, 6H, 2-H_B, as well as 3-, 4-, and 8'-H) and δ_A = 3.73 (m, 1H, 2-H_A); 4.31 (d, ^3J = 4.6 Hz, 1H, 3'-H), 7.03 (s, 1H, 5-H), 7.12 (d, ^3J = 8.0 Hz, 1H, 7-H), 7.47 (d, ^3J = 8.1 Hz, 1H, 8-H), 10.68 (broad s, 2H, 1-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 9.7 (C-10'), 17.4 (C-11), 18.6 (C-9'), 20.4 (C-12), 21.9 (C-6'), 25.9 (C-2), 30.1 (C-4), 33.8 (C-5'), 46.9 (C-7'), 47.1 (C-8'), 51.3 (C-4'), 53.0 (C-3), 54.1 (C-1'), 59.6 (C-3'), 123.5 (C-8), 128.3, 130.5, and 130.8 (C-5, C-6, C-7, and C-10), 139.3 (C-9), 211.6 (C-2'). – MS (EI, 70 eV): *m/z* (%) = 162 (10) [M^+ – bromocamphor-sulfonate$^-$], 161 (100) [M^+ – bromocamphor-

sulfonic acid], 146 (22) [M^+ – bromocamphor-sulfonic acid – CH_3], 131 (10) [M^+–bromocamphor-sulfonic acid–CH_4N].

$C_{21}H_{30}BrSO_4N$	calcd.:	C 53.39	H 6.40	N 2.96
(472.4)	found:	C 53.27	H 6.64	N 3.16.

(–)-(3R)-1,2,3,4-Tetrahydro-3,6-dimethylquinoline (**14a**)

To a warm (ca. 60 °C) solution of 2.31 g (4.89 mmol) of **16a** in 200 mL of water an aqueous ammonia solution (conc. 25 cg/g) was added until a pH of ca. 11. The cloudy suspension was slowly cooled to room temp. and allowed to stand for 2 d at 5 °C. The precipitate formed was filtered off and dried *in vacuo* at room temp., to yield 0.68 g (86%) of **14a** as colorless needles with *m.p.* 38 °C. – $[\alpha]_D^{20} = -77$ ($c = 0.091$ in benzene). – IR (KBr): ν/cm^{-1} = 3405, 3345 (N-H), 3010 (aromatic C–H), 2952, 2915, 2864 (aliphatic C–H), 1615, 1587, 1515 (aromatic C=C), 1270, 810. – ^1H NMR ($CDCl_3$): δ/ppm = 1.03 (d, ^3J = 6.6 Hz, 3H, 11-H), ABCMNX signal-system with δ_X = 1.97–2.06 (m, 1H, 3-H_X), δ_M = 2.34–2.43 (m, 1H, 4-H_M), δ_A = 2.70–2.77 (m, 1H, 2-H_A), δ_N = 2.82–2.89 (m, 1H, 4-H_N), δ_B = 3.21–3.26 (ddd, ^2J = 11.0 Hz, ^3J = 3.6 Hz, ^3J = 2.9 Hz, 1H, 2-H_B), δ_C = 3.40–3.80 (m, 1H, 1-H_C); 2.20 (s, 3H, 12-H), 6.42 (d, ^3J = 8.4 Hz, 1H, 8-H), 6.78 (d, superimposed by s, 2H, 5- and 7-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 19.0 (C-11), 20.4 (C-3), 27.5 (C-12), 35.5 (C-4), 49.1 (C-2), 114.2 (C-8), 121.3 (C-6), 126.3 and 127.3 (C-5 and C-7), 130.1 (C-10), 141.9 (C-9). – MS (EI, 70 eV): *m/z* (%) = 162 (11) [M^++H], 161 (100) [M^+], 160 (50) [M^+–H], 146 (23) [M^+–CH_3], 132 (21) [M^+–C_2H_5], 131 (21) [M^+–CH_4N], 118 (10) [M^+–C_2H_5N].

$C_{11}H_{15}N$	calcd.:	C 81.94	H 9.38	N 8.69
(161.2)	found:	C 81.75	H 9.53	N 8.57.

(+)-(3R)-N-(4-Bromobenzenesulfonyl)-1,2,3,4-tetrahydro-3,6-dimethylquinoline (**17a**)

To a warm (ca. 60 °C) solution of 0.81 g (5.00 mmol) of **14a** and 0.86 mL of *N*-ethyl-diisopropylamine ("Hünig's Base") in 10 mL of dry ethanol a solution of 1.28 g (5.00 mmol) of 4-bromobenzenesulfonyl chloride in 20 mL of dry ethanol was added dropwise with stirring during 15 min. The yellow solution was stirred for another 30 min at 60 °C, cooled to room temp., and 30 mL of water was added, forming a white precipitate. The reaction mixture was extracted three times with 30 mL each of dichloromethane. The combined extracts were dried with $MgSO_4$. The solvent was distilled off in a rotary evaporator affording a colorless solid. This solid was dissolved in 10 mL of hot ethanol and the solution was allowed to stand for 1 d at 5 °C. The crystals formed were filtered off, washed with a small amount of cold ethanol and dried *in vacuo*, to yield 1.06 g (56%) of **17a** as colorless plates with *m.p.* 123.5–124.5 °C. By slow crystallization of **17a** from a hot solution in ethanol, crystals suitable for an X-ray analysis were formed; cf. end of the Experimental Part, Fig. 1, and refs. [2, 27]. – $[\alpha]_D^{23} = +63$ (c=0.186 in methanol). – IR (KBr): ν/cm^{-1} = 3414 (O-H), 2952, 2925 (aliphatic C–H), 1349, 1342, 1159, (SO_2), 827, 739, 598, 572. – ^1H NMR ($CDCl_3$): δ/ppm = 0.89 (d, ^3J = 6.6 Hz, 3-H, 11-H), ABMNX signal-system with δ_X = 1.58–1.69 (m, 1H, 3-H_X), δ_M = 2.00 (dd, ^2J = 16.4 Hz, ^3J = 10.8 Hz, 1H, 4-H_M), δ_N = 2.49 (dd, ^2J = 16.2 Hz, ^3J = 5.0 Hz, 1H, 4-H_N), δ_A= 2.98 (dd, ^2J = 13.3 Hz, ^3J = 11.1 Hz, 1H, 2-H_A), δ_B = 4.09 (ddd, ^2J = 13.3 Hz, ^3J = 4.4 Hz, ^4J = 1.6 Hz, 1H, 2-H_B); 2.25 (s, 3H, 12-H), 6.78 (s, 1H, 5-H), 6.96 (d, ^3J = 9.2 Hz, 1H 7-H), 7.40–7.52 (two d, 4H, 14/14'- and 15/15'-H), 7.63 (d, ^3J = 8.4 Hz, 1H, 8-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 19.1 (C-11), 20.8 (C-12), 27.5 (C-3), 35.5 (C-4), 53.2 (C-2), 124.2 (C-8), 127.5 (C-10), 127.7 (C-6), 128.6 (C-14/14'), 129.8 (C-16), 130.2 (C-7), 132.3 (C-15/15'), 133.5 (C-5), 134.9 (C-13), 138.8 (C-9). – MS (EI, 70 eV): *m/z* (%) = 381 and 379 (15) [M^+], 160 (100) [M^+–$SO_2C_6H_4Br$], 145 (21) [M^+–$SO_2C_6H_4Br$–CH_3].

