Azinyl Sulfides, Part LXIII[+]

1-Alkyl-4-(arylamino)quinolinium-3-thiolates and 7-Alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Salts

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Keywords: *N*-Alkylquinolinium salts / Fused 1,4-benzothiazines / Quinolinium thiolates / Nucleophilic aromatic substitutions

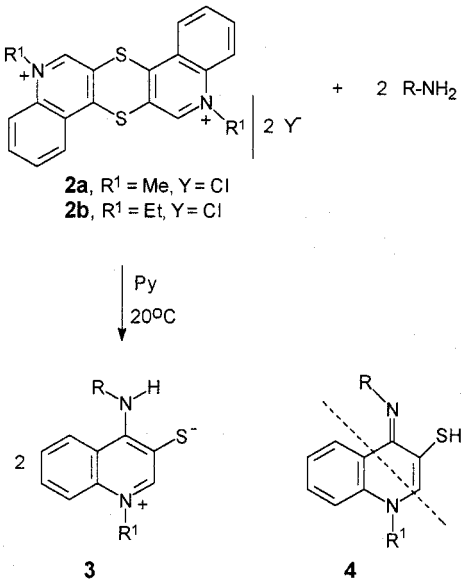
Reactions of 5,12-dialkylthioquinanthrenediinium bis-salts **2** with anilines in pyridine solution performed under oxygen-free atmosphere at room temperature yielded 1-alkyl-4-(arylamino)quinolinium-3-thiolates **3e**–**3i**. Similar treatment of **2** and anilines or of **3** at 20–70 °C in the presence of air led to 7-alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium salts **7**. The NMR assignment of quinolinium thiolate **3** has been supported by a ^{15}N NMR analysis. The structure of **7** has been established by both X-ray analysis and chemical transformations.

Introduction

4-Aminoquinolines, including 4-arylamino derivatives, exhibit a wide range of biological activities.[1,2] With this in mind, we have previously studied the amination of thioquinanthrene **1** (i.e. 1,4-dithiino[2,3-*c*:5,6-*c*′]diquinoline) using amines, amine salts, and sodium phenylamide.[3] No reactions were observed with either aliphatic or aromatic amines, or with aliphatic amine salts. In the case of the reaction of **1** with aromatic amine salts (180 °C), the formation of 12*H*-quino[3,4-*b*]-1,4-benzothiazines **11** and 4-arylaminoquinolines was observed, these being disproportionation products of the hypothetical initially formed 4-arylamino-3-quinolinethiols.[3] On the other hand, 5,12-dialkylthioquinanthrenediinium bis-salts **2** were found to react smoothly with primary alkyl amines, even within 2 hours at room temperature, to form 1-alkyl-4-(alkylamino)quinolinium-3-thiolates **3a**–**d** instead of the expected 1-alkyl-4-alkylimino-1,4-dihydro-3-quinolinethiols **4**.[4] The formation of the 4-aminoquinolinium species **3** may be rationalized in terms of the high basicity of 4-iminoquinolines,[5] making them capable of proton abstraction from thiols **4**. In order to evaluate this hypothesis and in an effort to reduce the donating properties of the 4-imino exocyclic nitrogen atom, we replaced the electron-donating *N*-methyl(alkyl) group at the exocyclic nitrogen atom with an electron-withdrawing *N*-phenyl group. This led to the present study on the reactions of 5,12-dialkylthioquinanthrenediinium bis-salts **2** with anilines.

Results and Discussion

As for alkylamines, the reactions of 5,12-dialkylthioquinanthrenediinium bis-salts **2** with primary arylamines were



3 **4**

Scheme 1

Table 1. 1-Alkyl-4-(alkylamino)- and 1-alkyl-4-(arylamino)quinolinium-3-thiolates **3**

R^1	R	Time	Product	Yield [%]
Me	Me, Et, *i*Bu	2 h	**3a**–**c**	86/80/70[4]
Et	Me	2 h	**3d**	80[4]
Me	Ph	7 d	**3e**	65
Me	4-$CH_3C_6H_4$	7 d	**3f**	70
Me	3-$CH_3C_6H_4$	7 d	**3g**	65
Me	4-ClC_6H_4	7 d	**3h**	63
Et	Ph	7 d	**3i**	58
Me	4-$NO_2C_6H_4$	10 d	–	–

[+] Part LXII: L. Skrzypek, *Heterocycles* **1999**, *51*, 2111–2118.

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  1434–193X/00/0816–2947 $ 17.50+.50/0

carried out in pyridine solution at room temperature, although the complete consumption of bis-salts **2** required much longer reaction times. Under the exclusion of air (see below), the reaction of **2** with arylamines (aniline, *m*- and *p*-toluidine, *p*-chloroaniline) led to 1-alkyl-4-(arylamino)-quinolinium-3-thiolates **3e−3i** (Scheme 1, Table 1). In the case of the reactions with *m*-chloroaniline and *o*-toluidine, the amines were consumed to a similar extent, but the respective thiolates **3** could not be isolated in pure form. No reaction was observed between **2** and *p*-nitroaniline.

The structures of 1-alkyl-4-(alkylamino)quinolinium-3-thiolates **3a−d** have previously been established on the basis of their ^{1}H NMR spectra (in chloroform solutions) since the signals of the *NH*-methyl and *NH*-methylene protons show splitting by an adjacent proton ($^3J_{H,H}$ = 6 Hz), which confirms that the alkylamino substituent is attached at the 4-position.[4] Also, ^{1}H-^{1}H NOEs are observed between the *NH*-methyl or *NH*-methylene protons and 5-H, and between the N^1-methyl or N^1-methylene protons and 2-H and 8-H. Furthermore, the presence of the exocyclic −NH− moiety in **3a** could also be proved by ^{15}N NMR spectroscopy as the ^{15}N signal of the exocyclic nitrogen atom shows a splitting with $^1J_{N-H}$ = 80 Hz.[6] Finally, an X-ray analysis of the isobutyl derivative **3c** has corroborated the NMR-based conclusions.[4]

The ^{1}H NMR spectra of 1-alkyl-4-(arylamino)quinolinium-3-thiolates **3e−3i** also reveal the presence of an N−H moiety (δ = 10.02−11.38). Thus, the structures of the reaction products derived from **2** and arylamines can also be represented by formula **3**. As the signals of the aromatic protons of **3e−3i** are overlapping, their complete ^{1}H NMR assignments were deduced with the help of two-dimensional ^{1}H-^{15}N NMR spectral experiments on **3f**. ^{1}H-^{15}N GHMQC spectra of **3f** in $CDCl_3$ are presented in Figure 1. They show two-bond ^{1}H-^{15}N correlations between the endocyclic nitrogen (δ_N = − 235.13) and both 2-H (δ_H = 8.56) and the CH_3N protons (δ_H = 4.08), as well as a three-bond correlation between the endocyclic nitrogen (δ_N = −235.13) and 8-H (δ_H = 7.58−7.68).

