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SYNTHESIS AND PROPERTIES OF *sym*-TRIAZINE DERIVATIVES. 18*. SYNTHESIS OF N-SUBSTITUTED 2,4-DIAMINO-6-(BENZOTHIAZOLYL-2-THIOMETHYL)-*sym*-TRIAZINES

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The condensation of methyl benzothiazolyl-2-thioacetate with N-substituted biguanides in the presence of sodium methylate gave 2-amino-4-(RR'-amino)-6-(benzothiazolyl-2-thiomethyl)-sym-triazines. In a number of cases the 1,1-disubstituted 5-(benzothiazolyl-2-thioacetyl)biguanides could also be separated and these could be cyclized by refluxing in DMF to the corresponding substituted sym-triazines described. The latter type of compound was also synthesized by treating 2-amino-4-trichloromethyl-6-(benzothiazolyl-2-thiomethyl)-sym-triazine with primary and secondary aliphatic and heterocyclic amines or by the reaction of N-substituted 2,4-diamino-6-chloromethyl-sym-triazines with 2-mercaptobenzothiazole.

Keywords: benzothiazole, biguanides, 2,4-diamino-*sym*-triazines, condensation.

There are literature reports that benzothiazolyl substituted *sym*-triazines show high antimicrobial and fungicidal activity [2-4] and are also used as efficient antioxidants and stabilizers for hydrocarbon fuels, lubricants, and polymeric materials [5-8]. Methods are known for the preparation of such bisheterocyclic compounds based on the reaction of chloro substituted *sym*-triazines with amines and mercaptans of the benzothiazole series [2-4, 9-11].

In a continuation of our investigation of the synthesis of heteryl substituted *sym*-triazines [11-14] we now report the preparation of N-substituted 2,4-diamino-*sym*-triazines which contain the benzothiazolyl-2-thiomethyl fragment.

It is known [12, 13, 15] that N-substituted 2,4-diamino-6-alkyl(aryl, heteryl)-*sym*-triazines are formed via the condensation of biguanides with acid derivatives like acid chlorides, esters, anhydrides, and imino esters. To synthesize the heterocycles indicated above we have used the condensation of methyl benzothiazolyl-2-thioacetate (**1**) with N-substituted biguanide hydrochlorides **2a-j** in the presence of base (method A) (Scheme1).

It was found that improved yields (see Table 1) of the N-substituted 2,4-diamino-6-(benzothiazolyl-2-thiomethyl)-*sym*-triazines **3a-j** can be achieved by refluxing the reagents in methanol in the presence of sodium methylate at a molar ratio of ester **1**: biguanide hydrochloride **2a-j**: MeONa of 1: 1: 1.25. It should be noted that the reaction time and the yields of the target *sym*-triazines depend on the nature of the substituent in the starting

* For Communication 17 see [1].

