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SYNTHESIS AND PROPERTIES OF DERIVATIVES OF *sym*-TRIAZINE. 16.* SYNTHESIS OF AMINE AND DIAMINE DERIVATIVES OF *sym*-TRIAZINE CONTAINING STERICALLY HINDERED PHENOL GROUPS FROM 6-ALKYL(ARYL)THIO-2,4-BIS(TRICHLOROMETHYL)-*sym*-TRIAZINE

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*The reaction of 6-alkyl(aryl)thio-2,4-bis(trichloromethyl)-*sym*-triazines with ammonia and primary and secondary amines is studied. It is shown that, depending on the reaction conditions, the replacement of either one or both of the trichloromethyl groups takes place. 6-Alkyl-(aryl)thio-2-amino-4-trichloromethyl- and 6-alkyl(aryl)thio-2,4-diamino-*sym*-triazines containing sterically hindered phenol groups are synthesized.*

In a continuation of our investigations in the area of amine derivatives of *sym*-triazine including sterically hindered phenol groups [2-5], we report in the present paper on the preparation of compounds of this type from 6-alkyl(aryl)thio-2,4-bis(trichloro-methyl)-*sym*-triazines (Ia-d).

It is known [4, 6-10] that trichloromethyl groups bound to the *sym*-triazine ring behave as pseudohalogens and are easily replaced by the action of nucleophilic reagents, with the splitting out of chloroform. However, up to now there has been a lack of information concerning the participation in such reactions of the above named bis(trichloromethyl) substituted Ia-d. We studied the reactions of the latter with ammonia, dimethylamine, morpholine, furfurylamine, and γ-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylamine. It has been established that the replacement of trichloromethyl groups in *sym*-triazines Ia-d can occur stepwise; depending on the reaction conditions replacement of either one or both of the CCl_3 groups takes place.

As a result of treating *sym*-triazines Ic, d with aqueous ammonia or dimethylamine at 30-35°C, only one Cl_3C group is replaced, and 2-amino- (IIa, b) or 2-dimethylamino-6-arylthio-4-trichloromethyl-*sym*-triazines (IIc, d) are formed in good yield (Table 1). The replacement of one trichloromethyl group in compounds Ia-d by the other amines studied was carried out in an inert solvent (benzene or dioxane) at the same temperature using a small excess (~10%) of amine in the presence of an equimolar amount of triethylamine. This gave the corresponding N-substituted 2-amino-4-trichloromethyl-*sym*-triazine (IIe-l) in a 76-86% yield.

The replacement of both trichloromethyl groups in *sym*-triazines Ic, d with amine or dimethylamine groups succeeds only if the reaction is carried out under more rigorous conditions in a nonaqueous medium. Thus, 2,4-diamino- (IIIa, b) and 2,4-bis(dimethyl-amino)-6-arylthio-*sym*-triazines (IIIc, d) were obtained in good yield by passing gaseous ammonia into solutions of triazines Ic, d in DMF at 150-155°C. The products of the replacement of both Cl_3C groups in *sym*-triazines Ia-d by the other amines, compounds IIIe, were synthesized in yields of 64-79% by heating the reactants (120-130°C) in the presence of triethylamine (I:amine:Et_3N mole ratio of 1:2, 1:2.1) in dioxane or toluene under pressure.

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*For paper 15 see [1].

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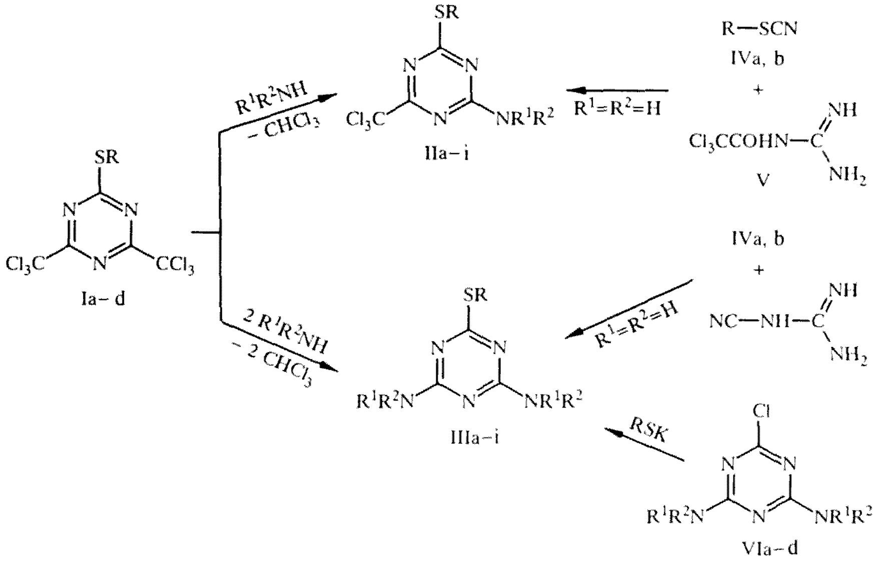