A one-bond correlation between the exocyclic nitrogen (δ_N = −254.01) and the N−H proton (δ_H = 10.38) ($^1J_{N-H}$ = 87.1 Hz) as well as a three-bond correlation with the *ortho* protons of the phenyl group (δ_H = 7.15−7.23) were also detected (see Figure 1).

The reactivity of the thiolate function in **3e** and **3i** was verified by alkylation with dimethyl sulfate or methyl iodide, which led to the previously reported[7] 4-arylaminoquinolinium salts **5a**, **5b**. Salts **5** were then converted to the 4-aryliminoquinolines **6** (see Scheme 2).

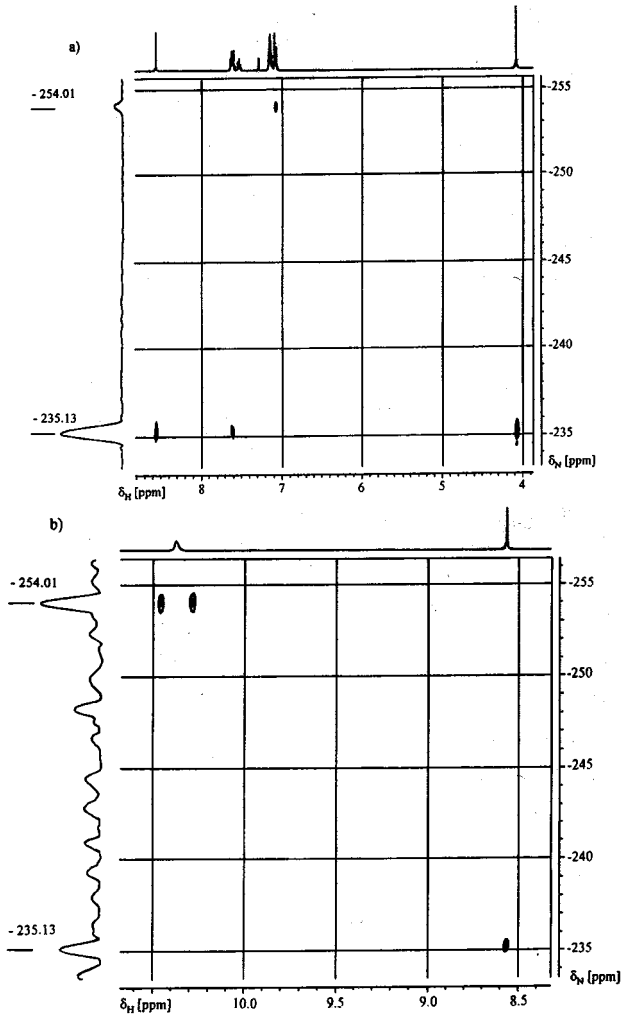


Figure 1. Two-dimensional ^{1}H,^{15}N NMR (GHMQC) spectra of 1-methyl-4-(4-methylphenylamino)quinolinium-3-thiolate **3f**; (a) mixing time 0.08 s; (b) mixing time 0.02 s

7-Alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Salts 7

In the course of this study, high oxidation susceptibility of the 1-alkyl-4-(arylamino)quinolinium-3-thiolates **3e−i** was observed. Thus, in order to prepare **3e−i** from **2**, the reaction mixtures have to be protected from air. In the presence of acids (e.g. HCl) or acid donors (e.g. tertiary amine hydrochlorides), 4-(arylamino)quinolinium-3-thiolates **3e−i** were found to undergo oxidative transformation by atmospheric oxygen to red-colored products **7** having the empirical formulae $R^1-C_9H_5-NS-NHC_6H_3ZCl$ (after recrystallization from ethanol). It was found that the same products could be prepared in good yield directly from **2a** or **2b** and $ZC_6H_4-NH_2$ when the reaction mixture was not protected from air. The reactions of *m*-substituted anilines (Z = 3-CH_3 or Z = 3-Cl) with **2a** led to mixtures containing both possible isomeric 2- and 4-(CH_3 or Cl) substituted salts **7d** and **7e** or **7g** and **7h** in ratios of ca. 11:9 (as concluded from ^{1}H NMR spectra).

Fortunately, the product of the reaction of 5,12-dimethylthioquinanthrenediinium bis(chloride) **2a** with aniline (pyridine, 70 °C, 2 h, air atmosphere) deposited directly from the reaction mixture as a 1:4 hydrate of a semi-pyridine complex with 7-methyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium chloride **7a** in the form of crystals suitable for X-ray analysis (Figure 2, Table 2).

The atom arrangement presented in Figure 2 does not permit a distinction between formulae **7** and **8**. However,

