Scientific paper

Ring Expansion of *N*-Aminobenzothiazolium Salts to Benzothiazines and Benzothiadiazines

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Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

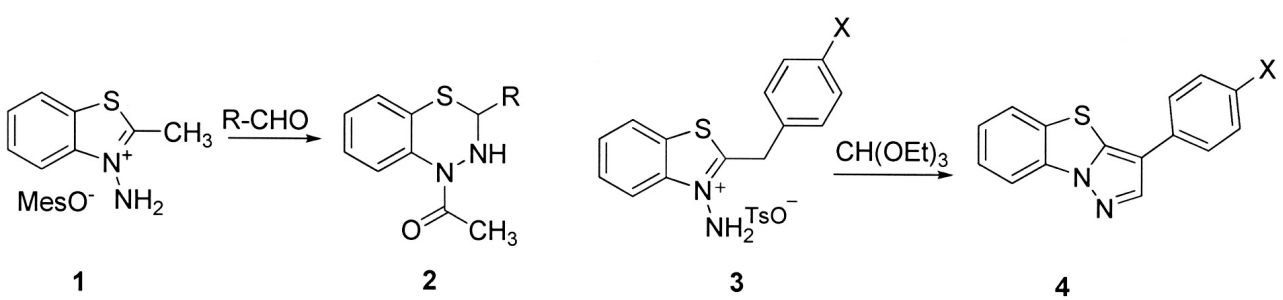
Abstract

N-amino-2-benzylbenzothiazinium salts when reacted with aldehydes were found to undergo ring expansion reactions to give either benzothiadiazines or benzothiazines. This ambident reactivity was found to be influenced by the conjugative nature of the aldehyde used.

Keywords: Ring expansion, thiadiazine, thiazine, ambident reactivity, reaction mechanism

1. Introduction

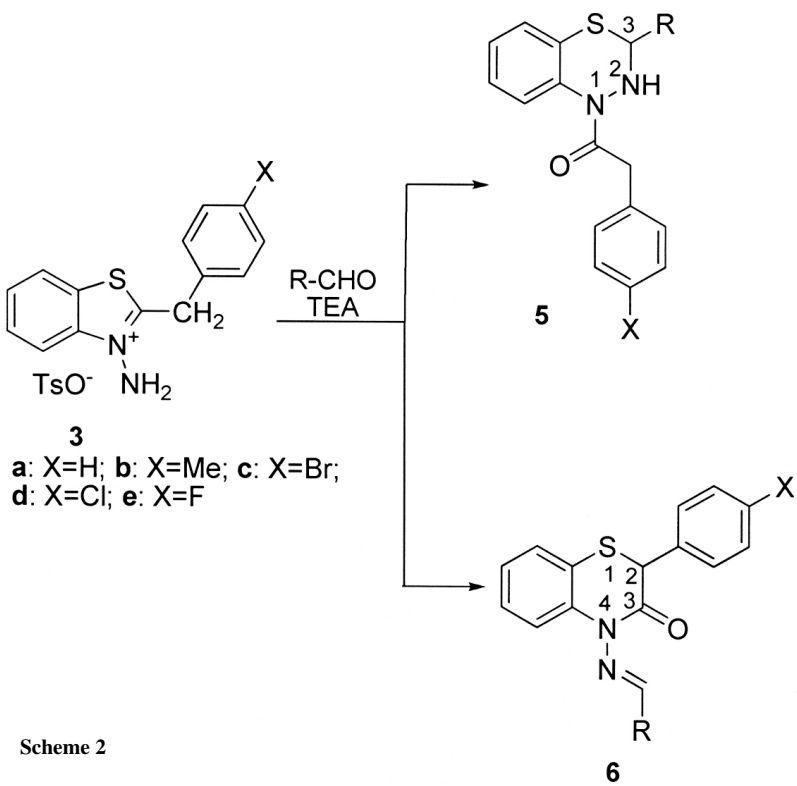
As mentioned in one of our recent publication,[1] very limited information is known concerning the chemistry of *N*-aminobenzothiazolium salts. Three decades ago, Tamura and his co-workers described that treatment of *N*-amino-2-methylbenzothiazolium mesylate (**1**) with aldehydes gives rise to a [1,3,4]benzothiazine derivative (**2**).[1,2] Quite recently we have published, furthermore, that benzyl substituted *N*-aminobenzothiazolium salts (**3**) related to (**1**) are convenient starting materials for cyclization to tricyclic fused pyrazoles (**4**) (Scheme 1).[1] As the benzyl substituted salts (**3**) in our hands contained an activated methylene group in the side chain, their conversion with aldehydes seemed of practical interest, which prompted us to extend our investigations into this direction.