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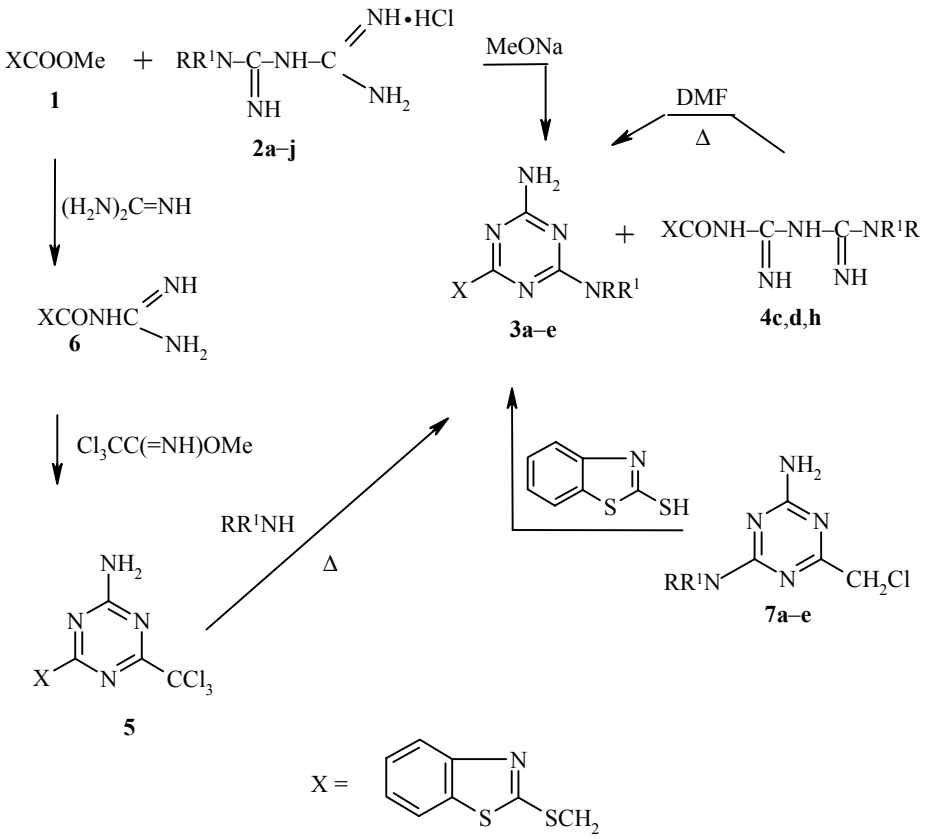
Scheme1



2-4 a R = Me, R^1 = H; **b** R = R^1 = Me; **c** R = Me, $R^1 = C_{18}H_{37}$; **d** R = R^1 = Bu; **e** R = *cyclo*-C_6H_{11}, R^1 = H; **f** R = Ph, R^1 = H; **g** R = 4-MeC_6H_4, R^1 = H; **h** R = R^1 = $PhCH_2$; **i** RR^1N = morpholino; **j** RR^1N = piperidino; **k** R = C_8H_{17}, R^1 = H; **l** R = furfuryl, R^1 = H; **7 a** R = R^1 = Me; **b** R = Ph, R^1 = H; **c** R = 4-MeC_6H_4, R^1 = H; **d** RR^1N = morpholino; **e** RR^1 = piperidino

biguanides. For example, with the use of the biguanide hydrochlorides **2a,b,e,i,j**, the corresponding 2,4-diamino-*sym*-triazines are formed in good yields (78-86%) after refluxing the reaction mixture in methanol for 8-10 h. The *sym*-triazines **3f,g** were prepared in 64-68% yields by heating the ester **1** with N-phenyl- (**2f**) and N-(p-tolyl)biguanide (**2g**) for 15-16 h. For the preparation of the *sym*-triazines **3c,d,h** from the N-methyl-N-octadecyl- (**2c**), N,N-dibutyl- (**2d**), and N,N-dibenzylbiguanide (**2h**) hydrochlorides a more prolonged heating was required (22-24 h); moreover, the yields of the indicated compounds did not exceed 45-52% and significant amounts (28-34%) of the 1,1-disubstituted 5-(benzothiazolyl-2-thioacetyl)biguanides **4c,d,h** were separated from the reaction mixtures. Evidently this is related to the significant steric strain caused by the bulky substituents in the indicated biguanides.

With prolonged refluxing in DMF the 5-acylbiguanides **4c,d,h** cyclize to the corresponding 2,4-diamino-*sym*-triazines **3c,d,h**. The formation of a similar 5-acylbiguanide when treating 5-nitrofuran-2-carboxylate ester with N-(4-nitrophenyl)biguanide and its conversion to 2-amino-4-(4-nitroanilino)-6-(5-nitrofuryl-2)-*sym*-triazine in low yield has been reported previously in the literature [16].