$C_{17}H_{18}BrNO_2S$	calcd.:	C 53.69	H 4.77	N 3.68
(380.3)	found:	C 53.73	H 5.12	N 3.64.

(–)-(3R)-1,2,3,4-Tetrahydro-3,6-dimethylquinolinium Perchlorate (**18a**)

To a solution of 0.20 g (1.24 mmol) of **14a** in 10 mL of diethyl ether 0.18 mL (2.10 mmol) of aqueous perchloric acid (conc. 70 cg/g) was added dropwise. After stirring for 10 min at 0 °C, the precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*, to give 0.23 g (71%) of **18a** as colorless needles with *m.p.* 157–161 °C. – $[\alpha]_D^{18} = -35$ (c = 0.098 in ethanol). – IR (KBr): ν/cm^{-1} = 3024 (aromatic C-H), 2976, 2961, 2934 (aliphatic C-H), 1609, 1588, 1508 (aromatic C=C), 1146, 1099, 1043 (ClO_4), 627. – ^1H NMR (CD_3OD): δ/ppm = 1.14 (d, ^3J = 6.7 Hz, 3H, 11-H), ABCMNX signal-system with δ_X = 2.10–2.27 (m, 1H, 3-H_X), δ_M = 2.49–2.58 (m, 1H, 4-H_M), δ_A and δ_N = 2.92–3.07 (m, 2H, 2-H_A and 4-H_N), δ_B = 3.50–3.55 (m, 1H, 2-H_B), δ_C = 4.65–4.93 (m, 2H, 1-H_C); 2.31 (s, 3H, 12-H), 7.14 (broad m, 3H, 5-, 7-, and 8-H). – ^{13}C NMR (CD_3OD): δ/ppm = 17.7 (C-11), 20.3 (C-3), 26.7 (C-12), 33.6 (C-4), 122.9 (C-8), 127.4, 128.8, 128.9, and 131.7 (C-5, C-6, C-7, and C-10), 140.3 (C-9). – MS (FD): *m/z* (%) = 423 (50) [$2M^+$–ClO_4^-], 163 (13) [M^+–ClO_4^- + H^+], 162 (12) [M^+–ClO_4^-), 161 (100) [M^+–$HClO_4$].

$C_{11}H_{16}ClNO_4$	calcd.:	C 45.76	H 6.63	N 4.85
•1.5 H_2O (288.7)	found:	C 46.16	H 6.86	N 4.77.

[(3R)+(3S)]-1,2,3,4-Tetrahydro-3,6-dimethylquinolinium Hydrochloride (**15c**), *with an excess of the (3S)-form* (**15b**) (Scheme 2)

From the mother liquor, obtained from the preparation and recrystallization of **16a**, containing the (+)-(3*R*)-sulfonate **16a** as minor compound and (–)-(3*S*)-sulfonate **16b** as major compound, the solvent was distilled off in a rotary evaporator. The solid residue was dissolved at 40 °C in 200 mL of water, and to the solution an aqueous ammonia solution (conc. 25 cg/g) was added until a pH of ca. 11. The cloudy solution was extracted three times with 100 mL each of diethyl ether. The combined ether extracts were dried with $MgSO_4$, filtered, the ether was distilled off in a rotary evaporator, and the residue was dried *in vacuo*, affording 5.59 g of crude **14c** as colorless solid with $[\alpha]_D^{19} = +0.5$ (c = 0.134 in benzene). As described before for (±)-**15c**, 5.50 g (34.11 mmol) of **14c** was converted into its hydrochloride by passing dry gaseous hydrogen chloride into a solution of this solid in 250 mL of dry diethyl ether, to give 6.46 g (96%) of the enriched hydrochloride **15c** as hygroscopic, colorless crystals with *m.p.* 187 °C. – IR, mass, ^1H and ^{13}C NMR spectrum as well as elemental analysis are practically identical with that of (±)-**15c** described before (*cf.* Scheme 1).

(–)-(3S)-1,2,3,4-Tetrahydro-3,6-dimethylquinolinium (1S)-endo-3-Bromocamphor-anti-8-sulfonate [8, 25] (**16b**)

To a warm (ca. 60 °C) solution of 6.30 g (31.86 mmol) of crude enriched **15c** in 250 mL of water a warm (ca. 60 °C) solution of 5.25 g (16.0 mmol) of (–)-(1*S*)-ammonium *endo*-3-bromocamphor-*anti*-8-sulfonate {Aldrich; purity 99%; $[\alpha]_D^{21} = -83$ ($c = 0.4$ in water)} in 40 mL of water was added with stirring. After slow cooling to room temp., the solution was allowed to stand for 24 h at 5 °C. The precipitate formed was filtered off and dried *in vacuo*, to yield 5.12 g (68%) of enriched **16b** as colorless needles with *m.p.* 195 °C. – $[\alpha]_D^{19} = -5$ ($c = 0.049$ in methanol). – In order to get diastereomerically pure **16b**, the product was three times recrystallized from acetone.

First recrystallization: 5.10 g (10.80 mmol) of enriched **16b** was recrystallized from 100 mL of acetone. The hot solution was filtrated, slowly cooled to room temp., and then allowed to stand for 24 h at –17 °C. The precipitate formed was filtered off, washed with a small amount of acetone, and dried *in vacuo*, to give 3.15 g of further enriched **16b** as colorless needles with *m.p.* 199 °C. – $[\alpha]_D^{19} = -23$ ($c = 0.063$ in methanol).

Second recrystallization: Analogously, 3.10 g (6.56 mmol) of enriched **16b** from the first recrystallization was again recrystallized from 450 mL of acetone to give 2.70 g of further enriched **16b** as colorless needles with *m.p.* 203 °C. – $[\alpha]_D^{19} = -31$ ($c = 0.061$ in methanol).

Third recrystallization: Analogously, 2.75 g (5.82 mmol) of enriched **16b** from the second recrystallization was again recrystallized from 500 mL of acetone to give 2.30 g (ca. 45%) of diastereomerically pure **16b** as colorless needles with *m.p.* 203 °C. – $[\alpha]_D^{19} = -31$ ($c = 0.056$ in methanol). – IR, mass, ^{1}H and ^{13}C NMR spectrum are practically identical with that of **16a** (cf. Scheme 1).