Scheme 1

2. Results and Discussion

Reaction of butyraldehyde with benzyl substituted *N*-aminobenzothiazolium salts (**3**) containing different substituents on the aryl group proceeded similar to that described by Tamura *et al.*[2,3]



3
a: X=H; **b**: X=Me; **c**: X=Br;
d: X=Cl; **e**: X=F

Scheme 2

5	R	X	yield (%)
a	C_3H_7	Me	49
b	C_3H_7	H	48
c	C_3H_7	Cl	49
d	C_3H_7	F	25
e	C_3H_7	Br	10
f	cyclohexyl	H	23

6	R	X	yield (%)
a	C_3H_7	Br	36
b	4-CH_3-C_6H_4	Br	30
c	4-CH_3-C_6H_4	Cl	33
d	4-CH_3-C_6H_4	H	28
e	4-CH_3-C_6H_4	F	20
f	4-CH_3-C_6H_4	Me	64
g	4-CH_3O-C_6H_4	H	32
h	4-CH_3O-C_6H_4	Cl	20
i	C_6H_5	H	26

Thus, transformation of **3a,b,d,e** resulted in formation of benzothiadiazines **5a-d** in moderate yields (25–49%). Conversion of the *p*-bromophenyl derivative **3c** with butyraldehyde, however, under the same reaction conditions yielded a mixture of two components: besides the expected benzothiadiazine (**5e**), a benzothiazine compound (**6a**) was also obtained (Scheme 2).

In order to explore a more extended synthetic possibility of this new type of ring expansion, the *N*-amino salts **3a-e** were transformed also by aryl aldehydes. Unexpectedly, in these reactions no benzothiadiazines (**5**) were formed but, instead, benzothiazines **6b-h** were isolated from the reaction mixtures.

Analysis of the ^{1}H-NMR spectra of **5** and **6** clearly indicate the structural differences between the two compounds. The compound with the benzothiadiazine structure (**5**) possesses an isolated methylene group (singlet at 4.0 ppm) and two protons (NH at 3.62 ppm, H3 at 4.4 ppm) coupled to each other. Contrarily, two singlet protons (H2 at 4.76 and N=CH 8.87 ppm) characterize the benzothiazine structure in compound **6**.

Benzothiazines of related structure have been already described by Takamizawa[4] and, furthermore, similar ring transformation with benzothiazoles without any *N*-amino moiety has been observed by Florio *et al.*[5,6]

The observed ambident reactivity of **3** raised the question of a possible mechanism. The most plausible pathways of this dual behavior are illustrated in Fig 1.

Thus, most probably, the first step is reaction of the *N*-amino function of **3** with the aldehyde to give an intermediate bearing an *N*-azomethine side chain (**a**) which will be attacked by the hydroxide anion to give an addition product (**b**). In order to rationalize the later events involving ring transformations, one has to assume that this species undergoes deprotonation followed by an S–C cleavage to result in a ring opening to (**c**) which can adopt conformers (**d**) and (**f**). In conformer (**d**), an intramolecular attack ("A route") is favoured by the vicinity of the thiolate anion to the azomethine-carbon atom to yield (**e**) which can be shifted to the more stable tautomeric form (**5**). In the case of conformer (**f**), however, another cyclization ("B route") can occur: the sulphur atom can here attack the olefinic carbon atom adjacent to the aryl group to give (**g**) which, in the presence of air, can undergo spontaneous oxidation to **6**.