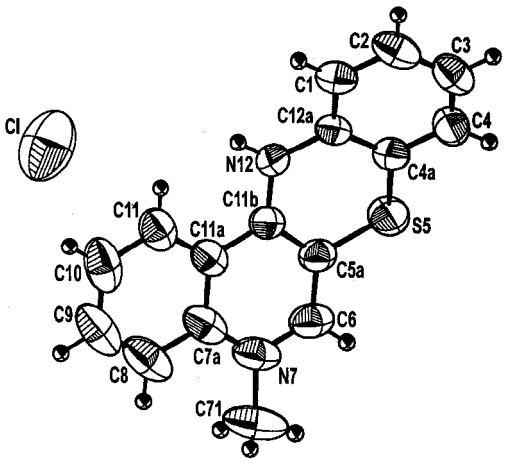
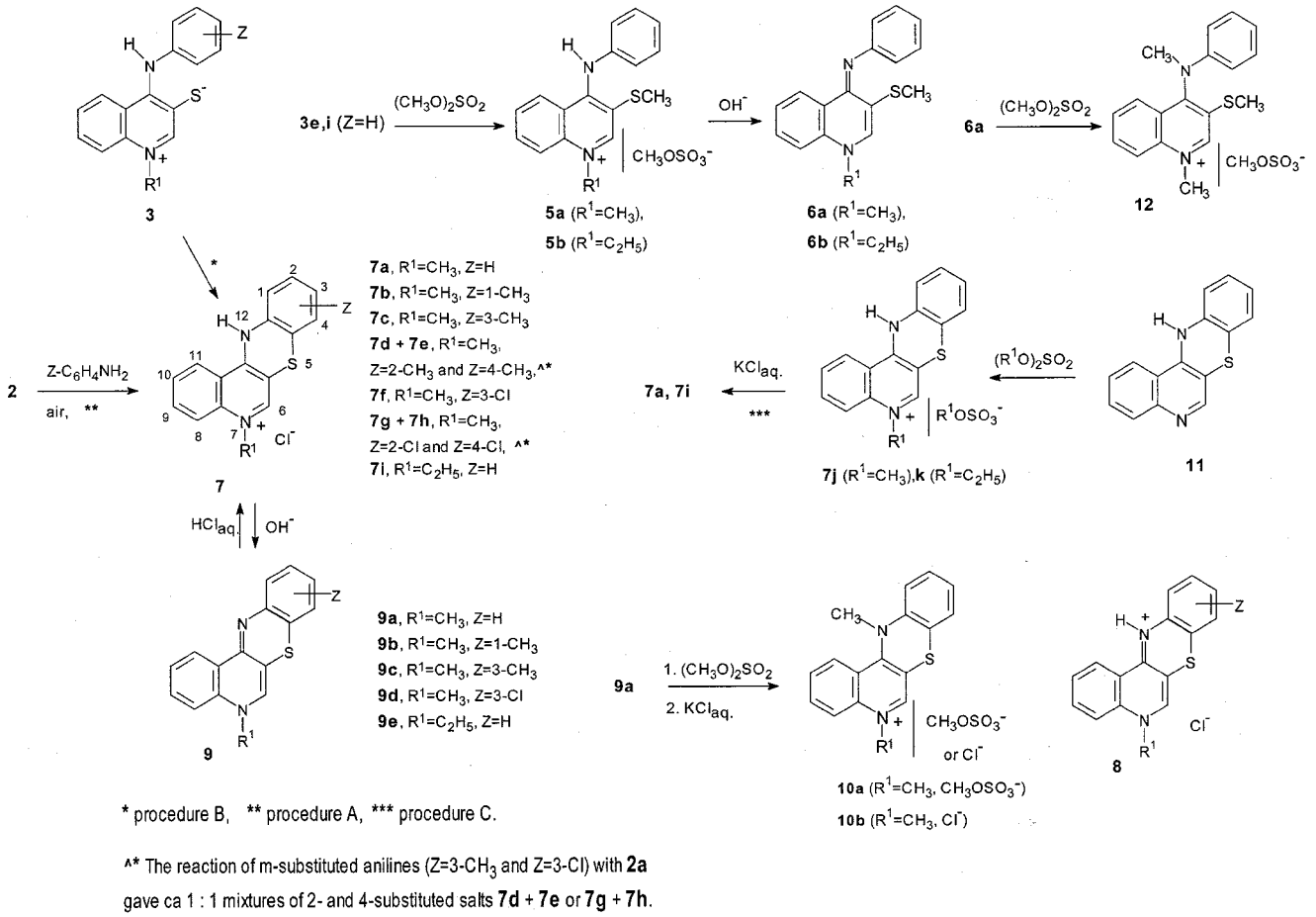


Figure 2. ORTEP representation of **7a** showing atom labelling scheme

Table 2. Selected bond lengths [Å] and angles [deg.] in **7a** · 1/2 Py · 1/4 H_2O

Bond lengths [Å]			
C4a−S5	1.764(2)	N7−C7a	1.363(4)
C4a−C12a	1.399(3)	N7−C71	1.492(5)
S5−C5a	1.758(2)	C7a−C11a	1.435(4)
C5a−C6	1.376(3)	C11a−C11b	1.436(3)
C5a−C11b	1397(3)	C11b−N12	1.357(3)
C6−N7	1.343(3)	N12−C12a	1.415(3)
Bond angles [°]			
S5−C4a−C12a	120.5(2)	C6−N7−C7a	121.1(2)
C4a−S5−C5a	98.8(2)	N7−C7a−C11a	119.9(3)
S5−C5a−C11b	121.8(2)	C7a−C11a−C11b	118.3(2)
S5−C5a−C6	117.2(2)	C5a−C11b−C11a	118.0(2)
C6−C5a−C11b	120.7(2)	C5a−C11b−N12	121.2(2)
C5a−C6−N7	121.9(2)	C11b−N12−C12a	123.3(2)
C6−N7−C71	117.0(3)	C4a−C12a−N12	121.1(2)



Scheme 2

the N7−C71 [1.492(3) Å] and C11b−N12 [1.357(3) Å] bond lengths and the C6−N7−C7a bond angle [121.1(2)°] are typical of those reported for 1-methyl-4-aminopyridinium salts[8] and differ from the corresponding structural parameters of 14-methyl-1,4-thiazino[2,3-*c*;6,5-*c*′]diquinoline.[9] Thus, the structure of the product of the reaction of **2a** with aniline should be depicted as the quinolinium-type salt **7a** rather than as the 1,4-thiazinium derivative **8** (see Scheme 2). The salts **7** could also be obtained by quaternization of quinobenzothiazines **11** with dialkyl sulfates (R^1 = CH_3, C_2H_5) followed by anion exchange. Taking into account the longer synthesis of **11**, this route is, however, less effective than those starting from **2** or **3** (Table 3).

The salts **7** were dehydrochlorinated to give the iminoquinoline-type product **9**. The starting hypothesis regarding the formation of betaines **3** instead of imines **4** seems to be

Table 3. Preparation of 7-alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium salts **7** from bis-salts **2**, from thiolates **3**, and from quinobenzothiazine **11**

Entry	Substrates	Procedure	Product(s)	Yield [%]
1	**2a**, aniline	A	**7a**	65
2	**2a**, *o*-toluidine	A	**7b**	66
3	**2a**, *p*-toluidine	A	**7c**	70
4	**2a**, *m*-toluidine	A	**7d** + **7e**	68
5	**2a**, *p*-chloroaniline	A	**7f**	63
6	**2a**, *m*-chloroaniline	A	**7g** + **7h**	54
5	**2b**, aniline	A	**7i**	58
6	**3e**	B	**7a**	75
7	**3f**	B	**7c**	72
8	**3g**	B	**7d** + **7e**	69
9	**3h**	B	**7f**	71
10	**11** via **7j**	C	**7a**	78
11	**11** via **7k**	C	**7i**	78

borne out by the ease of the reactions of iminoquinolines **6** and **9** with hydrochloric acid or with dialkyl sulfates, which lead to the 4-aminoquinolinium-type products **12** and **10**, respectively.