When the reaction of the ester **1** with the biguanide hydrochlorides **2b,i** was carried out in the presence of an equimolar amount of MeONa in refluxing methanol for 8 h the corresponding *sym*-triazines **3b,i** were obtained in low yields (44-47%) and a significant amount of the starting ester **1** was also separated from the reaction mixture.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	Found, % / Calculated, %				mp, °C*	R_f (solvent system)	^{1}H NMR spectrum, δ, ppm (*J*, Hz)					Yield, % (preparation method)
		C	H	N	S			CH_2S (2H, s)	NH_2 (2H, br. s)	NH (1H, br. s)	Benzothiazole ring protons (4H, m)	Other protons	
1	2	3	4	5	6	7	8	9	10	11	12	13	14
3a	$C_{12}H_{12}N_6S_2$	47.66 / 47.84	4.02 / 3.94	27.81 / 27.63	20.66 / 21.05	154.0-155.5	0.32 (a)	3.95	6.38	5.64	7.54-7.62	3.36 (3H, br. s, CH_3N)	73 (A)
3b	$C_{13}H_{14}N_6S_2$	87.88 / 49.05	4.48 / 4.40	26.60 / 26.41	20.02 / 20.12	141-143	0.52 (a)	3.90	6.92	—	7.65-7.92	3.25 (6H, d, *J* = 2.5, $(CH_3)_2N$)	86 (A), 75 (B), 84 (C)
3c	$C_{30}H_{48}N_6S_2$	64.62 / 64.74	8.57 / 8.63	15.29 / 15.11	11.72 / 11.51	148-149	0.20 (a)	4.25	6.78	—	7.90-8.02	1.12 (3H, t, CH_3); 1.32-1.80 (32H, m, CH_2); 3.50 (3H, s, CH_3N); 3.90 (2H, t, CH_2N)	45 (A)
3d	$C_{19}H_{26}N_6S_2$	56.60 / 56.72	6.41 / 6.46	21.10 / 20.89	15.95 / 15.92	56.0-57.5	0.37 (a)	4.18	6.54	—	7.64-7.75	1.15 (6H, t, $2CH_3$); 1.35-1.88 (8H, m, $4CH_2$); 3.74 (4H, m, $2CH_2N$)	44 (A), 76 (B)
3e	$C_{17}H_{20}N_6S_2$	54.92 / 4.84	5.50 / 5.37	22.33 / 22.58	17.32 / 17.20	229-230	0.22 (b)	4.04	7.02	6.05	7.84-8.06	1.84-2.38 (11H, m, CH_2, CH)	74 (A), 70 (B)

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12	13	14
3f	$C_{17}H_{14}N_6S_2$	55.62 55.73	3.77 3.82	22.80 22.95	17.60 17.48	223-224	0.32 (b)	3.88	6.68	5.58	7.74-7.90	6.92-7.04 (5H, m, H_{Ph})	87 (A) 78 (C)
3g	$C_{18}H_{16}N_6S_2$	56.95 56.84	4.12 4.21	21.91 22.10	17.05 16.84	119-120	0.40 (b)	4.10	6.45	5.71	7.94-8.10	2.04 (3H, s, CH_3); 6.88-7.04 (4H, m, H_{Ar})	62 (A), 80 (C)
3h	$C_{25}H_{22}N_6S_2$	63.95 63.83	4.52 4.68	18.01 17.87	13.54 13.62	254-255	0.50 (b)	3.93	6.80	—	7.67-7.80	3.25 (4H, s, 2 NCH_2H_{Ph}); 6.96-7.14 (10H, m, H_{Ph})	48 (A)
3i	$C_{15}H_{16}N_6OS_2$	49.91 50.00	4.52 4.44	23.51 23.33	17.62 17.78	158-159	0.51 (a)	4.33	6.88	—	7.88-8.02	3.34-3.72 (8H, m, $4CH_2$)	82 (A), 80 (B), 92 (C)
3j	$C_{16}H_{18}N_6S_2$	53.44 53.63	5.11 5.03	23.35 23.46	18.08 17.88	154-156	0.57 (a)	4.44	6.94	—	7.64-7.98	3.48-3.68 (10H, m, $5CH_2$)	76 (A), 70 (B), 88 (C)
3k	$C_{19}H_{26}N_6S_2$	56.83 56.72	6.38 6.46	20.77 20.89	16.04 15.82	162-163	0.44 (b)	3.94	6.60	5.63	7.52-7.67	1.05 (3H, t, CH_3); 1.30-1.52 (12H, m, $6CH_2$), 3.84 (2H, m, CH_2N)	64 (B)
3l	$C_{16}H_{14}N_6OS_2$	52.02 51.89	3.69 3.78	22.88 22.70	17.16 17.30	105.0-106.5	0.67 (b)	4.20	6.50	5.55	7.58-7.72	3.52 (2H, s, CH_2N); 6.58 (1H, dd, 3-H_{Fur}, J_{35} = 0.7); 6.84 (1H, dd, 4-H_{Fur}, J_{34} = 3.3); 7.72 (1H, dd, 5-H_{Fur}, J_{45} = 1.8)	76 (B)
5	$C_{12}H_8Cl_3N_5S_2$	36.80 36.69	1.95 2.04	18.02 17.83	16.18 16.30	172.0-173.5	0.34 (a)	3.94	6.68	—	7.67-7.84	—	78