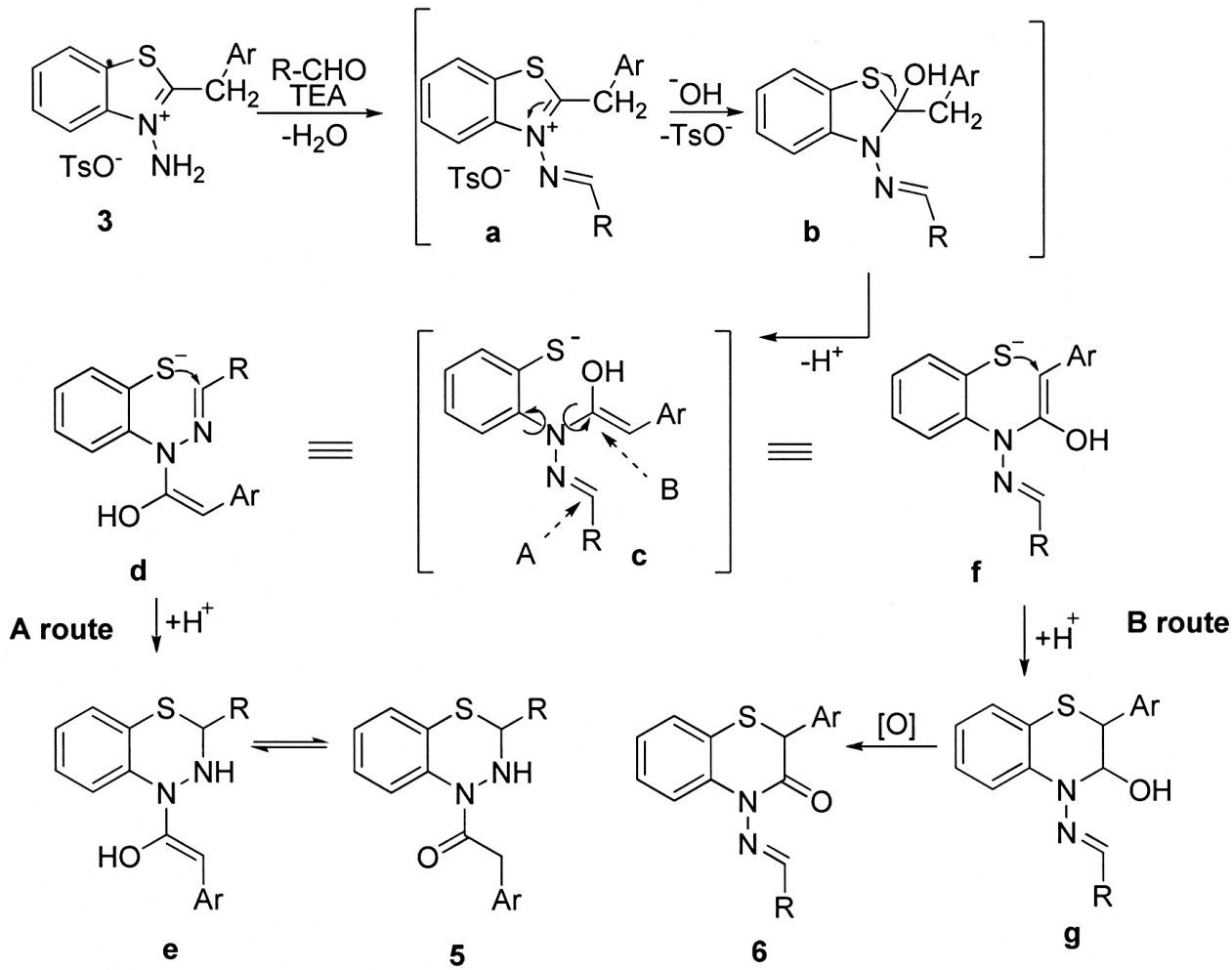


Fig 1. Possible reaction mechanism of the ring expansion of *N*-amino-2-benzylbenzothiazolium salts (**3**) to benzothiadiazines (**5**) and/or benzothiazines (**6**).

This mechanism supposes that the relative electrophilicities of the azomethine-carbon atom and the olefinic carbon atom against the thiolate nucleophile may play the main role to decide whether **5** or **6** are formed. The fact that with all aryl aldehydes the B route was observed seems to be in good accordance with this supposition as the conjugation with participation of the N1 atom of the ring and the aryl group deactivates the azomethine-carbon atom (*i.e.* this atom becomes partially negative). One can, however, also assume by comparing of the outcomes of most of the reactions carried out with butyraldehyde with those carried out with arylaldehydes that a steric hindrance of the aryl group might direct the nucleophilic attack to the olefinic carbon atom, whereas in the case of smaller substituents the azomethine-carbon atom takes part in the reaction.

In order to exclude or to support this possibility, amino salt **3a** was reacted with benzaldehyde and cyclohexyl aldehyde. These two aldehydes exert nearly similar steric hindrance, but their conjugative properties are entirely different. The finding that exlusively **5f** was formed with cyclohexyl aldehyde, whereas with benzaldehyde only **6i** was obtained seems to support the importance of the conjugation rather than the possible steric hindrance.

Upon these results one can conclude that the pathway of the experienced ring expansion of *N*-amino-2-benzylbenzothiazolium salts (**3**) strongly depends on the conjugation ability of the applied aldehyde. Thus, in the case of aliphatic or alicyclic aldehydes formation of thiadiazines is preferred, whereas in reactions with aryl aldehydes the reaction is directed towards formation of benzothiazines.

3. Experimental

Melting Points were determined on a Büchi apparatus and are uncorrected. The IR spectra were recorded on

a Thermo Nicolet Avatar 320 FT-IR spectrometer. NMR measurements were performed on Varian INOVA-200 or Varian INOVA-400 spectrometers equipped with a 5 mm inverse detection z-gradient probe. ^{1}H and ^{13}C NMR spectra were measured at room temperature (25 °C) in an appropriate solvent. ^{1}H and ^{13}C chemical shifts are expressed in ppm (δ) referenced to residual solvent signals. The elemental analysis has been carried out with an Elementar Vario EL III apparatus (at the Analytical Laboratory for Organic Chemistry, Chemical Research Center, Hungarian Academy of Sciences, H-1025 Budapest, Pusztaszeri út 59).