$C_{21}H_{30}BrSO_4N$	calcd.:	C 53.39	H 6.40	N 2.96
(472.4)	found:	C 53.48	H 6.39	N 3.04.

(+)-(3S)-1,2,3,4-Tetrahydro-3,6-dimethylquinoline (**14b**)

To a warm (ca. 60 °C) solution of 2.15 g (4.55 mmol) of **16b** in 200 mL of water an aqueous ammonia solution (conc. 25 cg/g) was added until a pH of ca. 11. The cloudy suspension was slowly cooled to room temp. and allowed to stand for 3 d at 5 °C. The precipitate formed was filtered off and dried *in vacuo* at room temp., to yield 0.70 g (95%) of **14b** as colorless crystals with *m.p.* 38 °C. – $[\alpha]_D^{20} = +70$ ($c = 0.026$ in benzene). – IR, mass, ^{1}H and ^{13}C NMR spectrum are practically identical with that of **14a** described before (*cf.* Scheme 1).

$C_{11}H_{15}N$	calcd.:	C 81.94	H 9.38	N 8.69
(161.2)	found:	C 81.07	H 9.72	N 8.44.

Syntheses of the Camphanoyl Amides 19a–c for Determination of the Enantiomeric Excess of 14a and 14b [26] (Scheme 3)

a) (–)-(1'S, 3R)-N-Camphanoyl-1,2,3,4-tetrahydro-3,6-dimethylquinoline (**19a**)

To a solution of 50.0 mg (0.31 mmol) of **14a** and 3.67 mg (0.03 mmol) of 4-(dimethylamino)pyridine in 0.75 mL of dry dichloromethane and 0.16 mL of dry pyridine 84.5 mg (0.39 mmol) (–)-(1*S*)-camphanoyl chloride {Fluka; purity > 98%; $[\alpha]_D^{20} = -18 \pm 1$ ($c = 2$ in CCl_4); *e.e.* = 99%} was added with stirring under dry argon. The reaction mixture was stirred for 24 h at room temp. After addition of 30 mL of dichloromethane, the solution was subsequently extracted with 100 mL of an aqueous saturated Na_2CO_3 solution and with 100 mL of water. The organic layer was dried with Na_2SO_4, filtrated, the solvent was distilled off in a rotary evaporator, and the solid residue was dried *in vacuo*. The crude **19a** was purified by flash chromatography on silica gel (column diameter 0.5 cm) with diethyl ether/*n*-hexane (1:1) as eluant (R_f-value of **19a** = 0.45, as determined by TLC on silica gel). The product-containing fractions were combined, the solvent was removed in a rotary evaporator, and the residue was dried *in vacuo*, to give 80.0 mg (76%) of **19a** as colorless crystals with *m.p.* 162 °C. – $[\alpha]_D^{19} = -123$ ($c = 0.160$ in ethanol). – IR (KBr): ν/cm^{-1} = 1780 (C=O, ester), 1657 (C=O, amide). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.00 (d, $^3J = 6.7$ Hz, 3H, 11-H), 1.05 and 1.07 (two s, 2×3H, 21- and 22-H), 1.17 (s, 3H, 20-H), 1.68–1.74 (m, 1H, 18-H_A), 1.84–2.01 (two m, 3H, 18-H_B and 19-H), 2.22 (s, 3H, 12-H), ABMNX signal-system with δ_M and δ_X = 2.29–2.41 (m, 2H, 3-H_X and 4-H_M), δ_N = 2.83–2.91 (m, 1H, 4-H_N), δ_A = 2.95–3.03 (m, 1H, 2-H_A), δ_B = 4.29–4.35 (m, 1H, 2-H_B); 6.86–6.91 (d, superimposed by s, 2H, 5- and 7-H), 7.33 (d, $^3J = 8.2$ Hz, 1H, 8-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 9.7 (C-20), 16.7 (C-11), 17.8 (C-22), 19.3 (C-21), 29.5 and 30.6 (C-18 and C-19), 31.6 (C-3), 35.2 (C-23), 51.6 (C-4), 53.9 (C-17), 56.0 (C-2), 92.4 (C-14), 124.9, 126.3, and 129.6 (C-5, C-7, and C-8), 134.8 (C-9), 135.0 (C-10), 167.0 (C-13), 178.6 (C-16). – MS (EI, 70 eV): *m/z* (%) = 342 (15) [M$^+$], 341 (100) [M$^+$–H].

$C_{21}H_{27}NO_3$	calcd.:	C 73.87	H 7.97	N 4.10
(341.5)	found:	C 73.75	H 7.85	N 4.14.

b) (–)-(1'S,3S)-N-Camphanoyl-1,2,3,4-tetrahydro-3,6-dimethylquinoline (**19b**)

Synthesis analogous to **19a** from **14b**; yield 67 mg (63%) **19b** as colorless crystals with *m.p.* 118 °C – $[\alpha]_D^{19} = -52$ ($c = 0.104$ in ethanol). – IR, mass, ^{1}H and ^{13}C NMR spectrum are similar to that of **19a**.

$C_{21}H_{27}NO_3$	calcd.:	C 73.87	H 7.97	N 4.10
(341.5)	found:	C 73.91	H 7.60	N 4.03.

c) (–)-[(1'S),(3R)+(3S)]-N-Camphanoyl-1,2,3,4-tetrahydro-3,6-dimethylquinoline (**19c**; 1:1 mixture of diastereomers)

Synthesis analogous to **19a** from racemic **14c** (= **14a** + **14b** [19]); yield 80 mg (76%) **19c** as colorless crystals with *m.p.* 126 °C. – $[\alpha]_D^{19} = -89$ ($c = 0.070$ in ethanol). – IR, mass, ^{1}H and ^{13}C NMR spectrum are similar to that of **19a**; most NMR signals twofold.

$C_{21}H_{27}NO_3$	calcd.:	C 73.87	H 7.97	N 4.10
(341.5)	found:	C 73.51	H 7.89	N 3.96.

d) Determination of the e.e.-values of **14a** and **14b**

Whereas the ^{1}H NMR spectrum of isochiral [18] **19c** showed for 2-H two multiplets of equal intensity at δ ca. 4.0 and ca. 4.3 ppm, the corresponding 2-H signal of the respective minor diastereomeric amide in monochiral **19a** and **19b** was practically not visible. This corresponds to an enantiomeric excess of *e.e.* > 98% for **19a** and **19b**, and hence also for **14a**

and **14b**, from which **19a,b** was prepared (for further details see ref. [2]).