* Compounds were crystallized as follows: **3a** from ethanol; **3b,e,k,l** from a mixture of 2-propanol–water (1:1.5); **3c** from a mixture of acetone–hexane (3:1); **3d** from 1-butanol; **3f** from a mixture of DMF–water (1:2); **3g** from a mixture of methyl cellosolve–water (1.5:1); **3h** from a mixture of ethanol–water (4:1); **3i** from a mixture of dioxane–water (2:1); **3j** from a mixture of benzene–hexane (3:1); and **5** from a mixture of 2-propanol–water (2:1).

It was found that exchange of methanol for a higher boiling solvent (ethanol, dioxane, 1-butanol, methyl cellosolve) did not lead to a marked increase in the yields of the 2,4-diamino-*sym*-triazines **3a-j**. At the same time, the use of two equivalents of sodium methylate in the condensation of ester **1** with the biguanide hydrochlorides **2a,b,f,i** leads to a lowering of the yield of the corresponding *sym*-triazines **3a,b,f,i** (up to 50-54%) and to the formation of unidentified, high melting side products (mp >300°C) which were poorly soluble in the majority of organic solvents.

It has previously been shown [14, 17, 18] that the reaction of 2-amino-4-trichloromethyl-*sym*-triazines with primary and secondary aliphatic amines gives the N-substituted 2,4-diamino-*sym*-triazines as a result of nucleophilic substitution of the CCl_3 group. In our work we used this method to prepare the *sym*-triazines **3b,d,e,i,l**. For this purpose we used the reaction of 2-amino-6-(benzothiazolyl-2-thiomethyl)-4-trichloromethyl-*sym*-triazine (**5**) with aliphatic and heterocyclic amines (method B).

The starting trichloromethyl-*sym*-triazine **5** was synthesized in 78% yield by the condensation of equimolar amounts of N-(benzothiazolyl-2-thioacetyl)guanidine (**6**) and the methyl imino ester of trichloroacetic acid in absolute ethanol. 2-Amino-4-dimethylamino-*sym*-triazine **3b** was obtained in 75% yield by passing gaseous dimethylamine into a solution of the *sym*-triazine **5** in DMF at 150-155°C. The best yield (68-80%) of the N-substituted 2,4-diamino-*sym*-triazines **3d,e,i-l** was achieved by heating the *sym*-triazine **5** at 140-155°C with an excess of the corresponding amines in dioxane or DMF under pressure.

In order to prepare the N-substituted 2,4-diamino-*sym*-triazines **3b,f,g,i,j** we have also used the reaction of the N-substituted 2,4-diamino-6-chloromethyl-*sym*-triazines (**7a-e**) with 2-mercaptobenzothiazole (method C). The reaction was performed by refluxing (4-5 h) the reagents in aqueous ethanol in the presence of a small excess of base. Under these conditions the *sym*-triazines indicated above are formed in 78-92 % yields.