3. 1. General Procedure for Ring Expansion of *N*-aminobenzothiazolium Salts

To a mixture of a solution of the appropriate *N*-aminobenzothiazolium 4-methylbenzenesulfonate (**3**, 1 mmol) in acetonitrile (30 mL) and triethylamine (0.5 mL), the appropriate aldehyde (2 mmol) was added. The reaction mixture was heated under reflux and was monitored by TLC. After disappearance of the starting benzothiazolium salt (8–24 h), the obtained solution was evaporated onto *silica*. The product was then separated by flash chromatography using *silica* as adsorbent and hexane-ethyl acetate 10:1 as the eluent.

1-(3-Propyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)-2-*p*-tolylethanone (5a). This compound was obtained by starting from 3-amino-2-(4-methylbenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3b**, 1 mmol, 0.426 g) and butyraldehyde (0.2 mL) to give pale yellow crystals (0.160 g, 49%), mp 61–64 °C. *Anal*. Calcd for $C_{19}H_{22}N_2OS$ (326.15): C, 69.90; H, 6.79; N, 8.58; S, 9.82. Found: C, 70.09; H, 7.12; N, 8.48; S, 10.16. IR (KBr) ν_{max}: 3242, 2959, 1665, 1516, 1472, 1362, 1281, 1126, 1111, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.95 (3H, t, *J* = 7 Hz, C3"$\underline{H}_3$), 1.5 (2H, m, C2"$\underline{H}_2$), 1.65 and 1.84 (2H, m, C1"$\underline{H}_2$) 2.32 (3H, s, C$\underline{H}_3$'), 3.58 (1H, d, *J* = 7 Hz, N$\underline{H}$), 3.96 (2H, m, COC$\underline{H}_2$), 4.40 (1H, m, H3), 7.05 (3H, m, H5, H6, H7), 7.14 (2H, m, H3', H5'), 7.24 (2H, m, H2', H6'), 7.76 (1H, m, H8). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 18.7, 21.0, 37.0, 41.0, 63.4, 124.0, 124.1, 125.5, 126.1, 127.1, 129.0 (2C), 129.2 (2C), 131.9, 133.3, 136.3, 172.0.

2-Phenyl-1-(3-propyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)ethanone (5b). This compound was obtained by starting from 3-amino-2-benzyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.411 g) and butyraldehyde (0.2 mL) to give pale yellow crystals(0.149 g, (48%), mp 114–116 °C. *Anal*. Calcd for $C_{18}H_{20}N_2OS$ (312.13): C, 69.20; H, 6.45; N, 8.97; S, 10.26. Found: C, 69.44; H, 6.80; N, 8.91; S, 10.63. (KBr) ν_{max}: 3241, 2959, 1665, 1471, 1364, 1281, 1129, 914, 746 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.95 (3H, t, *J* = 6.5 Hz, C3"$\underline{H}_3$), 1.5 (2H, m, C2"$\underline{H}_2$), 1.62 and 1.82 (2H, m, C1"$\underline{H}_2$), 3.62 (1H, d, *J* = 7 Hz, H2), 4.0 (2H, m, C(O) C$\underline{H}_2$), 4.4 (1H, m, H3), 7.0–7.12 (3H, m, H5, H6, H7), 7.20–7.40 (5H, m, H2', H3', H4', H5', H6'), 7.76 (1H, d, *J* = 8 Hz, H8). ^{13}C NMR ($CDCl_3$) δ (ppm): 14.0 (C3"), 19.0 (C2"), 37.2 (C1"), 41.7 (C(O) C$\underline{H}_2$), 63.6 (C3), 124.3 and 124.4 and 125.8 (C5, C6, C8), 126.3 (C4a), 127.0 (C7), 127.3 and 127.4 and 128.8 and 129.4 (C1', C2', C3', C4', C5', C6'), 135.2 (C8a), 172.3 (C=O).

2-(4-Chlorophenyl)-1-(3-propyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)ethanone (5c). This compound was obtained by starting from 3-amino-2-(4-chlorobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3d**, 1 mmol, 0.445 g) and butyraldehyde (0.2 mL) to give pale yellow crystals (0.170 g 49%), mp 114–116 °C. *Anal*. Calcd for $C_{18}H_{19}ClN_2OS$ (346.09) C, 62.33; H, 5.52; N, 8.08; S, 9.24. Found: C, 62.29; H, 5.47; N, 8.03; S, 9.22. IR (KBr) ν_{max}: 3273, 2959, 1674, 1475, 1356, 1283, 1128, 1088, 804, 753 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.97 (3H, t, *J* = 7 Hz, C3"$\underline{H}_3$), 1.55 (2H, m, C2"$\underline{H}_2$), 1.62 and 1.82 (2H, m, C1"$\underline{H}_2$), 3.61 (1H, d, *J* = 7 Hz, N$\underline{H}$), 3.97 (2H, m, C(O) C$\underline{H}_2$, 4.44 (1H, m, H3), 7.0–7.10 (3H, m, H5, H6, H7), 7.20–7.40 (4H, m, H2', H3', H5', H6'), 7.71 (1H, m, H8). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 18.8, 37.0, 40.6, 63.3, 124.1, 124.2, 125.7, 125.9, 127.2, 127.3, 128.6 (2C), 130.5 (2C), 132.8, 133.5, 170.7.