Experimental Section

General Remarks: Melting points are uncorrected. − ^{1}H NMR spectra (at 300 MHz) were recorded on a Varian VXR 300 spectrometer. Proton chemical shifts are reported relative to TMS or DSS (δ_H = 0.0) as internal standards. The protons of compounds **3a**, **5a**, **6a**, **7a**, and **9a** were assigned on the basis of NOE experiments. ^{14}N and ^{15}N NMR spectra were recorded on a Bruker AM 500 spectrometer at 36.142 MHz and 50.698 MHz, respectively. Nitrogen NMR chemical shifts were measured with respect to 0.1 M nitromethane in acetone (δ_N = 0.0) as an external standard. − EI mass spectra were determined on an LKB GC MS 2091 spectrometer at 15 eV and 70 eV at temperatures of 80−100 °C. − TLC analyses were performed on alumina 60 F neutral plates (type E, Merck) using mixtures of chloroform/ethanol (15:1 or 10:1, *v*/*v*) as eluents.

5,12-Dialkylthioquinanthrenediinium bis(chlorides) **2a** (R^1 = CH_3) and **2b** (R^1 = C_2H_5) were prepared by quaternization of thioquinanthrene **1** with dialkyl sulfates, followed by anion exchange.[10]

1-Alkyl-4-(arylamino)quinolinium-3-thiolates 3e−i. − Typical Procedure: Nitrogen was passed through a suspension of 1 mmol of the bis-salt **2** in dry pyridine (10 mL) at room temp. for 15 min. Aniline (2.5 mmol) was then added and nitrogen was passed for a further 15 min. The mixture was then stirred under nitrogen at room temperature for 7 days. Thereafter, the solid deposited was filtered off and washed with diethyl ether to give a first crop of the thiolate **3**. The combined filtrate and washings were concentrated to dryness in vacuo to give a crude product, which was separated by column chromatography on alumina eluting with chloroform/ethanol, 10:1, *v*/*v*, to afford a second crop of **3**. For analytical purposes, thiolate **3** was recrystallized from ethanol.

1-Methyl-4-(phenylamino)quinolinium-3-thiolate (3e): Prepared from bis(chloride) **2a** and aniline. Yield: 0.35 g (65%); m.p. 262−265 °C . − ^{1}H NMR ([D$_6$]DMSO): δ = 4.16 (s, 3 H, NCH_3), 6.92−7.20 (m, 2 H, H_{arom}), 7.26−7.38 (m, 3 H, H_{arom}), 7.78−7.86 (m, 1 H, 6-H), 8.10−8.24 (m, 2 H, 7-H, 8-H), 8.72−8.82 (m, 1 H, 5-H), 8.99 (s, 1 H, 2-H), 11.25 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 264 (100) [M$^+$ − 2 H]. − $C_{16}H_{14}N_2S$ (266.36): calcd. C 72.16, H 5.30, N 10.53, S 12.02; found C 72.38, H 5.20, N 10.11, S 12.20.

1-Methyl-4-(4-methylphenylamino)quinolinium-3-thiolate (3f): Prepared from bis(chloride) **2a** and *p*-toluidine. Yield: 0.39 g (70%); m.p. 202−206 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.31 (s, 3 H, CH_3), 4.18 (s, 3 H, NCH_3), 6.92−7.09 (m, 2 H, H_{arom}), 7.12−7.24 (m, 2 H, H_{arom}), 7.28−7.38 (m, 1 H, 6-H), 7.49−7.58 (m, 1 H, 8-H), 7.59−7.70 (m, 1 H, 7-H), 7.82−7.90 (m, 1 H, 5-H), 8.76 (s, 1 H, 2-H), 10.02 (s, 1 H, NH). − ^{15}N NMR (GHMQC) ($CDCl_3$): δ = −235.13 (s, NCH_3), −254.01 (d, J_{N-H} = 87.1 Hz, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M$^+$ − 2 H]. − $C_{17}H_{16}N_2S$ (280.39): calcd. C 72.82, H 5.75, N 9.99, S 11.43; found C 72.75, H 5.68, N 10.11, S 11.30.

1-Methyl-4-(3-methylphenylamino)quinolinium-3-thiolate (3g): Prepared from bis(chloride) **2a** and *m*-toluidine. Yield: 0.37 g (65%); m.p. 198−200 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.33 (s, 3 H, CH_3), 4.09 (s, 3 H, NCH_3), 6.94−7.28 (m, 6 H, H_{arom}), 7.52−7.68 (m, 3 H, H_{arom}), 8.57 (s, 1 H, 2-H), 10.38 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M$^+$ − 2 H]. − $C_{17}H_{16}N_2S$ (280.39): calcd. C 72.82, H 5.75, N 9.99, S 11.43; found C 72.91, H 5.68, N 10.08, S 11.35.

1-Methyl-4-(4-chlorophenylamino)quinolinium-3-thiolate (3h): Prepared from bis(chloride) **2a** and *p*-chloroaniline. Yield: 0.38 g (63%); m.p. 245−247 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 4.17 (s, 3 H, NCH_3), 6.98−7.10 (m, 2 H, H_{arom}), 7.32−7.42 (m, 2 H, H_{arom}), 7.62−7.78 (m, 1 H, 6-H), 7.92−8.18 (m, 2 H, 7-H, 8-H), 8.30−8.48 (m, 1 H, 5-H), 8.94 (s, 1 H, 2-H), 10.95 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 299 (100) [M$^+$ − 2 H]. − $C_{16}H_{13}ClN_2S$ (300.81): calcd. C 63.89, H 4.36, N 9.31, S 10.63, Cl 11.79; found C 63.94, H 4.45, N 9.25, S 10.57, Cl 11.88.

1-Ethyl-4-(phenylamino)quinolinium-3-thiolate (3i): Prepared from bis(chloride) **2b** and aniline. Yield: 0.33 g (59%); m.p. 223−226 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.54 (t, 3 H, *J* = 7.5 Hz, CH_3), 4.43 (q, 2 H, *J* = 7.5 Hz, CH_2), 7.22−7.28 (m, 1 H, 8-H), 7.31−7.40 (m, 1 H, 7-H), 7.59−7.66 (m, 1 H, 5-H), 8.60 (s, 1 H, 2-H), 10.38 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M$^+$ − 2 H]. − $C_{17}H_{16}N_2S$ (280.39): calcd. C 72.82, H 5.75, N 9.99, S 11.43; found C 72.79, H 5.68, N 10.15, S 11.34.