(+)-(3R,3'R)-1,3-Bis(1,2,3,4-tetrahydro-2,6-dimethylquinolin-1-yl)-trimethinium Perchlorate (**5a**) [8, 12] (Scheme 4)

A solution of 0.54 g (3.35 mmol) of **14a** and 0.28 g (1.68 mmol) of 1,1,3,3-tetramethoxypropane in 1 mL of dry ethanol was stirred at room temp. for 30 min, then 0.37 g of aqueous perchloric acid (conc. 70 cg/g) was added and the stirring was continued for 1 h. The yellow precipitate formed was filtered off and purified by extraction with 5 mL of boiling ethanol in a simple solid–liquid extractor. The extraction solution was then allowed to stand for 24 h at –17 °C. The precipitate formed was filtered off (using a D4 glass frit) and dried *in vacuo*, to yield 0.24 g (31%) of **5a** as yellow crystals with *m.p.* 260 °C (dec.). $-[\alpha]_D^{22} = +78$ ($c = 0.043$ in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 398 (4.740), 251 (4.210). – IR (KBr): ν/cm^{-1} = 3101, 3022 (aromatic C–H), 2964, 2930, 2879 (aliphatic C–H), 1618, 1594, 1583, 1499 (aromatic C=C), 1301, 1278, 1221, 1108, 1065 (ClO_4). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.15 (d, ^{3}J= 6.6 Hz, 6H, 11/11'-H), ABMNX signal-system with δ_X = 2.01–2.06 (m, 2H, 3/3'-H_X), δ_M = 2.32–2.38 (m, 2H, 4/4'-H_M), δ_A=2.68–2.74 (m, 2H, 2/2'-H), δ_N = 3.28–3.35 (m, 2H, 4/4'-H_N), δ_B = 4.03–4.08 (m, 2H, 2/2'-H_B); 2.26 (s, 6H, 12/12'-H), 6.07 (t, ^3J = 11.6 Hz, 1H, 14-H), 6.88 (s, 2H, 5/5'-H), 7.08 (m, 2H, 7/7'-H), 7.54 (d, ^3J = 8.4 Hz, 2H, 8/8'-H), 8.45 (d, ^3J = 11.6 Hz, 2H, 13/13'-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 18.6 (C-11/11'), 20.8 /c-12/12'), 28.3 (C-3/3'), 34.9 (C-4/4'), 53.9 (C-2/2'), 95.8 (C-14), 118.3 (C-5/5'), 129.2, 129.3, and 130.0 (C-6/6', C-7/7', and C-8/8'), 135.2 (C-10/10'), 137.0 (C-9/9'), 157.9 (C-13/13'). – MS (FD): *m/z* (%) = 360 (26) [$M^+ - ClO_4^-$], 359 (100) [$M^+ - HClO_4$].

$C_{25}H_{31}ClN_2O_4$	calcd.:	C 65.42	H 6.81	N 6.10
(459.0)	found:	C 65.30	H 6.97	N 5.94.

(–)-(3S,3'S)-1,3-Bis(1,2,3,4-tetrahydro-2,6-dimethylquinolin-1-yl)-trimethinium Perchlorate (**5b**)

Synthesis analogous to **5a**, from 0.70g (4.34 mmol) of **14b**, 0.36 g (2.17 mmol) of 1,1,3,3-tetramethoxypropane, and 0.48 g aqueous perchloric acid (conc. 70 cg/g) in ethanol, to give 0.32 g (32%) of **5b** as yellow crystals with *m.p.* 260 °C (dec.). $-[\alpha]_D^{22} = -78$ ($c = 0.0032$ in ethanol). – UV/Vis, IR, mass, ^{1}H and ^{13}C NMR spectrum are identical with that of **5a**.

$C_{25}H_{31}ClN_2O_4$	calcd.:	C 65.42	H 6.81	N 6.10
(459.0)	found:	C 64.93	H 6.57	N 6.04.

(+)-(3R,3'R)-1,5-Bis(1,2,3,4-tetrahydro-3,6-dimethylquinolin-1-yl)-pentamethinium Bromide (**10a**) [8,12] (Scheme 4)

To a solution of 0.79 g (4.87 mmol) of **14a** and 0.19 g (2.44 mmol) of dry pyridine in 5 mL of dry diethyl ether with stirring at room temp. a solution of 0.26 g (2.44 mmol) of cyanogen bromide in 4 mL of dry diethyl ether was added dropwise. The yellow solution was stirred for 2 h at room temp. and then allowed to stand for 24 h at –17 °C. The red precipitate formed was filtered off. The volume of the mother liquor was reduced by half in a rotary evaporator, and the solution was again allowed to stand for 24 h at –17 °C. The second precipitate formed was filtered off, combined with the first precipitate, and dried *in vacuo*. The crude product was purified by recrystallization from acetone (ca. 450 mL), to yield 0.23 g (20%) of **10a** as red needles with *m.p.* 230 °C. $-[\alpha]_D^{18} = +322$ (c = 0.017 in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 501 (5.023), 274 (4.093). – IR (KBr): ν/cm^{-1} = 3384, 3006 (aromatic C–H), 2955, 2924 (aliphatic C–H), 1615, 1588, 1567, 1528, 1469 (aromatic C=C), 1219, 1197, 1155. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.07 (d, ^3J = 6.6 Hz, 6 H, 11/11'-H), ABMNX signal-system with δ_X = 2.04–2.10 (m, 2H, 3-H_X), δ_M = 2.31–2.36 (m, 2H, 4/4'-H_M), δ_A= 2.68–2.75 (m, 2H, 2/2'-H_A), δ_N= 3.16–3.24 (m, 2H, 4/4'-H_N), δ_B = 3.87–3.93 (m, 2H, 2/2'-H_B); 2.21 (s, 6H, 12/12'-H), 6.31 (dd, appearing as t, 2H, 14/14'-H), 6.83 (s, 2H, 5/5'-H), 7.04 (d, ^3J = 8.3 Hz, 2H, 7/7'-H), 7.52 (d, ^3J = 8.3 Hz, 2H, 8/8'-H), 8.62 (d, ^3J = 11.9 Hz, 2H, 13/13'-H), 8.81 (t, ^3J = 12.7 Hz, 1H, 15-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 18.4 (C-11/11'), 20.6 (C-12/12'), 28.0 (C-3/3'), 34.8 (C-4/4'), 53.4 C-2/2'), 108.5 (C-14/14'), 118.0 (C-5/5'), 128.5, 128.9, and 129.7 (C-6/6', C-7/7', and C-8/8'), 135.1 (C-10/10'), 136.2 (C-9/9'), 155.2 (C-13/13'), 167.5 (C-15). – MS (FD): *m/z* (%) = 386 (7) [M^+–Br$^-$], 385 (44) [M^+–HBr], 58 (100) [$C_3H_8N^+$].

$C_{27}H_{33}BrN_2 \cdot 2H_2O$	calcd.:	C 64.66	H 7.44	N 5.59
(501.5)	found:	C 64.96	H 7.45	N 5.65.

