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Synthesis of Partially Saturated N-Substituted 4*H*-3,1-Benzothiazine-2(1*H*)-thiones

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Summary. Acid-catalyzed reaction of 2-arylidenecyclohexanones **1** with N-substituted dithiocarbamic acids **2** gave open-chain addition products **3** and **4**. Dehydration of **3** and **4** afforded only one of the three possible isomeric N-substituted 4*H*-3,1-benzothiazine-2(1*H*)-thiones **5** and **6**.

Keywords. N-Substituted 4*H*-3,1-benzothiazine-2(1H)-thiones; Synthesis; ^{1}H- and ^{13}C-spectroscopy.

Synthese von partiell gesättigten N-substituierten 4*H*-3,1-Benzothiazin-2-(1*H*)-thionen

Zusammenfassung. Die säurekatalysierte Reaktion von 2-Arylidencyclohexanonen **1** mit N-substituierten Dithiocarbaminsäure **2** ergab die offenkettigen Additionsprodukte **3** und **4**. Die Dehydratation von **3** und **4** führte ausschließlich zu einem der drei möglichen N-substituierten 4*H*-3,1-Benzothiazin-2(1*H*)-thion-Isomeren **5** und **6**.

Introduction

The chemistry and pharmacology of 3,1-benzothiazines have scarcely been investigated. The synthetic works were focused on preparation and simple transformation of the compounds. Transformation of 4-aryl-3,1-benzothiazine-2-thiones into 4,1-benzothiazepine derivatives is one of the most important results of the latter studies [1]. As a result of the pharmacological investigations, a few 4-aryl-2-(thi)oxo-, and 4-aryl-2-amino-3,1-benzothiazine derivatives with CNS [2–4], analgesic [5, 6], and antimicrobial [7, 8] effects were reported.

Earlier, we have shown that reaction of dithiocarbamic acid with 2-arylidenecyclohexanones is a versatile route for synthesis of 4-aryl-4*H*-3,1-benzothiazine-2(1*H*)-thiones [9]. As a continuation of our earlier work, we report here the results obtained by treating 2-arylidenecyclohexanones **1 a–f** with N-substituted dithiocarbamic acids **2 a** and **2 b**. In these reactions formation of partially saturated N-substituted 4*H*-3,1-benzothiazine-2(1*H*)-thiones was expected, which were considered to be the first representatives of N-substituted 3,1-benzothiazines.

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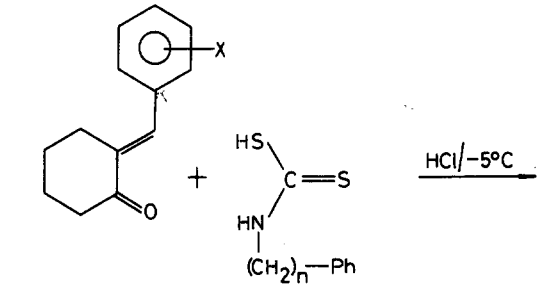
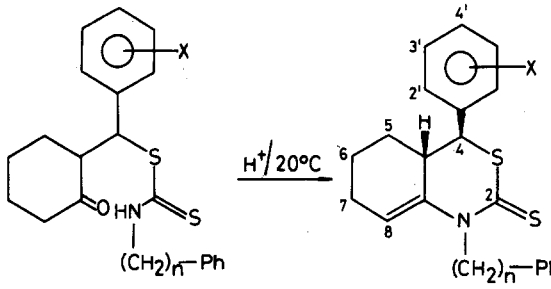
Results and Discussion

The reaction of 2-arylidenecyclohexanones **1 a–f** with dithiocarbamic acids **2 a** and **2 b** was carried out in acidic aqueous acetone solutions at −5°C to yield the open-chain addition products **3 a–f** and **4 a–d** (Scheme 1). The appearance of the $\nu_{(NH)}$ and $\nu_{(C=O)}$ signals in their IR spectra proved unambiguous evidence of the progress of the addition reactions as well as the open-chain structure of the products. The ^{1}H-NMR (60 MHz, *DMSO-d_6*) spectra were rather complex suggesting equilibrium between the open-chain and cyclic N,O-hemiketal structures [9] of the compounds.