The characteristics for the *sym*-triazines synthesized **3a-l** and **5** are given in Table 1. The composition and the structure of these compounds were confirmed from elemental analytical data and from IR and ^{1}H NMR spectroscopy. Thus the IR spectra show absorption maxima of varying intensity characteristic of stretching (1565-1550, 1530-1520, 1440-1425 cm^{-1}), breathing (1115-1110, 1015-1000 cm^{-1}), out of plane (815-800 cm^{-1}) and in plane (730-695 cm^{-1}) straining vibrations of the *sym*-triazine ring [12-14, 18-21]. In the spectrum of the trichloromethyl-*sym*-triazine **5** these bands are shifted to low frequency when compared with the spectra of the 2,4-diamino-*sym*-triazines **3a-l**. Along with the vibrations indicated there are also absorption bands characteristic of benzothiazole fragments [20]: 1605-1595, 1530-1515, 1465-1455, 1395-1380 (ν condensed thiazole ring), 1160-1100 (β CH), 1080-1065 (thiazole breathing vibration), and at 950-930 (γ CH) and 800-785 cm^{-1} (β ring).

There are two broad absorption bands in the range 3460-3340 cm^{-1} (ν_{as} NH) and 3190-3120 cm^{-1} (ν_s NH) in the NH stretching band region of the spectra of compounds **3a-l** and **5**. Such a position and the nature of the doublet for the NH stretching vibration indicates the presence of a strong hydrogen bond [14, 17, 19] in these compounds. The strong absorption maxima in the range 1620-1665 cm^{-1} are assigned to NH scissoring vibrations of the primary amino groups and this is typical of associated amino derivatives of *sym*-triazine [12, 14, 22].

The spectra of the N-substituted 2,4-diamino-*sym*-triazines **3a,e-g,k,l** also show weak absorption bands in the region 3370-3300 cm^{-1} (ν_s NH) and absorption bands of varying intensity in the range 1525-1510 cm^{-1} (NH scissoring vibrations) which are assigned to vibrations of the secondary heteroaromatic amino groups [11, 13, 14, 18, 23].

The ^{1}H NMR spectra of the synthesized *sym*-triazines (see Table 1) show signals for the primary amino group protons as broadened singlets with an intensity of two proton units in the range 6.15-7.02 ppm [12-14]. The signals for the protons of the secondary NH groups in the spectra of compounds **3a,e-g,k,l** appear as broadened singlets in the range 5.50-6.05 ppm and are typical of *sym*-triazine amino derivatives of this type [11, 14]. The protons of the benzothiazole fragments appear as multiplet signals at 7.40-8.14 ppm. The signals for the protons of the thiomethylene groups are observed as singlets in the range 3.88-4.25 ppm for all of these compounds.

EXPERIMENTAL

IR spectra were taken on a Bruker IFS-48 instrument for KBr tablets or as a suspension in vaseline oil. ^{1}H NMR spectra were recorded on a Bruker WP-250 (250 MHz) spectrometer for DMSO-d_6 solutions using TMS internal standard. Monitoring of the course of the reaction and the purity of the compounds obtained was performed using TLC on Brockmann activity grade III Al_2O_3 in the solvent systems benzene–methanol 20:1 (a) and benzene–2-propanol, 10:1 (b) and visualized using iodine vapor.

The characteristics of the synthesized compounds are given in Table 1.

The starting methyl benzothiazolyl-2-thioacetate (**1**) [24, 25], the N-substituted biguanides **2a-j** [26-28] and N-substituted 2,4-diamino-6-chloromethyl-*sym*-triazines **7a-e** [27, 29] were prepared as indicated in the reported work.

N-Substituted 2,4-Diamino-6-(benzothiazolyl-2-thiomethyl)-*sym*-triazines (3a,b,e-g,i-j). A. The biguanide hydrochloride **2a,b,e-g,i-j** (20 mmol) was added portionwise to a stirred solution of sodium methylate which had been prepared from sodium (0.57 g, 25 mmol) in absolute methanol (75 ml). The reaction mixture was stirred for 0.5 h at 20°C, the ester **1** (4.78 g, 20 mmol) was added portionwise, the product was refluxed with stirring until the starting ester **1** had disappeared (8-10 h for the preparation of the *sym*-triazines **3a,b,e,i,j** or 15-16 h for the *sym*-triazines **3f,g** according to TLC), and then evaporated to dryness at reduced pressure. The residue was washed with water, dried, and crystallized from the appropriate solvent (see Table 1).