1-Alkyl-3-methylthio-4-(phenylamino)quinolinium Methyl Sulfates (5): A suspension of 1-alkyl-4-(phenylamino)quinolinium-3-thiolate **3e** or **3i** (2 mmol) in dimethyl sulfate (10 mmol) was stirred at 40 °C for 1 h. The mixture was then cooled to room temperature, whereupon anhydrous diethyl ether (20 mL) was added. The solid obtained was collected by filtration and washed with further diethyl ether. The white product was dried in vacuo to give the salt **5**.

1-Methyl-3-methylthio-4-(phenylamino)quinolinium Methyl Sulfate (5a): Yield: 0.39 g (ca. 100%). − ^{1}H NMR (D_2O): δ = 2.42 (s, 3 H, SCH_3), 3.74 (s, 3 H, OCH_3), 4.20 (s, 3 H, NCH_3), 7.21−7.29 (m, 2 H, H_{arom}), 7.31−7.39 (m, 1 H, H_{arom}), 7.41−7.54 (m, 3 H, H_{arom}), 7.59−7.65 (m, 1 H, 8-H), 7.88−8.01 (m, 2 H, 5-H, 7-H), 8.79 (s, 1 H, 2-H). − MS (EI, 15 eV): *m*/*z* (%) = 280 (100) [M$^+$ − HCH_3SO_4]. − $C_{18}H_{20}N_2O_4S_2$ (392.48): calcd. C 55.08, H 5.14, N 7.14, S 16.34; found C 55.01, H 5.21, N 7.02, S 16.34.

1-Ethyl-3-methylthio-4-(phenylamino)quinolinium Ethyl Sulfate (5b): Yield: 0.42 g (ca. 100%). − ^{1}H NMR (D_2O): δ = 1.57 (t, 3 H, *J* = 7.2 Hz, CH_3), 2.41 (s, 3 H, SCH_3), 3.75 (s, 3 H, OCH_3), 4.62 (q, 2 H, *J* = 7.2 Hz, CH_2), 7.17−7.24 (m, 2 H, H_{arom}), 7.25−7.32 (m, 1 H, H_{arom}), 7.35−7.50 (m, 3 H, H_{arom}), 7.58−7.65 (m, 1 H, H_{arom}),

7.93−8.09 (m, 2 H, H_{arom}), 8.84 (s, 1 H, 2-H). − MS (EI, 15 eV): *m*/*z* (%) = 295 (100) [M^+ − HCH_3SO_4]. − $C_{20}H_{24}N_2O_4S_2$ (420.54): calcd. C 57.12, H 5.75, N 6.66, S 15.25; found C 57.32, H 5.54, N 6.48, S 15.11.

1-Alkyl-3-methylthio-1,4-dihydro-4-phenyliminoquinolines (6): In a single portion, 5% aqueous sodium hydroxide solution (5 mL) was added to a cold solution of methyl sulfate **5a** or ethyl sulfate **5b** in water (10 mL). The solid formed was collected by filtration, washed with water, and dried in air. It was subsequently purified by column chromatography on alumina eluting with chloroform/ethanol, 10:1, *v*/*v*.

1-Methyl-3-methylthio-1,4-dihydro-4-phenyliminoquinoline (6a): Yield: 0.23 g (82%); m.p. 133−134 °C. − ^{1}H NMR ([D_6]DMSO): δ = 2.16 (s, 3 H, SCH_3), 3.70 (s, 3 H, NCH_3), 6.62−6.69 (m, 2 H, H_{arom}), 6.81−6.92 (m, 1 H, H_{arom}), 6.95−7.06 (m, 1 H, H_{arom}), 7.15−7.24 (m, 2 H, H_{arom}), 7.42−7.55 (m, 3 H, H_{arom}), 7.78 (s, 1 H, 2-H). − MS (EI, 15 eV): *m*/*z* (%) = 280 (100) [M^+]. − $C_{17}H_{16}N_2S$ (280.39): calcd. C 72.82, H 5.75, N 9.99, S 11.43; found C 72.62, H 5.48, N 10.09, S 11.30

1-Ethyl-3-methylthio-1,4-dihydro-4-phenyliminoquinoline (6b): Yield: 0.22 g (74%); oil. − ^{1}H NMR ([D_6]DMSO): δ = 1.22−1.29 (t, 3 H, *J* = 7.3 Hz, CH_3), 2.19 (s, 3 H, SCH_3), 4.12−4.24 (q, 2 H, *J* = 7.3 Hz, CH_2), 6.62−6.68 (m, 1 H, H_{arom}), 6.62−6.70 (m, 2 H, H_{arom}), 6.82−6.92 (m, 1 H, H_{arom}), 6.94−7.04 (m, 1 H, H_{arom}), 7.15−7.24 (m, 2 H, H_{arom}), 7.44−7.58 (m, 3 H, H_{arom}), 7.79 (m, 1 H, 2-H). − MS (EI, 15 eV): *m*/*z* (%) = 294 (100) [M^+]. − $C_{18}H_{18}N_2S$ (294.41): calcd. C 73.43, H 6.16, N 9.51, S 10.89; found C 73.28, H 6.09, N 9.63, S 10.80

7-Alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chlorides (7). − Procedure A [from bis(chloride) **2** and anilines]**:** A mixture of 5,12-(dimethyl)thioquinanthrenediium bis(chloride) **2a** (1 mmol), dry pyridine (10 mL), and aniline (2.5 mmol) was stirred under air for 2 h at 70 °C. The mixture was subsequently cooled to room temp. and the benzothiazinium salt **7** thus obtained was collected by filtration and washed with diethyl ether. The crude product was purified by recrystallization from ethanol.

Procedure B (from quinolinium thiolate **3**)**:** A mixture of quinolinium thiolate **3** (1 mmol), dry pyridine (10 mL), and triethylamine hydrochloride (2.5 mmol) was stirred under air for 2 h at 70 °C. The salt **7** was isolated and purified as in Procedure A.

Procedure C (from alkyl sulfates **7f** or **7g** and aqueous potassium chloride)**:** A solution of 7-alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium alkyl sulfate **7f** or **7g** (1 mmol) in water (2 mL) was poured into a saturated aqueous solution of potassium chloride (5 mL). The resulting mixture was cooled to room temperature and the solid formed was filtered off, dried in air, and recrystallized from ethanol.