1 2a n=1
2b n=2



3 n=1
4 n=2
5 n=1
6 n=2

	a	b	c	d	e	f
X	H	4-OMe	4-Me	4-Cl	3-OMe	4-Br

Scheme 1

In order to obtain the expected 3,1-benzothiazines we tried to apply the dehydration methods (Method A: *p-TSA*/Benzene; Method B: *TFA*/Benzene; Method C: $(C_2H_5)_2O-BF_3/CHCl_3$) used in our earlier work, which proved to be slightly selective in dehydration of the configurationally different cyclic dithiocarbamic acid adducts of 2-arylidenecyclohexanones [9]. These methods, however, failed, even if longer reaction times were used. Thus, compounds **3 a–f** and **4 a–d** were dehydrated in acetic anhydride using sulphuric acid as catalyst. ^{1}H-NMR (60 MHz, $CDCl_3$) analysis of the crude reaction products showed that dehydration of **3 a–f** and

Table 1. ^{1}H-NMR data (chemical shifts, δ/ppm and coupling constants/Hz) of compounds **5a–f** and **6a–d** in *DMSO-d_6* or $CDCl_3$ solution[a] at 250.14 MHz. Further signals: CH_3 (X), s (3 H): 3.79 (**5b**), 2.34 (**5c**), 3.76 (**5e**, **6b**), 2.30 (**6c**), *Ph*CH_2 (side chain in **6a–d**): XY-part of an ABXY-system, ~ 3.0 and ~ 3.15, 2 × m (2 × 2 H)

Compound	CH_2 (5, 6) 2 × m (2 × 2 H)	CH_2 (7) m (2 H)	H-4a m (1 H)	H-4 d (1 H)[b]	NCH_2[c] 2 × d/m (2 × 1 H)	H-8 ~ t (1 H)[d]	*Ar*H (Pos. 4 + side chain) m's/d's (9/10 H)[e]
5a	~ 1.25, ~ 1.45	2.05	2.98[f]	4.64	5.62, 5.86	5.77	7.2–7.5
5b	~ 1.4, ~ 1.5	2.10	2.82	4.35	5.46, 5.99	5.66	6.88[g], 7.2–7.4[h]
5c	~ 1.45, ~ 1.55	2.10	2.85	4.35	5.46, 6.00	5.66	7.1–7.4
5d	~ 1.3, ~ 1.5	2.08	3.00	4.71	5.60, 5.86	5.79	~ 7.25[h], ~ 7.35[h], 7.46[g], 7.52[g]
5e	~ 1.3, ~ 1.5	2.05	3.02	4.62	5.58, 5.88	5.76	6.92[i], 7.02[j], 7.2–7.4[h]
5f	~ 1.35, ~ 1.5	2.10	3.08	4.35	5.46, 5.95	5.68	7.2–7.4[h], 7.47[g]
6a	1.15– 1.6	2.15	~ 2.6	4.52	~ 4.55, ~ 4.8	6.00	7.2–7.4
6b	1.2– 1.6	2.15	2.55	4.45	~ 4.55, ~ 4.8	5.99	6.93[g], ~ 7.3[h]
6c	1.1– 1.6	2.15	2.55	4.48	~ 4.4, ~ 4.8	6.04	~ 7.2[h], ~ 7.3[h]
6d	1.1– 1.6	2.15	~ 2.6	4.57	~ 4.2, ~ 4.8	6.02	~ 7.2–7.5

[a] Solvent *DMSO-d_6* for **5a**, **d**, **f** and **6a–d**, $CDCl_3$ for **5b**, **c**, **e**

[b] *J* (H-4, H-4a): 11.7 ± 0.2

[c] AB-type spectrum (2 × d) for **5a–f**, *J* (A, B): 16.0 ± 0.2, AB-part (2 × m) of an ABXY-system for **6a–d**

[d] *J*: 4.0 ± 0.1

[e] Total intensity 10 H (**5a**, **6a**), 9 H (**5b–f**, **6b–d**)

[f] ~ d (*J*: 11.3)

[g] A or B part (intensity: 2 H) of the AA'BB'-type multiplet of the *para*-disubstituted aromatic ring (Pos. 4), *J* (A, B): 8.8 (**5b**, **6b**), ~ 9 (**5d**), 8.4 (**5f**)