(–)-(3S,3'S)-1,5-Bis(1,2,3,4-tetrahydro-3,6-dimethylquinolin-1-yl)-pentamethinium Bromide (**10b**)

Synthesis analogous to **10a**, from 0.56 g (3.47 mmol) of **14b** and 0.14 g (1.74 mmol) of dry pyridine, dissolved in 5 mL of dry diethyl ether, and 0.18 g (1.74 mmol) of cyanogen bromide, dissolved in 4 mL of dry diethyl ether; yield 0.18 g (22%) of **10b** as red needles with *m.p.* 228–230 °C (from acetone). – $[\alpha]_D^{23} = -324$ ($c = 0.015$ in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 502 (5.029), 274 (4.048). – IR, mass, ^{1}H and ^{13}C NMR spectrum are identical with that of **10a**.

$C_{27}H_{33}BrN_2 \cdot 2H_2O$	calcd.:	C 64.66	H 7.44	N 5.59
(501.5)	found:	C 64.51	H 7.73	N 5.54.

(+)-(3R)-1-(1,2,3,4-Tetrahydro-3,6-dimethylquinolin-1-yl)-3-(1,2,3,4-tetrahydro-6-methylquinolin-1-yl)trimethinium Perchlorate (**4a**) (Scheme 5)

a) 1,2,3,4-Tetrahydro-6-methylquinoline (**20**) [3, 30, 31]

Synthesis according to ref. [12] by reduction of 6-methylquinoline (Aldrich; purity 98%) with Raney-nickel in KOH/H_2O/CH_3OH.

b) 1,3-Bis(1,2,3,4-tetrahydro-6-methylquinolin-1-yl)-trimethinium Perchlorate (**1**) [3]

To a solution of 4.42 g (30.0 mmol) of **20** in 10 mL of ethanol 2.46 g (15.0 mmol) of 1,1,3,3-tetramethoxypropane was first added, with stirring, and then 3.3 mL of aqueous perchloric acid (conc. 70 cg/g) at 0 °C. Stirring was continued for 1h at 0 °C, and the yellow precipitate formed was filtered off. The volume of the mother liquor was reduced by half in a rotary evaporator, and the solution was allowed to stand for 30 min at 0 °C. The second precipitate formed was filtered off, combined with the first precipitate and both were dried *in vacuo*. Recrystallization from dry ethanol (ca. 800 mL) yields 1.87 g (29%) of **1** as yellow needles with *m.p.* 286–290 °C. – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 396 (4.739), 250 (4.187). – IR (KBr): ν/cm^{-1} = 3107, 3022 (aromatic C–H), 2950

(aliphatic C–H), 1620, 1593, 1497 (aromatic C=C), 1369, 1292, 1099 (ClO_4). – ^{1}H NMR (CD_3SOCD_3): δ/ppm = 1.92–1.96 (m, 4H, 3/3'-H), 2.23 (s, 6H, 12/12'-H), 2.71–2.75 (m, 4H, 4/4'-H), 3.88–3.92 (m, 4H, 2/2'-H), 6.26 (t, ^3J = 11.4 Hz, 1H, 14-H), 7.05 (s, 2H, 5/5'-H), 7.12 (d, ^3J = 8.4 Hz, 2H, 7/7'-H), 7.37 (d, ^3J = 8.4 Hz, 2H, 8/8'-H), 8.74 (d, ^3J = 11.4 Hz, 2H, 13/13'-H). – ^{13}C NMR (CD_3SOCD_3): δ/ppm = 20.2 (C-12/12'), 21.4 (C-4/4'), 25.9 (C-3/3'), 47.1 (C-2/2'), 96.1 (C-14), 117.7 (C-5/5'), 128.1, 130.0, and 130.2 (C-6/6', C-7/7', and C-8/8'), 135.7 and 135.9 (C-9/9' and C-10/10'), 158.7 (C-13/13'). – MS (FD): *m/z* (%) = 332 (32) [M^+ +H–ClO_4], 331 (100) [M^+ –ClO_4].

$C_{23}H_{27}ClN_2O_4$	calcd.:	C 64.11	H 6.31	N 6.50
(430.9)	found:	C 63.90	H 6.14	N 6.30.

c) 3-(1,2,3,4-Tetrahydro-6-methylquinolin-1-yl)prop-2-enal (**21**)

A suspension of 4.12 g (9.56 mmol) of **1** in 200 mL of water in a distillation apparatus, consisting of a 500 mL round-bottom three-necked flask with steam-injection tube, packed column (height 10 cm) with Claisen still-head and water-cooled condenser as well as receiving flask, was subjected to a steam distillation. After the first distillate was obtained, 0.76 g (19.0 mmol) of solid NaOH was added to the hot suspension, whereupon **1** was completely dissolved. The steam distillation was then continued for 30 min. The distillate, containing the tetrahydroquinoline formed, was discarded, and the remaining light-yellow solution was allowed to stand for ca. 12 h at room temperature. The cloudy solution was then extracted three times with 200 mL each of diethyl ether. The combined ether extracts were washed with 200 mL of water; the organic phase was separated and dried with $MgSO_4$. The ether was removed by distillation in a rotary evaporator affording an orange-coloured oil as residue. To this oil 200 mL of petroleum ether (*b.p.* 40–60 °C) was added, and the emulsion was heated under reflux to the boiling point. To the hot emulsion petroleum ether was added until a clear solution was formed. The solution was cooled to room temp. and allowed to stand for 24 h at –17 °C. The yellow precipitate formed was filtered off, washed with petroleum ether and dried *in vacuo* to yield 0.76 g (40%) of **21** as yellow plates with *m.p.* 44–45 °C. – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 323 (4.568), 229 (4.242). – IR (KBr): ν/cm^{-1} = 3009 (aromatic C-H), 2948, 2746 (aliphatic C–H), 1650 (C=O), 1619, 1598, 1580, 1501 (aromatic C=C), 1169, 1156. – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.93–2.01 (tt, appearing as quint, ^3J = 6.2 and 6.4 Hz, 2H, 3-H), 2.24 (s, 3H, 12-H), 2.66 (t, ^3J = 6.2 Hz, 2H, 4-H), 3.47 (t, ^3J = 6.4 Hz, 2H, 2-H), 5.46 (dd, ^3J = 13.0 and ca. 8.0 Hz, 1H, 14-H), 6.89 (s, 1H, 5-H), 6.98 (broad m, 2H, 7- and 8-H), 7.69 (d, ^3J = 13.0 Hz, 1H, 13-H), 9.26 (d, ^3J = 13.0 Hz, 15-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 20.6 (C-12), 22.4 (C-3), 27.2 (C-4), 46.4 (C-2), 105.3 (C-14), 116.1 (C-5), 128.3, 128.8, and 129.7 (C-6, C-7, and C-8), 133.2 (C-10), 137.3 (C-9), 153.0 (C-13), 190.3 (C-15). – MS (EI, 70 eV): *m/z* (%) = 202 (13) [M^+ +H], 201 (100) [M^+], 200 (17) [M^+–H], 185 (13) [M^+–H–CH_3].