7-Methyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (7a): Prepared according to Procedures A, B, and C; m.p. 248 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 4.14 (s, 3 H, NCH_3), 7.02−7.08 (m, 2 H, H_{arom}), 7.10−7.20 (m, 1 H, 10-H), 7.52−7.61 (m, 1 H, 8-H), 7.78−7.88 (m, 1 H, 9-H), 8.00−8.09 (m, 2 H, H_{arom}), 8.66 (s, 1 H, 6-H), 9.00 (m, 1 H, 11-H), 9.01 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 264 (100) [M^+ − HCl]. − $C_{16}H_{13}ClN_2S$ (300.81): calcd. C 63.98, H 4.36, N 9.31, S 10.66, Cl 11.79; found C 63.75, H 4.48, N 9.24, S 10.30, Cl 11.70.

1,7-Dimethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (7b): Prepared according to Procedure A; m.p. 235 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 2.49 (s, 3 H, CH_3), 4.21 (s, 3 H, NCH_3), 6.82−7.15 (m, 3 H, H_{arom}), 7.70−7.90 (m, 1 H, 10-H), 8.00−8.20 (m, 2 H, 8-H, 9-H), 8.61−8.70 (m, 1 H, 11-H), 8.87 (s, 1 H, 6-H), 10.15 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+ − HCl]. − $C_{17}H_{15}ClN_2S$ (314.83): calcd. C 64.86, H 4.80, N 8.90, S 10.18, Cl 11.26; found C 64.32, H 4.70, N 8.76, S 10.28, Cl 11.14.

3,7-Dimethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (7c): Prepared according to Procedures A and B; m.p. 233 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 2.19 (s, 3 H, CH_3), 4.11 (s, 3 H, NCH_3), 6.78−6.85 (m, 1 H, H_{arom}), 6.87−7.02 (m, 1 H, H_{arom}), 7.32−7.38 (m, 1 H, H_{arom}), 7.78−7.88 (m, 1 H, 10-H), 8.00−8.10 (m, 2 H, 8-H, 9-H), 8.61 (s, 1 H, 6-H), 8.83−8.90 (m, 1 H, 11-H), 10.93 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+ − HCl]. − $C_{17}H_{15}ClN_2S$ (314.83): calcd. C 64.86, H 4.80, N 8.90, S 10.18, Cl 11.16; found C 64.10, H 4.72, N 8.82, S 10.24, Cl 11.29.

A Mixture of 2,7-Dimethyl- and 4,7-Dimethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chlorides (7d and 7e): Prepared according to Procedures A and B; m.p. 252 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 2.14 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 4.11 (s, 3 H, NCH_3), 4.12 (s, 3 H, NCH_3), 6.85−7.06 (m, 8 H, H_{arom}), 7.40−7.46 (m, 2 H, 10_{arom}), 7.74−7.84 (m, 2 H, H_{arom}), 7.98−8.08 (m, 2 H, H_{arom}), 8.65 (s, 1 H, 6-H), 8.66 (s, 1 H, 6-H), 9.02−9.12 (m, 2 H, 11-H), 11.07 (s, 1 H, NH), 11.29 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+ − HCl]. − $C_{17}H_{15}ClN_2S$ (314.83): calcd. C 64.86, H 4.80, N 8.90, S 10.18, Cl 11.16; found C 64.55, H 4.72, N 8.80, S 10.25, Cl 11.39.

3-Chloro-7-methyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (7f): Prepared according to Procedure A; m.p. 178 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 4.83 (s, 3 H, NCH_3), 6.96−6.99 (m, 2 H, H_{arom}), 7.32−7.42 (m, 2 H, H_{arom}), 7.62−7.78 (m, 1 H, 10-H), 7.92−8.18 (m, 2 H, 8-H, 9-H), 8.30−8.48 (m, 1 H, 11-H), 8.94 (s, 1 H, 6-H), 10.95 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 299 (100) [M^+ − HCl]. − $C_{16}H_1Cl_{22}N_2S$ (335.25): calcd. C 57.32, H 3.61, N 8.36, S 9.56, Cl 21.15; found C 57.42, H 3.57, N 8.30, S 9.60, Cl 21.28.

A Mixture of 2-Chloro-7-methyl- and 4-Chloro-7-methyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chlorides (7g and 7h): Prepared according to Procedure A; m.p. 249 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 4.12 (s, 3 H, NCH_3), 4.15 (s, 3 H, NCH_3), 7.02−7.22 (m, 4 H, H_{arom}), 7.35−7.47 (m, 1 H, H_{arom}), 7.60−7.72 (m, 1 H, H_{arom}), 7.75−7.90 (m, 2 H, H_{arom}), 7.96−8.15 (m, 4 H, H_{arom}), 8.62−8.70 (m, 2 H, H_{arom}), 8.83−9.05 (m, 2 H, H-11), 10.99 (s, 1 H, NH), 11.16 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 299 (100) [M^+ − HCl]. − $C_{16}H_{12}Cl_2N_2S$ (335.25): calcd. C 57.32, H 3.61, N 8.36, S 9.56, Cl 21.15; found C 57.48, H 3.47, N 8.27, S 9.70, Cl 21.08.

7-Ethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (7i): Prepared according to Procedure A; m.p. 254 °C (decomp.). − ^{1}H NMR ([D_6]DMSO): δ = 2.19 (t, 3 H, *J* = 7.3 Hz, CH_3), 4.11 (q, 2 H, *J* = 7.3 Hz, CH_2), 6.78−6.85 (m, 1 H, H_{arom}), 6.87−7.02 (m, 1 H, H_{arom}), 7.32−7.38 (m, 1 H, H_{arom}), 7.78−7.88 (m, 1 H, 10-H), 8.00−8.10 (m, 2 H, 8-H, 9-H), 8.61 (s, 1 H, 6-H), 8.83−8.90 (m, 1 H, 11-H), 10.93 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+ − HCl]. − $C_{17}H_{15}ClN_2S$ (314.83): calcd. C 64.86, H 4.80, N 8.90, S 10.18, Cl 11.17; found C 64.10, H 4.72, N 8.82, S 10.24, Cl 11.29.