[h] Overlapping m's, intensity: 7 H (**5b**, **f**, **6b**), 3 + 2 H (**5d**), 6 H (**5e**), 5 + 4 H (**6c**)

[i] H-4 (4-aryl group), dd (1 H)

[j] H-2, 6 (4-aryl group), overlapping d's (2 H)

Table 2. ^{13}C-NMR chemical shifts (δ/ppm) of compounds **5a–f** and **6a–d** in *DMSO-d_6* and/or $CDCl_3$ solution at 20 or 63 MHz[a]. Further signals: CH_3(X): 55.3 (**5b**), 21.1 (**5c**), 56.9[c] (**5e**), 54.9 (**6b**), 22.3 (**6c**); *Ph*CH_2 (side chain): 34.2 (**6a, b**), 34.0 (**6c, d**); C_{Ar}-2, 3, 5, 6: four lines between 128.0 and 132.0 ppm for **5d** and **6c, d**, three lines for **5a, c** and **6a, d** because of overlap of two lines at 130.5 (**5a**) and 130.0 (**6a**) or of appearance of one line out of the interval given above at 126.8 (**5c**), 116.0[c] (**6b**, C-3, 5). Two lines are in the above interval and two are separated for **5b, f** at 114.5[c] (C-3, 5) and 126.7 (**5b**) and 126.7 and 132.2[c] (**5f**, C-3, 5). There are two plus four[c] lines for **5e**, three in the interval given above and three further ones at 115.9 (C-2[c]), 122.2 (C-6[c]) and 161.4 (C-3[c])

Compound	C=S(2)	C-4[b]	C-4a	C-5, 7	C-6	C-8	C-8a	NCH_2[b]	C_{Ar}-1	C_{Ar}–C[c]	C_{Ar}-4	C_{Ar}-4[c]
5a	192.4	55.2	40.2	26.0, 27.4	19.6	118.8	140.1	56.9	138.0[b]	138.1[b]	128.5	129.9
5b	192.5	54.3	39.9	24.9, 26.2	18.6	117.0	139.4	56.4	136.5	128.2	127.1	159.7
5c	192.7	54.7	39.9	25.0, 26.4	18.7	116.9	139.6	56.4	133.5	136.6	127.2	138.4
5d	192.1	54.4	40.0	26.0, 27.4	19.5	119.0	139.9	56.9	137.3[b]	137.9[b]	128.6	134.0
5e	192.4	55.1	40.1	26.0, 27.5	19.6	118.7	140.2	56.9[d]	138.0	139.7	128.5	115.4
5f	191.8	54.3	39.7	24.8, 26.3	18.6	117.3	139.0	56.4	135.7	136.3	127.2	122.4
6a	191.0	55.2	39.7	26.0, 26.9	19.2	119.0	140.3[b]	55.4	138.5	139.9[b]	128.0	129.8
6b	191.3	55.2	39.9	26.0, 26.9	19.2	118.8	140.5	56.8	139.9	130.2	128.0	160.8
6c	191.0	55.2	39.5	25.9, 26.8	19.0	119.0	139.9[b]	55.0	140.3	135.5	128.0	139.2[b]
6d	190.6	55.1	39.6	25.8, 26.9	19.0	119.1	140.0	55.4	139.0	137.6	127.8	134.4

[a] Solvent: *DMSO-d_6* (**5a, d, e**, and **6a–d**) or $CDCl_3$ (**5b, c, f**, and **6c, d**), measuring frequency: 20.14 MHz (**5b, c, f**) or 62.89 MHz (**5a, d, e**, and **6a–d**)

[b] Interchangeable assignments

[c] 4-aryl group

[d] Two overlapping lines

4a–d furnished only one of the three possible 3,1-benzothiazine isomers **5a–f** and **6a–d** (Scheme 1) [10].

The ^{1}H- and ^{13}C-NMR data of compounds **5a–f** and **6a–d** are given in Tables 1 and 2 and provide convincing evidence of the structures of the new products. The values (ca. 11.7 Hz) of *J* (H-4, H-4a) coupling constants prove [11] the 1,3-diaxial arrangements of the hydrogens involved and consequently the *cis*-equatorial position of the 4-aryl group relative to the H-4a and the heteroring, respectively. Both 7-methylen hydrogens have couplings of the same magnitude to H-8 (the olefinic signal is a pseudo-triplet split by ca 4 Hz). All evidence suggests a preferred conformation for the flexible compounds, with the alicycle in half-chair form (where C-6 and C-7 have "up and down" position to the plane of C-4a, 7, 8, 8a atoms) and the hetero ring in a twisted-boat form (Fig. 1).