2-(4-Fluorophenyl)-1-(3-propyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)ethanone (5d). This compound was obtained by starting from 3-amino-2-(4-flurorobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3e**, 1 mmol, 0.430 g) and butyraldehyde (0.2 mL) to give pale yellow crystals (0.170 g 49%), mp 130–131 °C. *HRMS* (EI): M^+, found: 330.1203. $C_{18}H_{19}FN_2OS$ required: 330.1202. IR (KBr) ν_{max}: 3274, 2960, 1669, 1511, 1475, 1434, 1358, 1279, 1217, 1127, 819, 754 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.96 (3H. t, *J* = 7 Hz, C3"$\underline{H}_3$), 1.53 (2H, m, C2"$\underline{H}_2$), 1.62 and 1.90 (2H, m, C1"$\underline{H}_2$) 3.62 (1H, d, *J* = 7 Hz, N$\underline{H}$), 3.96 (2H, m, C(O) C$\underline{H}_2$), 4.46 (1H, m, H3), 7.06 (5H, m, H5, H6, H7, H3', H5'), 7.30 (2H, m, H2', H6'), 7.74 (1H, m, H8). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 18.8, 37.1, 40.4, 63.4, 115.3 (2C, d, $^2J_{C,F}$ = 23.5 Hz), 124.0, 124.1 (C8, C6), 125.7, 126.1, 127.2, 130.6 (2C, d, $^3J_{C,F}$ = 9 Hz), 133.1, 162.0 (d, $^1J_{C,F}$ = 235 Hz), 171.8.

2-(4-Bromophenyl)-1-(3-propyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)ethanone (5e). This compound was obtained by starting from 3-amino-2-(4-bromobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3c**, 1 mmol, 0.49 g) and butyraldehyde (0.2 mL) to give pale yellow crystals (0.040 g 10%), mp 96–98 °C. *Anal*. Calcd for $C_{18}H_{19}BrN_2OS$ (391.33): C, 55.25; H, 4.89; N, 7.16; S, 8.19. Found: C, 55.15; H, 4.85; N, 7.15; S, 8.31.IR (KBr) ν_{max}: 3275, 2958, 1675, 1475, 1359, 1284, 1128, 1071, 1012, 752 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ

(ppm): 0.95 (3H, t, J = 6.5 Hz, C3"$\underline{H}_3$), 1.4–1.8 (4H, m, C2"$\underline{H}_2$, C1"$\underline{H}_2$), 3.61 (1H, d, J = 7 Hz, H2-N$\underline{H}$), 3.95 (2H, m, C(O) C$\underline{H}_2$), 4.44 (1H, m, H3), 7.0–7.12 (3H, m, H5, H6, H7), 7.23 (2H, m, H3', H5'), 7.46 (2H, m, H2', H6'), 7.74 (1H, m, H8). ^{13}C NMR ($CDCl_3$) d (ppm): 12.5, 18.0, 35.9, 39.8, 62.2, 119.8, 123.1, 123.2, 124.7, 126.2, 128.2, 129.9 (2C), 130.7 (2C), 133.1, 170.5.

1-(3-Cyclohexyl-2,3-dihydro-1*H*-benzo[*e*][1,3,4]thiadiazin-1-yl)-2-phenylethanone (5f). This compound was obtained by starting from 3-amino-2-benzyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.411 g) and cyclohexanecarbaldehyde (0.25 mL) to give pale yellow crystals (0.08 g, 23%), mp 136–137 °C. *Anal*. Calcd for $C_{21}H_{24}N_2OS$ (352.16): C, 71.55; H, 6.86; N, 7.95. Found: C, 71.40; H, 7.06; N, 7.83. IR (KBr) ν_{max}: 3275, 2931, 2841, 1688, 1474, 1440, 1352, 1279, 1119, 757 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.23 and 1.73 and 2.06 (11H, m, H-cyclohexyl), 3.60 (1H, d, J = 7 Hz, N$\underline{H}$), 3.98 (2H, m, COC$\underline{H}_2$), 4.45 (1H, dd, J = 7 + 12 Hz, H3), 7.06 (3H, m, H5, H6, H7), 7.28 (5H, m, H2', H3', H4', H5', H6'), 7.74 (1H, m, H8). ^{13}C NMR ($CDCl_3$) δ (ppm): 25.7, 25.2, 28.5, 29.4, 41.0, 42.2, 69.1, 123.9, 124.0, 125.5, 126.7, 127.4, 128.5 (2C), 129.2 (2C), 133.3, 135.2, 172.3.