$C_{13}H_{15}NO$	calcd.:	C 77.58	H 7.51	N 6.96
(201.3)	found:	C 77.58	H 7.42	N 6.77.

d) (+)-(3R)-Perchlorate **4a**

A solution of 58.0 mg (0.29 mmol) of propenal **21** and 76.0 mg (0.29 mmol) of (–)-(3*R*)-**18a** in 5 mL of dry ethanol was stirred for 30 min at 50 °C. After cooling to room temp., the precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*, to give 0.12 g (93%) of **4a** as yellow crystals with *m.p.* 238–240 °C. – $[\alpha]_D^{28}$ = +48 (*c* = 0.058 in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 397 (4.788), 288 (3.706), 251 (4.239). – IR (KBr): ν/cm^{-1} = 3098, 3022 (aromatic C–H), 2935 (aliphatic C–H), 1619, 1594, 1583, 1500 (aromatic C=C), 1098 (ClO_4). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.08 (d, ^3J = 6.6 Hz, 3H, 11-H), 1.96–2.02 (m, 3H, 3/3'-H), 2.19 (s, 6H, 12/12'-H), 2.27–2.33 (m, 1H, 4-H_A), 2.58–2.68 (m, 3H, 4'-H and 2-H_A), 3.20–3.29 (m, 1H, 4-H_B), 3.83–3.88 (t, ^3J = 6.2 Hz, 2H, 2'-H), 3.94–4.00 (m, 1H, 2-H_B), 6.01 (t, ^3J = 11.7 Hz, 1H, 14-H), 6.83 (s, 2H, 5/5'-H), 7.01 (d, ^3J = 8.4 Hz, 2H, 7/7'-H), 7.43–7.48 (m, 2H, 8/8'-H), 8.46 (d, ^3J = 11.7 Hz, 2H, 13/13'-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 18.4 (C-11), 20.7 (C-12), 22.0 (C-12'), 26.7 (C-3), 28.2 (C-3'), 34.9 (C-4/4'), 48.1 (C-2'). 53.9 (C-2), 95.7 (C-14), 118.2 and 118.5 (C-5 and C-5'), 129.1, 129.3, 129.7, and 129.9 (C-6/6', C-7/7', and C-8/8'), 135.1 (C-10/10'), 136.8 and 136.9 (C-9 and C-9'), 157.7 and 157.9 (C-13 and C-13'). – MS (FD): *m/z* (%) = 360 (5) [M^+–$HClO_4$ + CH_3], 359 (26) [M^+–$HClO_4$ + CH_2], 346 (40) [M^+–ClO_4^-], 345 (100) [M^+–$HClO_4$].

$C_{24}H_{29}ClN_2O_4$	calcd.:	C 64.78	H 6.57	N 6.30
(445.0)	found:	C 64.75	H 6.76	N 6.31.

(+)-(3R)-1-(1,2,3,4-Tetrahydro-3,6-dimethylquinolin-1-yl)-5-(1,2,3,4-tetrahydro-6-methylquinolin-1-yl)pentamethinium Perchlorate (**9a**) [3, 8, 28] (Scheme 6)

a) 1,5-Bis(1,2,3,4-tetrahydro-6-methylquinolin-1-yl)pentamethinium Bromide (**6**)

To a solution of 3.00 g (20.39 mmol) of tetrahydroquinoline **20** and 0.76 g (9.61 mmol) of dry pyridine in 10 mL of dry ethanol was added with stirring at room temp. a solution of 1.08 g (10.20 mmol) of cyanogen bromide in 10 mL of dry diethyl ether. Stirring was continued for 1h, the red precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*. The crude product (1.20 g) was recrystallized from dry acetone (ca. 1000 mL), to yield 1.10 g (25%) of **6** as red needles with *m.p.* 230 °C. – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 500 (5.016), 274 (4.203). – IR (KBr). ν/cm^{-1} = 3422 (O-H), 3004 (aromatic C–H), 2935 (aliphatic C–H), 1615, 1587, 1569, 1525, 1495, 1459 (aromatic C=C), 1350, 1308, 1215, 1192, 1160. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.06–2.08 (m, 4H, 3/3'-H), 2.27 (s, 6H, 12/12'-H), 2.72–2.76 (m, 4H, 4/4'-H), 3.83–3.87 (m, 4H, 2/2'-H), 6.43 (dd, appearing as t, 2H, 14/14'-H), 6.92 (s, 2H, 5/5'-H), 7.11 (m, 2H, 7/7'-H), 7.51 (d, ^3J = 8.4 Hz, 2H, 8/8'-H), 8.60 (d, ^3J = 11.6 Hz, 2H, 13/13'-H), 8.74 (m, 1H, 15-H). – ^{13}C NMR (CD_3SOCD_3): δ/ppm = 20.2 (C-12/12'), 21.5 (C-4/4'), 26.0 (C-3/3'), 47.0 (C-2/2'), 108.6 (C-14/14'), 117.8 (C-5/5'), 128.1, 129.7, and 130.2 (C-6/6', C-7/7', and C-8/8'), 135.3 and 135.6 (C-9/9' and C-10/10'), 155.0 (C-13/13'), 165.3 (C-15). – MS (FD): *m/z* (%) = 358 (29) [M^+–Br^-], 357 (100) [M^+–HBr].

$C_{25}H_{29}BrN_2 \cdot 3H_2O$	calcd.:	C 61.10	H 7.18	N 5.70
(491.4)	found:	C 61.69	H 6.74	N 5.86.

b) 5-(1,2,3,4-Tetrahydro-6-methylquinolin-1-yl)penta-2,4-dienal (**22**)