Experimental Part

Melting points were determined on a Boetius apparatus and are uncorrected. IR spectra were taken in KBr pellets with a Specord 75 IR spectrophotometer. ^{1}H-NMR spectra were recorded with a Perkin-Elmer R-12 equipment (60 MHz) or a Bruker WM-250 FT-spectrometer, using *TMS* as internal standard, at 35°C or 25°C, respectively. ^{13}C-NMR measurements were carried out at 25°C on Bruker WM-250 or WP-80 SY FT-spectrometers, at 63 or 20 MHz, respectively, using *TMS* as internal standard. Elemental analyses were performed in-house and at the Central Research Laboratory, University Medical School, Pécs.

2-Arylidenecyclohexanones [12] and N-substituted dithiocarbamic acids [13] used as starting materials were synthesized by literature methods. The (*E*)-configuration of the unsaturated ketones was based on ^{1}H-NMR investigations [14].

The isomeric composition of the reaction products was examined by ^{1}H-NMR spectroscopy (60 MHz), based on investigation of the well separated H-4 signals. TLC was performed on Kieselgel GF 254 plates (Merck) using benzene as eluant.

General Procedure for the Addition of Dithiocarbamic Acids **2a** *and* **2b** *to 2-Arylidenecyclohexanones* **1a–f**

To a solution of 0.075 mol of ammonium salt of N-benzyl- (**2a**), or N-(2-phenylethyl)-dithiocarbamic acid (**2b**) dissolved in 150 ml of 50% methanol (cooled to −5°C), 35 ml of 6.5*N* hydrochloric acid (cooled to −5°C) was added dropwise while stirring. Cooling and stirring were continued, and 0.035 mol of unsaturated ketone **1a–f** in 200 ml acetone (cooled to −5°C) was added to the reaction mixture. After stirring at this temperature for 4 h, the precipitate formed was filtered off, washed free of acid with water, dried, and crystallized from benzene/petroleum ether to give colourless crystals.

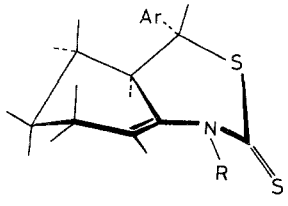


Fig. 1. Conformation of compounds **5** and **6**

2-(α-(N-Benzyl-thiocarbamoylthio)-benzyl)-cyclohexan-1-one (**3a**)

Yield: 83%, m.p. 108–111°C. IR (KBr): $\nu = 3320\,cm^{-1}$ (NH), 2925, 2945 cm^{-1} (CH_2), 1690 cm^{-1} (C=O). $C_{21}H_{23}NOS_2$ (369.54). Calcd. C 68.26, H 6.27, S 17.35; found C 68.34, H 6.21, S 17.10.

2-(α-(N-Benzyl-thiocarbamoylthio)-4-methoxybenzyl)-cyclohexan-1-one (**3b**)

Yield: 81%, m.p. 106–109°C. IR (KBr): $\nu = 3275\,cm^{-1}$ (NH), 2930 cm^{-1} (CH_2), 1695 cm^{-1} (C=O). $C_{22}H_{25}NO_2S_2$ (399.57). Calcd. C 66.13, H 6.31, S 16.05; found C 66.24, H 6.18, S 15.80.

2-(α-(N-Benzyl-thiocarbamoylthio)-4-methylbenzyl)-cyclohexan-1-one (**3c**)

Yield: 78%, m.p. 100–104°C. IR (KBr): $\nu = 3335\,cm^{-1}$ (NH), 2930, 2945 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{22}H_{25}NOS_2$ (383.57). Calcd. C 68.89, H 6.57, S 16.72; found C 68.64, H 6.78, S 16.67.