(*E*)-2-(4-Bromophenyl)-4-(butylideneamino)-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6a). This compound was obtained by starting from 3-amino-2-(4-bromobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3c**, 1 mmol, 0.49 g) and butyraldehyde (0.2 mL) to give pale yellow crystals 0.140 g (36%), mp 103–105 °C,. *Anal*. Calcd for $C_{18}H_{17}BrN_2OS$ (388.02): C, 55.53; H, 4.40; N, 7.20; S, 8.24. Found: C, 55.20; H, 4.23; N, 7.11; S, 8.27. IR (KBr) ν_{max}: 2954, 2924, 1656, 1585, 1485, 1475, 1333, 1268, 1012, 751 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 1.05 (3H, t, J = 8, C3'$\underline{H}_3$), 1.71 (2H, m, C2'$\underline{H}_2$), 2.55 (2H, m, C1'$\underline{H}_2$), 4.70 (1H, s, H2), 7.03 (1H, t, J = 8 Hz, H7), 7.23 (2H, m, H3", H5"), 7.30 (3H, m, H5, H6, H8), 7.41 (2H, m, H2", H6"), 8.15 (1H, t, J = 5 Hz, N=C$\underline{H}$). ^{13}C NMR ($CDCl_3$) δ (ppm): 13.7, 19.2, 35.2, 46.9, 118.1, 119.9, 122.3, 124.1, 127.3, 128.1, 129.6 (2C), 131.8 (2C), 133.7, 138.8, 161.8, 169.2.

(*E*)-2-(4-Bromophenyl)-4-(4-methylbenzylideneamino)-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6b). This compound was obtained by starting from 3-amino-2-(4-bromobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3c**, 1 mmol, 0.49 g) and 4-methylbenzaldehyde (0.2 mL) to give pale yellow crystals (0.131 g, 30%), mp 178–180 °C. *HRMS* (EI): M$^+$, found: 436.0252. $C_{22}H_{17}BrN_2OS$ requires: 436.0245. IR (KBr) ν_{max}: 2912, 1648, 1605, 1484, 1338, 1011, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.40 (3H, s, C$\underline{H}_3$'), 4.76 (1H, s, H2), 7.05 (1H, t, J = 8 Hz, H7), 7.26 (6H, m, H3", H5", H3', H5', H8, H5), 7.34 (1H, t, J = 8 Hz, H6), 7.43 (2H, m, H2", H6"), 7.76 (2H, m, H2', H6'), 8.88 (1H, s, N=C$\underline{H}$). ^{13}C NMR (CDC-l_3) δ (ppm): 21.8, 47.6, 119.1, 120.6, 122.5, 124.6, 127.6, 128.2, 128.7 (2C), 129.7 (2C), 129.9 (2C), 130.7, 132.0 (2C), 133.8, 139.5, 142.7, 162.1, 166.2.

(*E*)-2-(4-Chlorophenyl)-4-(4-methylbenzylideneamino)-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6c). This compound was obtained by starting from 3-amino-2-(4-chlorobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3d**, 1 mmol, 0.445 g) and 4-methylbenzaldehyde (0.2 mL) to give pale yellow crystals (0.130 g, 33%), mp 158–161 °C. *Anal*. Calcd for $C_{22}H_{17}ClN_2OS$ (392.08): C, 67.25; H, 4.36; N, 7.13; S, 8.16. Found: C, 66.85; H, 4.27; N, 7.04; S, 8.27. IR (KBr) ν_{max}: 2911, 1648, 1605, 1489, 1337, 1090, 749 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.41 (3H, s, CH_3'), 4.76 (1H, s, H2), 7.03 (1H, dd, J = 8.2 + 7.5 Hz, H7), 7.21 (1H, dd, J = 8.0 + 7.5 Hz, H6), 7.26 (4H, m, H3', H5', H3", H5"), 7.31 (2H, m, H2", H6"), 7.35 (1H, d, J = 8.2 Hz, H8), 7.42 (1H, d, J = 8.0 Hz, H5), 7.76 (2H, m, H2', H6'), 8.87 (1H, s, N=CH). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.7 ($\underline{C}H_3$), 47.3 (C2), 118.9 (C5), 120.5 (C8a), 124.4 (C7), 127.4 (C6), 128.0 (C8), 128.5 (C2', C6'), 128.8 (C3", C5"), 129.4 (C2", C6"), 129.6 (C3', C5'), 130.5 (C1'), 133.0 (C1"), 134.2 (C4"), 139.3 (C4a), 142.5 (C4'), 162.0 (C3), 166.1 (N=$\underline{C}$H).