A suspension of 0.18 g (4.40 mmol) of magnesium oxide in a solution of 1.00 g (2.29 mmol) of **6** in hot (ca. 60 °C) ethanol

in a distillation apparatus, consisting of a 250 mL round-bottom three-necked flask with steam injection tube, packed column (height ca. 10 cm) with Claisen still-head and water-cooled condenser as well as receiving flask, was subjected to steam distillation for ca. 2 h. The distillate, containing the tetrahydroquinoline formed, was discarded. The remaining yellowish solution was cooled to room temp. and then allowed to stand for 24 h at 5 °C. The precipitate formed was filtered off and dried *in vacuo* with P_4O_{10}. This solid was extracted with 100 mL of benzene, the extract was separated, and the benzene was distilled off in a rotary evaporator, to give a brown oil. After the addition of 5mL petroleum ether (*b.p.* 40–60 °C) to this oil with stirring, it crystallizes. The crystals were filtered off and dried *in vacuo*. Recrystallization from ca. 400 mL of petroleum ether (*b.p.* 40–60 °C) yields 0.36 g (69%) of **22** as yellow crystals with *m.p.* 119 °C. – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 394 (4.768), 307 (3.535), 275 (4.290), 267 (4.265), 256 (4.242). – IR (KBr): ν/cm^{-1} = 3450, 3041, 3022 (aromatic C–H), 2957, 2937, 2809 (aliphatic C–H), 1650 (C=O), 1589, 1573, 1499, 1470 (aromatic C=C), 1335, 1330. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.00–2.08 (tt, appearing as quint, ^3J = 6.2 and 6.3 Hz, 2H, 3-H); 2.31 (s, 3H, 12-H), 2.72 (t, ^3J = 6.2 Hz, 2H, 4-H), 3.58 (t, ^3J = 6.3 Hz, 2H, 2-H), 5.73 (dd, ^3J, = 12.7 and 11.5 Hz, 1H, 14-H), 6.01 (dd, ^3J = 14.5 Hz and 8.3 Hz, 1H, 16-H), 6.94–7.05 (m, 3H, 5-, 7-, and 8-H), 7.25 (dd, ^3J = 11.5 and 14.5 Hz, 1H, 15-H), 9.42 (d, ^3J = 8.3 Hz, 1H, 17-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 20.5 (C-12), 22.4 (C-3), 27.2 (C-4), 46.0 (C-2), 101.6 (C-14), 115.4 (C-5), 123.3 (C-15), 128.0, 128.1, and 129.6 (C-6, C-7, and C-8), 132.2 (C-10), 137.5 (C-9), 144.3 (C-16), 155.3 (C-13), 192.7 (C-17). – MS (EI, 70 eV): *m/z* (%) = 227 (18) [M$^+$], 81 (100) [M$^+$–$C_{11}H_{14}N$ +H].

$C_{15}H_{17}NO$	calcd.:	C 79.26	H 7.54	N 6.16
(227.3)	found:	C 79.31	H 7.55	N 6.14.

c) (+)-(3R)-Perchlorate **9a**

To a solution of 0.11 g (0.50 mmol) of pentadienal **22** in 3 mL of dry ethanol a solution of 0.13 g (0.50 mmol) of (–)-(3*R*)-**18a** in 5 mL of dry ethanol was added at room temp. with stirring. Then, the reaction mixture was stirred for 30 min at 50 °C. After cooling to room temp., the precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*, to yield 0.22 g (94%) of **9a** as red needles with *m.p.* 219 °C. – $[\alpha]_D^{28}$ = +153 (*c* = 0.104 in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 501 (5.018), 274 (4.175), 235 (4.556). – IR (KBr): ν/cm^{-1} = 3423 (O-H), 3004 (aromatic C–H), 2923 (aromatic C-H), 1614, 1588, 1569, 1528, 1495 (aromatic C=C), 1351, 1218, 1195, 1157, 1092 (ClO_4). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.08 (d, ^3J = 6.6 Hz, 3H, 11-H), 1.97–2.08 (m, 3H, 3/3'-H), 2.21 and 2.22 (two s, 6H, 12/12'-H), 2.28–2.37 (m, 1H, 4-H_A), 2.63–2.67 (m, 3H, 4'-H and 2-H_A), 3.11–3.19 (m, 1H, 4-H_B), 3.71–3.76 (m, 2H, 2'-H), 3.82–3.88 (m, 1H, 2-H_B), 6.32 (dd, appearing as t, 2H, 14/14'-H), 6.86 (s, 2H, 5/5'-H), 7.02 (d, ^3J = 8.2 Hz, 2H, 7/7'-H), 7.24–7.29 (m, 2H, 8/8'-H), 8.11–8.23 (t, superimposed by d, 3H, 13/13'-H and 15-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 18.4 (C-11), 20.6 (C-12), 21.9 (C-12'), 26.7 (C-3), 28.0 (C-3'), 34.9 (C-4/4'), 47.5 (C-2), 53.4 (C-2'), 108.7 (C-14/14'), 117.4 and 117.7 (C-5 and C-5'), 128.8, 129.0, 129.7, and 129.9 (C-6/6', C-7/7', and C-8/8'), 135.5 (C-10/10'), 136.2 (C-9/9'), 154.9 and 155.1 (C-13 and C-13'), 166.8 (C-15). – MS (FD): *m/z* (%) = 371 (5) [M$^+$–$HClO_4$], 370 (35) [M$^+$–H–$HClO_4$], 369 (100) [M$^+$–2H–$HClO_4$].

$C_{26}H_{31}ClN_2O_4 \cdot H_2O$	calcd.:	C 63.68	H 6.80	N 5.72
(489.0)	found:	C 64.20	H 6.65	N 5.93.

(+)-(2S,3'R)-1-(1,2,3,4-Tetrahydro-2,6-dimethylquinolin-1-yl)-5-(1,2,3,4-tetrahydro-3,6-dimethylquinolin-1-yl)pentamethinium Perchlorate (**11a**) [3] (Scheme 7)

To a solution of 0.10 g (0.42 mmol) of (+)-(2*S*)-pentadienal **23a** [12] in 3 mL of dry ethanol was added at room temp. with stirring a solution of 0.11 g (0.42 mmol) of (–)-(3*R*)-perchlorate **18a** in 2 mL of dry ethanol. Then, the reaction mixture was heated for 30 min under reflux. After cooling to room temp., and subsequent addition of 5 mL of 2-propanol, the precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*, to give 0.19 g (93%) of **11a** as red needles with *m.p.* 149–151 °C. – $[\alpha]_D^{18}$ = +1458 (*c* = 0.024 in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 497 (4.996), 274 (4.040). – IR (KBr): ν/cm^{-1} = 3077 (aromatic C–H), 2929 (aliphatic C–H), 1614, 1588, 1570, 1528, 1495 (aromatic C=C), 1195, 1161, 1093 (ClO_4). – ^{1}H NMR ($CDCl_3$): δ/ppm = 1.05 (d, ^3J = 6.6 Hz, 3H, 11'-H), 1.22 (d, ^3J = 6.6 Hz, 3H, 11-H), 1.75–1.82 (m, 1H, 3-H_A), 2.02–2.11 (m, 2H, 3-H_B and 3'-H), 2.20 (s, 6H, 12/12'-H), 2.29–2.37 (m, 1H, 4'-H_A), 2.55–2.81 (m, 3H, 2'-H_A and 4-H), 3.13–3.21 (m, 1H, 4'-H_B), 3.81–3.87 (m, 1H, 2'-H_B), 4.47–4.49 (m, 1H, 2-H), 6.25–6.40 (m, 2H, 14/14'-H), 6.85 (d, ^3J = 8.0 Hz, 2H, 7/7'-H), 6.99 and 7.02 (two s, 2H, 5- and 5'-H), 7.19–7.27 (m, 2H, 8/8'-H), 8.08–8.19 (m, 3H, 13/13'-H and 15-H. – ^{13}C NMR ($CDCl_3$): δ/ppm = 17.2 (C-11), 18.6 (C-11'), 20.8 (C-12/12'), 23.3 (C-3), 28.2 (C-3'), 35.0 (C-4/4'), 51.8 (C-2'), 53.6 (C-2), 108.4 and 108.8 (C-14 and C-14'), 117.6 and 118.9 (C-5 and C-5'), 128.9, 129.1, 129.2, 129.9, and 130.1 (C-6/6', C-7/7', and C-8/8'), 135.4 (C-10/10'), 136.3 and 136.8 (C-9 and C-9'), 154.8 and 155.1 (C-13 and C-13'), 167.0 (C-15). – MS (FD): *m/z* (%) = 386 (16) [M$^+$–ClO_4^-], 385 (100) [M$^+$–$HClO_4$].