2-(α-(N-Benzyl-thiocarbamoylthio)-4-chlorobenzyl)-cyclohexan-1-one (**3d**)

Yield: 73%, m.p. 110–113°C. IR (KBr): $\nu = 3300\,cm^{-1}$(NH), 2940 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{21}H_{22}ClNOS_2$ (403.98). Calcd. C 62.44, H 5.49, S 15.87; found C 62.23, H 5.37, S 15.98.

2-(α-(N-Benzyl-thiocarbamoylthio)-3-methoxybenzyl)-cyclohexan-1-one (**3e**)

Yield: 85%, m.p. 103–105°C. IR (KBr): $\nu = 3225\,cm^{-1}$(NH), 2940 cm^{-1} (CH_2), 1695 cm^{-1} (C=O). $C_{22}H_{25}NO_2S_2$ (399.57). Calcd. C 66.13, H 6.31, S 16.05; found C 66.04, H 6.48, S 15.94.

2-(α-(N-Benzyl-thiocarbamoylthio)-4-bromobenzyl)-cyclohexan-1-one (**3f**)

Yield: 86%, m.p. 116–118°C. IR (KBr): $\nu = 3305\,cm^{-1}$(NH), 2935 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{21}H_{22}BrNOS_2$ (448.43). Calcd. C 56.25, H 4.94, S 14.30; found C 56.07, H 4.71, S 14.51.

2-(α-(N-(2-Phenylethyl)-thiocarbamoylthio)-benzyl)-cyclohexan-1-one (**4a**)

Yield: 80%, m.p. 119–122°C. IR (KBr): $\nu = 3355\,cm^{-1}$(NH), 2945 cm^{-1} (CH_2), 1690 cm^{-1} (C=O). $C_{22}H_{25}NOS_2$ (383.57). Calcd. C 68.89, H 6.57, S 16.72; found C 68.72, H 6.64, S 16.90.

2-(α-(N-(2-Phenylethyl)-thiocarbamoylthio)-4-methoxybenzyl)-cyclohexan-1-one (**4b**)

Yield: 87%, m.p. 114–116°C. IR (KBr): $\nu = 3355\,cm^{-1}$(NH), 2940 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{23}H_{27}NO_2S_2$ (413.59). Calcd. C 66.79, H 6.58, S 15.50; found C 66.57, H 6.43, S 15.71.

2-(α-(N-(2-Phenylethyl)-thiocarbamoylthio)-4-methylbenzyl)-cyclohexan-1-one (**4c**)

Yield: 85%, m.p. 126–128°C. IR (KBr): $\nu = 3315\,cm^{-1}$(NH), 2940 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{23}H_{27}NOS_2$ (397.59). Calcd. C 69.48, H 6.84, S 16.13; found C 69.39, H 6.71, S 16.37.

2-(α-(N-(2-Phenylethyl)-thiocarbamoylthio)-4-chlorobenzyl)-cyclohexan-1-one (**4d**)

Yield: 72%, m.p. 126–129°C. IR (KBr): $\nu = 3240\,cm^{-1}$(NH), 2930 cm^{-1} (CH_2), 1700 cm^{-1} (C=O). $C_{22}H_{24}ClNOS_2$ (418.01). Calcd. C 63.21, H 5.79, S 15.34; found C 63.07, H 5.63, S 15.47.

General Procedure for Dehydration of Compounds **3** *and* **4**

To the suspension of compounds **3** and **4** (0.03 mol) in 80 ml acetic anhydride 0.5 ml conc. sulphuric acid was added dropwise with stirring. Stirring was continued for ½ h. Then the mixture was cooled, the precipitate formed was filtered off, washed free of acid with water and dried. The product obtained was subjected to column chromatography (Merck, Kieselgel 60, 0.0063–0.2 mm; benzene) and crystallized from benzene/petroleum ether to give colourless crystals. For the ^{1}H-NMR spectra of compounds **5a–f** see Table 1, for the corresponding ^{13}C-NMR see Table 2.

trans-N-Benzyl-4-phenyl-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5a**)

Yield: 93%, m.p. 177–179°C. IR (KBr): $\nu = 2910, 2920, 2945\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1605, $1495\,cm^{-1}$ ($C=C_{Ar}$). $C_{21}H_{21}NS_2$ (351.52). Calcd. C 71.75, H 6.02, S 18.24; found C 71.68, H 5.93, S 18.14.