(*E*)-4-(4-Methylbenzylideneamino)-2-phenyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6d). This compound was obtained by starting from 3-amino-2-benzyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.411 g) and 4-methylbenzaldehyde (0.2 mL) to give **6d**, pale yellow crystals (0.105 g, 29%), mp 135–138 °C. *Anal*. Calcd for $C_{22}H_{18}N_2OS$ (358.11): C, 73.71; H, 5.06; N, 7.82; S, 8.95. Found: C, 73.35; H, 5.05; N, 7.78; S, 9.21. IR (KBr) ν_{max}: 3086, 3056, 2920, 1668, 1607, 1475, 1450, 1310, 1225, 765 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.41 (3H, s, C$\underline{H}_3$'), 4.82 (1H, s, H2), 7.05 (1H, t, J = 6 Hz, H7), 7.26 (10H, m, H3', H5', H3", H5", H2", H4", H6", H5, H6, H8), 7.77 (2H, m, H2', H6'), 8.92 (1H, s, N=C$\underline{H}$). ^{13}C NMR ($CDCl_3$) δ (ppm): 22.0, 48.0, 118.9, 121.0, 124.4, 127.3, 127.9 (2C), 128.1, 128.3, 128.4 (2C), 128.7 (2C), 129.5 (2C), 130.8, 134.6, 139.5, 142.4, 162.5, 165.8.

(*E*)-2-(4-Fluorophenyl)-4-(4-methylbenzylideneamino)-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6e). Starting from 3-amino-2-(4-flurorobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3e**, 1 mmol, 0.430 g) and 4-methylbenzaldehyde (0.2 mL) to give pale yellow crystals (0.075 g, 20%), mp 112–115 °C. *HRMS* (EI): M$^+$, found: 376.1055. $C_{22}H_{17}FN_2OS$ requires: 376.1046. IR (KBr) ν_{max}: 2927, 1653, 1603, 1506, 1476, 1330, 1229, 1161, 745 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.42 (3H, s, C$\underline{H}_3$'), 4.79 (1H, s, H2), 6.98 (2H, m, H2", H6") 7.06 (1H, t, J = 5 Hz, H7), 7.23 (1H, t, J = 5 Hz, H6), 7.27 (2H, m,

H3', H5'), 7.35 (2H, m, H3", H5"), 7.38 (1H, d, *J* = 5 Hz, H8), 7.43 (1H, d, *J* = 5 Hz, H5), 7.76 (2H, m, H2', H6'), 8.90 (1H, s, N=C<u>H</u>). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.8, 47.3, 115.6 (2C, d, $^2J_{C,F}$ = 26.5 Hz), 118.9, 120.7, 124.4, 127.3, 128.0, 128.5 (2C), 129.6 (2C), 129.8 (2C, d, $^3J_{C,F}$ = 9 Hz), 130.2, 130.5, 139.3, 142.5, 143.8, 162.5 (d, $^1J_{C,F}$ = 245 Hz), 166.0.

(*E*)-4-(4-Methylbenzylideneamino)-2-*p*-tolyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6f). This compound was obtained by starting from 3-amino-2-(4-methylbenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.426 g) and 4-methylbenzaldehyde (0.2 mL) to give pale yellow crystals (0.238 g, 64%), mp 155–157 °C. *Anal*. Calcd for $C_{23}H_{20}N_2OS$ (320.08): C, 74.16; H, 5.41; N, 7.52; S, 8.61. Found: C, 74.00; H, 5.43; N, 7.48; S, 8.65. IR (KBr) ν_{max}: 2915, 1651, 1605, 1510, 1476, 1446, 1333, 750, 503 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 2.25 (3H, s, C<u>H</u>$_3$"), 2.40 (3H, s, C<u>H</u>$_3$'), 4.80 (1H, s, H2), 7.04 (1H, t, *J* = 8 Hz, H7), 7.11 (2H, m, H3", H5"), 7.24 (1H, t, *J* = 8 Hz, H6), 7.26 (2H, m, H2", H6"), 7.27 (2H, m, H3', H5'), 7.35 (1H, d, *J* = 8 Hz, H8), 7.43 (1H, d, *J* = 8 Hz, H5), 7.75 (2H, m, H2', H6'), 8.92 (1H, s, N=C<u>H</u>). ^{13}C NMR ($CDCl_3$) δ (ppm): 21.3, 21.9, 47.9, 119.1, 121.4, 124.5, 127.4, 128.1, 128.2 (2C), 128.7 (2C), 129.6 (2C), 129.8 (2C), 130.9, 131.7, 138.2, 139.7, 142.6, 162.8, 166.0.