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-(N-methyloctadecylamino)-6-*sym*-triazine (3c) and 5-(Benzothiazolyl-2-thioacetyl)-1-methyl-1-octadecylbiguanide (4c). A. The biguanide hydrochloride **2c** (8.07 g, 20 mmol) was added portionwise to a stirred solution of sodium methylate which had been prepared from sodium (0.57 g, 25 mmol) in absolute methanol (100 ml). The reaction mixture was stirred for 0.5 h at 20°C, cooled to 0°C, and the NaCl residue was filtered off and washed on the filter with absolute methanol (20 ml). The ester **1** (4.78 g, 20 mmol) was added to the filtrate, mixture was refluxed with stirring for 22-24 h (monitored using TLC until the disappearance of the starting ester **1** from the reaction mixture) and then cooled to -5°C and held at this temperature for 0.5 h. The precipitate was filtered off, washed on the filter with cold methanol (20 ml), dried, and crystallized from a mixture of acetone–hexane (3:1) to give the product **3c** (5.0 g, 45%).

The filtrate was evaporated to dryness under reduced pressure and the residue was crystallized from a mixture of 2-propanol–water (2:1) to give the product **4c** (3.9 g, 34%); mp 64-66°C, R_f 0.44 (b). IR spectrum (KBr), ν, cm^{-1}: 1625, 1645 (C=N), 1690 (C=O), 3325-3350 (NH). ^{1}H NMR spectrum, δ, ppm: 8.84 (1H, br. s, CONH); 7.80-7.72 (4H, m, H_{arom}); 6.38 (H, br. s, NH); 6.04 (1H, br. s, NH); 4.08 (2H, s, CH_2S); 3.84 (2H, t, CH_2N); 3.45 (3H, s, MeN): 1.87-1.30 (32H, m, 16 CH_2); 1.12 (3H, t, CH_3). Found, %: C 62.58; H 8.80; N 14.82; S 11.04. $C_{30}H_{50}N_6OS_2$. Calculated, %: C 62.71; H 8.71; N 14.63; S 11.15.

A solution of the 5-acylbiguanide **4c** (1.65 g, 2.9 mmol) in DMF (15 ml) was refluxed for 3 h, cooled to 20°C, and poured into iced water (70 ml). The precipitate was filtered off, dried, and crystallized from a mixture of acetone–hexane (3:1) to give the *sym*-triazine **3c** (1.2 g, 75%).

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-dibutylamino-*sym*-triazine (3d) and 5-(Benzothiazolyl-2-thioacetyl)-1,1-dibutylbiguanide (4d) were prepared similarly from the biguanide hydrochloride **2d**. The 5-acylbiguanide **4d** (yield 28%) was obtained from the filtrate; mp 108-109°C (heptane–2-propanol, 4:1), R_f 0.18 (a). ^{1}H NMR spectrum, δ, ppm: 9.04 (1H, br. s, CONH); 7.70-7.61 (4H, m, H_{arom}); 6.54 (2H, br. s, NH); 6.04 (1H, br. s, NH); 3.90 (2H, s, CH_2S); 3.72 (2H, t, CH_2N); 1.54-1.33 (8H, m, 4 CH_2); 1.16 (6H, t, 2 CH_3). Found, %: C 54.14; H 6.80; N 19.85; S 15.37. $C_{19}H_{28}N_6OS_2$. Calculated, %: C 54.28; H 6.66; N 20.00; S 15.23.

Refluxing the 5-acylbiguanide **4d** in DMF for 2 h gave the *sym*-triazine **3d** in 80% yield.