trans-N-Benzyl-4-(4-metoxyphenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5b**)

Yield: 89%, m.p. 161–163°C. IR (KBr): $\nu = 2910, 2925\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1605, $1510\,cm^{-1}$ ($C=C_{Ar}$). $C_{22}H_{23}NOS_2$ (381.55). Calcd. C 69.25, H 6.08, S 16.81; found C 70.05, H 6.19, S 16.68.

trans-N-Benzyl-4-(4-methylphenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5c**)

Yield: 79%, m.p. 188–190°C. IR (KBr): $\nu = 2910, 2925\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1605, $1495\,cm^{-1}$ ($C=C_{Ar}$). $C_{22}H_{23}NS_2$ (365.55). Calcd. C 72.29, H 6.34, S 17.54; found C 72.57, H 6.21, S 17.44.

trans-N-Benzyl-4-(4-chlorophenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5d**)

Yield: 84%, m.p.: 183–185°C. IR (KBr): $\nu = 2940\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1605, $1490\,cm^{-1}$ ($C=C_{Ar}$). $C_{21}H_{20}ClNS_2$ (385.97). Calcd. C 65.35, H 5.22, S 16.61; found C 65.38, H 5.07, S 16.54.

trans-N-Benzyl-4-(3-methoxyphenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5e**)

Yield: 89%, m.p. 164–166°C. IR (KBr): $\nu = 2910, 2930, 2945\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1605, $1585\,cm^{-1}$ ($C=C_{Ar}$). $C_{22}H_{23}NOS_2$ (381.55). Calcd. C 69.25, H 6.08, S 16.81; found C 69.41, H 5.83, S 16.64.

trans-N-Benzyl-4-(4-bromophenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**5f**)

Yield: 87%, m.p. 164–166°C. IR (KBr): $\nu = 2915, 2930, 2945\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1590, $1485\,cm^{-1}$ ($C=C_{Ar}$). $C_{21}H_{20}BrNS_2$ (430.42). Calcd. C 58.60, H 4.68, S 14.90; found C 58.42, H 4.79, S 15.01.

trans-N-(2-Phenylethyl)4-phenyl-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**6a**)

Yield: 91%, m.p. 175–177°C. IR (KBr): $\nu = 2940\,cm^{-1}$ (CH_2), $1655\,cm^{-1}$ (C=C), 1600, $1495\,cm^{-1}$ ($C=C_{Ar}$). $C_{22}H_{23}NS_2$ (365.55). Calcd. C 72.29, H 6.34, S 17.54; found C 71.97, H 6.41, S 17.64.

trans-N-(2-Phenylethyl)4-(4-methoxyphenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**6b**)

Yield: 89%, m.p. 171–173°C. IR (KBr): $\nu = 2945\,cm^{-1}$ (CH_2), $1640\,cm^{-1}$ (C=C), 1610, $1510\,cm^{-1}$ ($C=C_{Ar}$). $C_{23}H_{25}NOS_2$ (395.58). Calcd. C 69.83, H 6.37, S 16.21; found C 70.04, H 6.19, S 16.37.

trans-N-(2-Phenylethyl)4-(4-methylphenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**6c**)

Yield: 81%, m.p. 197–199°C. IR (KBr): $\nu = 2940\,cm^{-1}$ (CH_2), $1640\,cm^{-1}$ (C=C), 1605, $1515\,cm^{-1}$ ($C=C_{Ar}$). $C_{23}H_{25}NS_2$ (379.58). Calcd. C 72.78, H 6.64, S 16.89; found C 72.64, H 6.81, S 17.03.

trans-N-(2-Phenylethyl)4-(4-chlorophenyl)-4a,5,6,7-tetrahydro-4H-3,1-benzothiazine-2(1H)-thione (**6d**)

Yield: 87%, m.p. 197–199°C. IR (KBr): $\nu = 2910$, $2930\,cm^{-1}$ (CH_2), $1650\,cm^{-1}$ (C=C), 1600, $1490\,cm^{-1}$ ($C=C_{Ar}$). $C_{22}H_{22}ClNS_2$ (400.00). Calcd. C 66.06, H 5.54, S 16.03; found C 65.83, H 5.78, S 16.14.

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