7-Alkyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Alkyl Sulfates (7j and 7k): A mixture of 12*H*-quino[3,4-*b*]-1,4-benzothiazine **11** (1 mmol) and dimethyl or diethyl sulfate (3 mmol) was kept at 80 °C for 2 or 6 h. It was then allowed to cool to room temp. and triturated with diethyl ether (10 mL). The solid produced was collected by

filtration and treated twice with diethyl ether as described above. The product was dried in vacuo.

7-Methyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Methyl Sulfate (7j): Yield: 0.54 g (ca. 100%). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.38 (s, 1 H, CH_3O), 4.14 (s, 3 H, NCH_3), 7.02−7.10 (m, 2 H, H_{arom}), 7.14−7.28 (m, 2 H, H_{arom}), 7.84−7.91 (m, 1 H, 10-H), 8.02−8.12 (m, 2 H, 8-H, 9-H), 8.60−8.68 (m, 2 H, 6-H, 11-H), 10.48 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 264 (100) [$M^+ - HCH_3SO_4$]. − $C_{17}H_{16}N_2O_4S_2$ (376.44): calcd. C 54.24, H 4.28, N 7.44, S 17.03; found C 54.11, H 4.09, N 7.32, S 17.14.

7-Ethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Ethyl Sulfate (7k): Yield: 0.40 g (ca. 100%). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.01 (t, 3 H, *J* = 7.2 Hz, CH_3), 1.42 (t, 3 H, *J* = 7.2 Hz, CH_3), 3.74 (q, 2 H, *J* = 7.2 Hz, CH_2), 4.61 (q, 2 H, *J* = 7.2 Hz, CH_2), 7.02−7.12 (m, 2 H, H_{arom}), 7.14−7.28 (m, 2 H, H_{arom}), 7.82−7.90 (m, 1 H, 10-H), 8.08−8.10 (m, 1 H, 9-H), 8.16 (m, 1-H, 8-H), 8.60−8.68 (m, 1 H, 11-H), 8.66 (s, 1 H, 6-H), 10.59 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [$M^+ - HC_2H_5SO_4$]. − $C_{19}H_{20}N_2O_4S_2$ (404.49): calcd. C 56.42, H 4.98, N 6.93, S 15.85; found C 56.30, H 4.75, N 6.84, S 15.96.

7-Alkyl-7*H*-quino[3,4-*b*]-1,4-benzothiazines (9): Quinobenzothiazinium chloride **7** (1 mmol) was dissolved in water (20 mL) at 50 °C. A small amount of insoluble material was filtered off. The filtrate was then made alkaline with 5% aqueous sodium hydroxide solution (10 mL). The solid produced was collected by filtration, washed with water, and dried in air to give crude **9**, which was purified by recrystallization from ethanol.

7-Methyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine (9a): Prepared from chloride **7a**. Yield: 0.26 g (ca. 100%); m.p. 248 °C (decomp.). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.48 (s, 3 H, CH_3), 6.62−6.68 (m, 1 H, H_{arom}), 6.72−6.79 (m, 1 H, H_{arom}), 6.48−6.92 (m, 1 H, 10-H), 7.06 (s, 1 H, 6-H), 7.18−7.29 (m, 2 H, H_{arom}), 7.48−7.56 (m, 1 H, 9-H), 8.15−8.19 (m, 1 H, 11-H). − MS (EI, 15 eV): *m*/*z* (%) = 264 (100) [M^+]. − $C_{16}H_{12}N_2S$ (264.34): calcd. C 72.70, H 4.58, N 10.60, S 12.13; found C 72.65, H 4.50, N 10.72, S 12.04.

1,7-Dimethyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine (9b): Prepared from chloride **7b**. Yield: 0.27 g (ca. 100%); m.p. 146−148 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.22 (s, 3 H, CH_3), 3.47 (s, 3 H, NCH_3), 6.42−6.49 (m, 1 H, H_{arom}), 6.61−6.68 (m, 1 H, H_{arom}), 6.74−6.79 (m, 1 H, H_{arom}), 7.00 (s, 1 H, 6-H), 7.18−7.27 (m, 2 H, 8-H, 10-H), 7.47−7.55 (m, 1 H, 9-H), 8.18−8.24 (m, 1 H, 11-H). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+]. − $C_{17}H_{14}N_2S$ (278.37): calcd. C 73.35, H 5.07, N 10.06, S 11.52; found C 73.24, H 5.10, N 10.15, S 11.40.

3,7-Dimethyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine (9c): Prepared from chloride **7c**. Yield: 0.27 g (ca. 100%); m.p. 248 °C (decomp.). − ^{1}H NMR ([D$_6$]DMSO): δ = 2.09 (s, 1 H, CH_3), 3.46 (s, 3 H, NCH_3), 6.48−6.50 (m, 1 H, 4-H), 6.62−6.72 (m, 2 H, 1-H, 2-H), 6.99 (s, 1 H, 6-H), 7.15−7.26 (m, 2 H, 8-H, 10-H), 7.46−7.57 (m, 1 H, 9-H), 8.10−8.18 (m, 1 H, 11-H). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+]. − $C_{17}H_{14}N_2S$ (278.37): calcd. C 73.35, H 5.07, N 10.06, S 11.52; found C 73.25, H 5.14, N 10.18, S 11.45.

3-Chloro-7-methyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine (9d): Prepared from chloride **7f**. Yield: 0.30 g (ca. 100%); m.p. 248 °C (decomp.). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.60 (s, 3 H, NCH_3), 6.65−6.72 (m, 1 H, H_{arom}), 6.75−6.85 (m, 1 H, 4-H), 6.78−6.92 (m, 1 H, H_{arom}), 7.10 (s, 1 H, 6-H), 7.20−7.32 (m, 2 H, 8-H, 10-H), 7.52−7.59 (m, 1 H, 9-H), 8.12−8.18 (m, 1 H, 11-H). − MS (EI, 15 eV): *m*/*z* (%) = 299 (100) [M^+]. − $C_{16}H_{11}ClN_2S$ (298.79): calcd. C 64.32, H 3.71, N 9.38, S 10.73, Cl 11.87; found C 64.48, H 3.64, N 9.36, S 10.78, Cl 11.93.