$C_{27}H_{33}ClN_2O_4$	calcd.:	C 66.86	H 6.86	N 5.77
(485.0)	found:	C 66.53	H 7.17	N 5.56.

(+)-(2S)-1-(1,2,3,4-Tetrahydro-2,6-dimethylquinolin-1-yl)-3-(1,2,3,4-tetrahydro-6-methylquinolin-1-yl)trimethinium Perchlorate (**2a**) [3, 12] (Scheme 8)

To a solution of 0.10 g (0.50 mmol) of propenal **21** in 5 mL of dry ethanol a solution of 0.13 g (0.50 mmol) of (–)-(2*S*)-perchlorate **24a** [12] in 2 mL of dry ethanol was added at room temp. with stirring. The reaction mixture was heated for 30 min under reflux. After cooling to room temp., the solution was allowed to stand for 24 h at ca. –17 °C. The precipitate formed was filtered off and dried *in vacuo*. The product was purified by hot extraction in a simple solid/liquid extractor with 5 mL of dry ethanol. The extraction solution was allowed to stand for 24 h at –17 °C, the precipitate formed was filtered off, washed with diethyl ether, and dried *in vacuo*, to yield 0.12 g (54%) of **2a** as yellow needles with *m.p.* 263 °C. – $[\alpha]_D^{19}$ = +245 (*c* = 0.047 in ethanol). – UV/Vis (ethanol): λ_{max}/nm (lg ε) = 394 (4.740), 250 (4.180). – IR (KBr): ν/cm^{-1} = 3097 (aromatic C–H), 2944 (aliphatic C–H), 1618, 1576, 1503 (aromatic C=C), 1291, 1083 (ClO_4). – ^{1}H NMR [$CDCl_3$; mixture of (*E,E,E,E*) and (*E,E,Z,E*) isomer; the signals of the

minor (*E,E,Z,E*) isomer with (*Z*) configuration at C-14'/C-15' are marked by a single quotation mark if possible]: δ/ppm = 1.23 (d, ^3J = 6.5 Hz, 3H, 11/11'-H), 1.76–1.83 (m, 1H, 3- or 3'-H_A), 1.95–2.04 (m, 3H, 17/17'-H and 3- or 3'-H_B), 2.10–2.21 (two, s, 3H each, 12/12'- and 26/26'-H), 2.29–2.31 (m, 1H, 3'- or 3-H_A), 2.60–2.65 (m, 4H, 19/19'- and 4/4'-H), 2.72–2.80 (m, 1H, 3'- or 3-H_B), 3.82–3.86 (m, 2H, 17/17'-H), 3.90–3.97 (m, 1H, 2- or 2'-H), 4.66–4.68 (m, 1H, 2'- or 2-H), 5.94–6.12 (m, 1H, 14/14'-H), 6.85–6.88 (m, 2H, 5/5'- and 20/20'-H), 6.99–7.19 (m, 2H, 7/7'- and 22/22'-H), 7.39–7.44 (m, 2H, 8/8'- and 23/23'-H), 8.38–8.44 (m, 2H, 13/13'- and 15/15'-H). – ^{13}C NMR ($CDCl_3$): the spectrum contains 28 signals the assignment of which was not possible. However, at δ/ppm = 95.2 and 95.4 two signals for C-14/14' and between δ/ppm = 157.5–158.0 four signals for C-13/13' and C-15/15' can be seen, which is in accordance with the existence of two diastereomers of **2a** in solution. – MS (FD): *m/z* (%) = 359 (6) [M^+–$HClO_4$ + CH_2], 347 (3) [M^+–ClO_4^- + H], 346 (33) [M^+ –ClO_4^-], 345 (100) [M^+–$HClO_4$].

$C_{24}H_{29}ClN_2O_4$	calcd.:	C 64.78	H 6.57	N 6.30
(445.0)	found:	C 64.40	H 6.63	N 6.53.

Crystal Structure Determination of 17a [27]

Colorless plates, crystallized from a hot saturated solution of **17a** in ethanol by cooling from 78 to 0 °C at low rate (ca. 10 °C/h), leaving the suspension for 3 d at 5 °C, decantation of the liquid phase, and drying of the remaining crystals at room temperature. – $C_{17}H_{18}BrNO_2S$, M_r = 380.3 g/mol; crystal size: 0.3 × 0.1 × 0.1 mm; monoclinic space group $P2_1$; Z = 4, a = 1038.7(1), b = 1079.2(1), c = 1562.8(1) pm; α = 90 °, β = 106.176(8)°, χ = 90 °; V = 1682.4(2)·10^{-30} m^3; d_{calcd} = 1.501 Mg/m^3; θ range 2.11–25.85°, reflections collected 13721, independent reflections 6033 (R_{int} = 0.0914), observed reflections 3329 [$I > 2\sigma(I)$], reflections used for refinement 6033, index ranges $-12 \le h \le 12$, $-13 \le k \le 13$, $-19 \le l \le 19$, phi range/increment 0-208/1°; program system used: SHELXS-96, SHELXL-96, SHELXTL, and STOE IPDS software. Empirical absorption correction, direct methods, full-matrix refinement at F^2 with all independent reflections, weighting scheme $w^{-1} = \sigma^2(F_0^2) + (0.0658\,P)^2 + 0.0000\,P$, with $P = (F_0^2 + 2\,F_c^2)/3$; hydrogen atoms: riding; non-hydrogen atoms were refined anisotropically; R index (all data): $wR2$ (based on F^2) = 0.1351, R index conventional [$I > 2\sigma(I)$] : $R1$ (based on F) = 0.0538; extremes of the final difference Fourier synthesis 0.52/–0.58 e ·$Å^{-3}$; "Flack parameter" (absolute structure): 0.000(14). – In the asymmetric unit of **17a** there are two molecules with different conformation of the tetrahydropyridine ring but with the same absolute (*R*)-configuration at C-3.

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