(*E*)-4-(4-Methoxybenzylideneamino)-2-phenyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6g). This compound was obtained by starting from 3-amino-2-benzyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.411 g) and 4-methoxybenzaldehyde (2 mmol, 0.272 g) to give pale yellow crystals (0.120 g, 32%), mp 135–137 °C. *Anal*. Calcd for $C_{22}H_{18}N_2O_2S$ (374.11): C, 70.57; H, 4.85; N, 7.48; S, 8.56. Found: C, 70.32; H, 5.06; N, 7.46; S, 8.51. IR (KBr) ν_{max}: 2916, 1658, 1599, 1514, 1316, 1260, 1168, 1030, 828, 752 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.85 (3H, s, OC<u>H</u>$_3$), 4.81 (1H, s, H2), 6.96 (2H, m, H3', H5'), 7.03 (1H, t, *J* = 8 Hz, H7), 7.31 (8H, m, H2", H3", H4", H5", H6", H5, H6, H8), 7.82 (2H, m, H2', H6'), 8.83 (1H, s, N=C<u>H</u>). ^{13}C NMR ($CDCl_3$) δ (ppm): 47.8, 55.4, 114.3 (2C), 118.7, 120.8, 124.1, 125.9, 127.1, 128.0 (2C), 128.1, 128.6 (2C), 130.1, 130.2 (2C), 134.6, 139.4, 162.3, 162.6, 165.8.

(*E*)-2-(4-Chlorophenyl)-4-(4-methoxybenzylideneamino)-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6h). This compound was obtained by starting from 3-amino-2-(4-chlorobenzyl)-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3d**, 1 mmol, 0.445 g) and 4-methoxybenzaldehyde (2 mmol, 0.272 g) to give pale yellow crystals (0.082 g, 20%), mp 145–147 °C. *Anal*. Calcd for $C_{22}H_{17}ClN_2O_2S$ (408.07): C, 64.62; H, 4.19; N, 6.85; S, 7.84. Found: C, 64.37; H, 4.26; N, 6.88; S, 8.24. IR (KBr) ν_{max}: 2930, 1650, 1598, 1514, 1489, 1315, 1258, 1170, 1028, 837, 756 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.84 (3H, s, OC<u>H</u>$_3$), 4.80 (1H, s, H2), 6.98 (2H, m, H3', H5'), 7.05 (1H, t, *J* = 8 Hz, H7), 7.21 (1H, d, *J* = 8 Hz, H8), 7.30 (5H, m, H6, H2", H3", H5", H6"), 7.41 (1H, d, *J* = 8 Hz, H5), 7.82 (2H, m, H2', H6'), 8.80 (1H, s, N=C<u>H</u>). ^{13}C NMR ($CDCl_3$) δ (ppm): 47.1, 55.4, 114.3 (2C), 118.8, 120.4, 124.3, 125.7, 127.3, 128.0, 128.8 (2C), 129.4 (2C), 130.3 (2C), 133.1, 134.1, 139.2, 161.9, 162.8, 166.2.

(*E*)-4-(Benzylideneamino)-2-phenyl-2*H*-benzo[*b*][1,4]thiazin-3(4*H*)-one (6i). This compound was obtained by starting from 3-amino-2-benzyl-1,3-benzothiazol-3-ium 4-methylbenzenesulfonate (**3a**, 1 mmol, 0.411 g) and benzaldehyde (2 mL) to give pale yellow crystals (0.089 g, 26%), mp 109–110 °C. *Anal*. Calcd for $C_{21}H_{16}N_2OS$ (344.10): C, 73.23; H, 4.68; N, 8.13. Found: C, 72.95; H, 4.44; N, 8.12. IR (KBr) ν_{max}: 3029, 1671, 1470, 1450, 1444, 1308, 1226, 1214, 756 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 4.82 (1H, s, H2), 7.05 (1H, t, *J* = 8 Hz, H7), 7.22 (1H, t, *J* = 8, H6), 7.4–7.5 (10H, m, H5, H8, H2", H3", H4", H5", H6', H3', H4', H5'), 7.86 (2H, m, H2', H6'), 9.02 (1H, s, N=C<u>H</u>). ^{13}C NMR ($CDCl_3$) δ (ppm): 47.6, 118.5, 120.6, 123.9, 126.7, 127.5 (2C), 127.6, 127.7, 127.9 (2C), 128.1 (2C), 128.3(2C), 131.2, 133.0, 134.0, 139.0, 162.1, 164.6.

4. Acknowledgment

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5. References

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Povzetek

Reakcije *N*-amino-2-benzilbenzotiazolijevih soli z aromatskimi aldehidi vodijo do razširitve obroča pri čemer nastanejo ustrezni benzotiadiazini ali benzotiazini. Substituenti na aromatskem obroču aldehida imajo zmeren vpliv na reaktivnost.