7-Ethyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine (9e): Prepared from chloride **7i**. Yield: 0.278 g (100%); m.p. 140−142 °C. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.23 (t, 3 H, *J* = 7.8 Hz, CH_3), 3.95 (q, 2 H, *J* = 7.8 Hz, CH_2), 6.62−6.69 (m, 1 H, H_{arom}), 6.71−6.81 (m, 2 H, H_{arom}), 6.84−6.92 (m, 1 H, H_{arom}), 7.05 (s, 1 H, 6-H), 7.16−7.24 (m, 2 H, 10-H), 7.12−7.17 (m, 1 H, 8-H), 7.48−7.56 (m, 1 H, 9-H), 8.15−8.22 (m, 1 H, 11-H). − MS (EI, 15 eV): *m*/*z* (%) = 278 (100) [M^+]. − $C_{17}H_{14}N_2S$ (278.37): calcd. C 73.35, H 5.07, N 10.06, S 11.52; found C 73.25, H 5.14, N 10.18, S 11.49.

7,12-Dimethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Methyl Sulfate (10a): A mixture of 7-methyl-7*H*-quino[3,4-*b*]-1,4-benzothiazine **9a** (1 mmol) and dimethyl sulfate (3 mmol) was kept at 80 °C for 2 h. It was then allowed to cool to room temperature and triturated with diethyl ether (10 mL). The solid produced was collected by filtration and treated twice with diethyl ether as described above. The product was dried in vacuo. Yield: 0.40 g (ca. 100%). − ^{1}H NMR ([D$_6$]DMSO): δ = 3.42 (s, 1 H, OCH_3), 4.14 (s, 3 H, NCH_3), 7.02−7.10 (m, 2 H, H_{arom}), 7.14−7.28 (m, 2 H, H_{arom}), 7.84−7.91 (m, 1 H, 10-H), 8.02−8.12 (m, 2 H, 8-H, 9-H), 8.60−8.68 (m, 2 H, 6-H, 11-H), 10.48 (s, 1 H, NH). − MS (EI, 15 eV): *m*/*z* (%) = 293 (100) [$M^+ - HCH_3SO_4$]. − $C_{19}H_{21}N_2O_4S_2$ (405.50): calcd. C 56.28, H 5.22, N 6.91, S 15.81; found 56.11, H 5.08, N 6.84, S 15.89.

7,12-Dimethyl-12*H*-quino[3,4-*b*]-1,4-benzothiazinium Chloride (10b): A solution of 7,12-dimethylquino[3,4-*b*]-1,4-benzothiazinium methyl sulfate **10a** (1 mmol) in water (2 mL) was poured into a saturated aqueous solution of potassium chloride (5 mL). The resulting mixture was allowed to cool to room temperature. The solid produced was collected by filtration, dried in air, and recrystallized from ethanol. Yield: 0.22 g (69%). − ^{1}H NMR ([D$_6$]DMSO): δ = 4.04 [s, 3 H, N(7)−CH_3], 4.31 [s, 3 H, N(12)−CH_3], 7.22−7.33 (m, 2 H, H_{arom}), 7.35−7.48 (m, 2 H, H_{arom}), 7.82−7.92 (m, 1 H, 10-H), 8.05−8.17 (m, 1 H, 9-H), 8.21−8.29 (m, 1 H, 8-H), 8.50−8.58 (m, 1 H, 11-H), 9.09 (s, 1 H, 6-H). − MS (EI, 15 eV): *m*/*z* (%) = 293 (100) [M^+ − HCl]. − $C_{18}H_{18}ClN_2S$ (329.86): calcd. C 65.54, H 5.50, N 8.49, S 9.72, Cl 10.75; found C 65.42, H 5.62, N 8.42, S 9.76, Cl 10.92.

1-Methyl-4-(methylphenylamino)-3-methylthioquinolinium Methyl Sulfate (12): A mixture of **6a** (1 mmol) and dimethyl sulfate (3 mmol) was kept at 80 °C for 2 h. It was then allowed to cool to room temp. and triturated with diethyl ether (10 mL). The solid produced was filtered off and triturated twice with diethyl ether as described above. The product was dried in vacuo. Yield: 0.40 g (ca. 100%). − ^{1}H NMR (D_2O): δ = 3.18 (s, 3 H, OCH_3), 3.76 (s, 3 H, $NCH_3C_6H_5$), 3.87 (s, 3 H, NCH_3), 6.97−7.05 (m, 2 H, H_{arom}), 7.18−7.28 (m, 2 H, H_{arom}), 7.42−7.52 (m, 2 H, H_{arom}), 7.60−7.78 (m, 3 H, H_{arom}), 8.21 (s, 1 H, 2-H). − MS (EI, 15 eV): *m*/*z* (%) = 295 (100) [$M^+ - CH_3SO_4$]. − $C_{19}H_{22}N_2S_2O_4$ (406.51): calcd. C 56.14, H 5.45, N 6.89, S 11.79; found C 56.48, H 5.72, N 6.70, S 11.92.

Crystallography:

Compound **7a** was found to co-crystallize with pyridine and water on cooling the mixture obtained following reaction of **2a** and aniline according to Procedure A. The composition of the co-crystallizate was confirmed by elemental analysis. A well-shaped crystal of dimensions 0.84 × 0.56 × 0.32 mm was mounted on an Enraf−Nonius CAD4 single-crystal diffractometer and data was

collected using monochromated Mo-K_α radiation. A monoclinic cell was established and the systematic absences indicated the space group $P2_1/c$. Of 4928 reflections collected in the ω-scan mode, 4754 were found to be independent (R_{int} = 0.029), $2.18 < \theta < 29.93°$, *hkl* range −13, 0, 0 to 13, 17, 19. Lorentz and polarization corrections were applied. The structure was solved by direct methods (SHELXS-90)[11] and refined by full-matrix least-squares analysis on F^2 (SHELXL-97).[12] Hydrogen atoms were geometrically positioned, except for the hydrogen attached to N12, which was located on difference Fourier maps, and the two H atoms of the water molecule, which were not located (low occupancy factors). The hydrogens were refined as "riding" on their carbons, except for 12-H on N12, for which the positional parameters were refined. The refinement converged at $R = 0.065$ [$I > 2\sigma(I)$] and $wR = 0.185$ (all data), $S = 1.038$. Largest peak and hole in the final difference map 0.430 and −0.258 eÅ^{-3}, respectively. The pyridine molecule was found to be located at the crystallographic center of symmetry. Due to the possible orientational disorder of this pyridine molecule over 6 equivalent positions and the consequent difficulty in resolving the nitrogen atom position, the model used in the refinement was a benzene molecule. The water molecule shows partial occupancy and the s.o.f. refined to a value of 0.25. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (depository number CCBC-127803). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44 (0)1223 336033; E-mail: teched@chemcrys.cam.ac.uk].

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Received January 21, 2000
[O00026]