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-dibenzylamino-*sym*-triazine (3h) and 5-(Benzothiazolyl-2-thioacetyl)-1,1-dibenzylbiguanide (4h) were prepared similarly from the biguanide hydrochloride **2h**. The 5-acylbiguanide **4h** was separated from the filtrate in 30% yield; mp 154-156°C (2-propanol–water, 1:1), R_f 0.21 (b). IR spectrum (KBr), ν, cm^{-1}: 1630; 1645 (C=N); 1685 (C=O); 3345-3360 (NH). Found, %: C 61.58; H 5.03; N 17.05; S 13.25. $C_{25}H_{24}N_6OS_2$. Calculated, %: C 61.47; H 4.92; N 17.21; S 13.11.

Refluxing the 5-acylbiguanide **4h** in DMF for 4.5 h gave the *sym*-triazine **3h** in 76% yield.

N-(Benzothiazolyl-2-thioacetyl)guanidine (6). Guanidine hydrochloride (2.38 g, 25 mmol) was added to a stirred solution of sodium methylate which had been prepared from sodium (0.57 g, 25 mmol) in methanol (80 ml). The reaction mixture was refluxed with stirring for 0.5 h and cooled to 20°C. A solution of the ester **1** (5.97 g, 25 mmol) in absolute methanol (50 ml) was added dropwise and the product was stirred for 6 h and evaporated to dryness under reduced pressure. The residue was washed with benzene (3 × 10 ml) and crystallized from aqueous ethanol to give the guanidine **6** (5.50 g, 87%); mp 97-98.5 (decomp.), R_f 0.42 (a). Found, %: C 45.19; H 3.94; N 20.87; S 24.34. $C_9H_{10}N_4OS_2$. Calculated, %: C 45.10; H 3.78; N 21.04; S 24.07.

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-trichloromethyl-*sym*-triazine (5). A mixture of the guanidine **6** (3.81 g, 15 mmol) and the methyl imino ester of trichloroacetic acid (2.64 g, 15 mmol) in absolute methanol (45 ml) was refluxed with stirring for 3 h, cooled to 20°C, and poured into iced water (150 ml). The precipitate was filtered off, dried, and crystallized from a mixture of 2-propanol–water (2:1) to give the *sym*-triazine **5** (4.59 g).

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-dimethylamino-*sym*-triazine (3b). B. A stream of dry dimethylamine was passed for 1 h through a stirred solution of the *sym*-triazine **5** (1.96 g, 5 mmol) in anhydrous DMF (40 ml) at 150-155°C. Solvent was removed under reduced pressure and the residue was washed with ether (2 × 15 ml) and crystallized from a mixture of 2-propanol–water (1:1.25) to give the *sym*-triazine **3b** (1.19 g).

2-Amino-6-(benzothiazolyl-2-thiomethyl)-4-cyclohexylamino-*sym*-triazine (3e). B. A mixture of the *sym*-triazine **5** (3.14 g, 8 mmol) and cyclohexylamine (5.54 g, 56 mmol) in anhydrous dioxane (45 ml) was held at 140-145°C for 6 h in a sealed ampule. After cooling to 20°C, the contents of the ampule was poured into iced water (150 ml). The precipitate was filtered off, washed on the filter with water, dried, and crystallized from a mixture of 2-propanol–water (1:1.5) to give the *sym*-triazine **3e** (2.08 g).

Similarly, the reaction of the *sym*-triazine **5** with dibutylamine, morpholine, piperidine, octylamine, or furfurylamine gave the corresponding *sym*-triazines **3d,i-e**.

N-Substituted 2,4-Diamino-6-(benzothiazolyl-2-thiomethyl)-*sym*-triazines (3b,f,g,i,j). C. 2-Mercaptobenzothiazole (3.34 g, 20 mmol) was added portionwise to a stirred solution of NaOH (0.88 g, 22 mmol) in ethanol (50%, 60 ml). The reaction mixture was stirred for 20 min at 20°C, the chloromethyl-*sym*-triazine (**7a-e**, 25 mmol) was added portionwise, and the product was refluxed with stirring for 4 h and then evaporated to dryness under reduced pressure. The residue was crystallized from the appropriate solvent (see Table 1) to give the *sym*-triazines **3b,f,g,i,j**.

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