Ia, IIIi, R = Me; Ib, IIb, IIIb R = $PhCH_2$; Ic, IIa, c, e, g, k, IVa R = 4-HO-3,5-(*t*-Bu)$_2C_6H_2$; Id, IId, f, g, *l*, IIId, f, g, *l*, IVb R = 4-HO-3,5-(*t*-Bu)$_2$-$C_6H_2CH_2$; IIa, b, IIIa, b $R^1 = R^2$ = H; IIc, d, IIIc, d, VIa $R^1 = R^2$ = Me; IIe, f, IIIe, f, VIb R^1R^2N = morpholino; IIg, h, IIIg, h, VIc R^1 = furfuryl, R^2 = H; IIi-*l*, IIIi-*l*, VId R^1 = 4-HO-3,5-(*t*-Bu)$_2C_6H_2(CH_2)_3$, R^2 = H

The compositions and structures of the synthesized amine (IIa-*l*) and diamine derivatives (IIIa-*l*) are in good agreement with their elemental analyses, PMR and IR spectra. The structures of some of the products were also supported by independently converging synthesis. For example, 2-amino-4-trichloromethyl-*sym*-triazines IIa, b are formed in high yield by boiling equimolar quantities of the corresponding thiocyanate (IVa, b) and N-(trichloroacetyl)guanidine (V) in ethanol. 2,4-Diamino-*sym*-triazines IIIa, b were synthesized by the condensation of thiocyanates IVa, b with dicyanadiamide in the presence of catalytic amounts of piperidine. N-Substituted 2,4-diamino-*sym*-triazines IIIc, e, g, j, k were obtained by the reaction of N-substituted 2,4-diamino-6-chloro-*sym*-triazines (VIa-d) with the K derivatives of benzylmercaptan or 3,5-di-*tert*-butyl-4-hydroxythiophenol in ethanol. All of the substances prepared by an independently converging synthesis were completely identical with the reaction products of a nucleophilic substitution of the trichloromethyl groups in *sym*-triazines Ib-d.

In the IR spectra of all of the compounds synthesized there are absorption maxima at 1560-1525, 1420-1400, 1115-1095, 1015-985, 825-805, and 715-695 cm^{-1} belonging to stretching, "breathing," and out-of-plane and in-plane deformation vibrations of the *sym*-triazine ring [1-5, 9, 11, 12]. In the spectra of *sym*-triazines IIa-*l*, which contain trichloromethyl groups, these are shifted to slightly lower frequencies compared to the analogous bands in the spectra of compounds IIIa-*l*. For all of the *sym*-triazines under discussion, one also finds absorptions due to the sterically hindered phenol residue: a rather narrow band at 3655-3635, characteristic of a screened phenolic hydroxyl [13]; two medium intensity bands in the 1265-1220 region connected with the vibrations of the Ar—OH bonds in screened phenols [14], and two groups of bands at 885-870 and 835-820 cm^{-1} (out-of-plane deformations of the tetrasubstituted benzene ring).

There are two broad bands in the spectra of 2-aminosubstituted IIa, b in the region of N—H stretches. One of them is shifted to the long wavelength side and appears at 3190-3090 (ν_s NH), the other has a smaller wavelength and occurs at 3460-3280 cm^{-1} (ν_{as} NH). These data are evidence of the presence in these compounds in the crystalline state of a strong hydrogen bond [5, 9, 11]. At 3500-3100 cm^{-1} in the spectra of 2,4-diaminosubstituted IIIa, b, there are four absorption bands: two narrow, at higher frequencies (3480-3465 and 3420-3410 cm^{-1}), and two broad at lower frequencies (3315-3280 and 3160-3130 cm^{-1}). This is evidence that there are two kinds of hydrogen bonds in these compounds in the crystalline state. By analogy with the data in [11, 15] concerning the vibrational spectra of melamine and ammeline (4,6-diamino-2-hydroxy-*sym*-triazine), the following assignments of these frequencies can be made: the two shortwave narrow bands apparently belong to the antisymmetric and symmetric stretches of the N—N bonds in the amine groups involved in a weak hydrogen bond, and the two longwave broad bands to the corresponding vibrations of amine groups forming a strong hydrogen bond.

TABLE 1. Characteristics of the Compounds Synthesized

Compound	Molecular formula	T_{mp}, °C	R_f (solvent system)	Yield, %*2
II a	$C_{18}H_{23}Cl_3N_4OS$	184...185,5	0,64 (a)	85 (81)
II b	$C_{19}H_{25}Cl_3N_4OS$	167...168	0,56 (b)	88 (84)
II c	$C_{20}H_{27}Cl_3N_4OS$	132...133,5	0,46 (b)	89
II d	$C_{21}H_{29}Cl_3N_4OS$	124...125	0,60 (b)	82
II e	$C_{22}H_{29}Cl_3N_4O_2S$	158...160	0,52 (a)	86
II f	$C_{23}H_{31}Cl_3N_4O_2S$	140...141,5	0,43 (b)	81
II g	$C_{23}H_{27}Cl_3N_4O_2S$	88...90	0,72 (c)	78
II h	$C_{24}H_{29}Cl_3N_4O_2S$	Oil	0,57 (b)	76
II i	$C_{22}H_{31}Cl_3N_4OS$	108...109	0,63 (c)	83
II j	$C_{28}H_{37}Cl_3N_4OS$	142...143	0,50 (c)	80
II k	$C_{35}H_{49}Cl_3N_4O_2S$	140...141	0,74 (a)	84
II *l*	$C_{36}H_{51}Cl_3N_4O_2S$	117...118	0,63 (b)	77
III a	$C_{17}H_{25}N_5OS$	250...252	0,34 (b)	85 (63)
III b	$C_{18}H_{27}N_5OS$	135...136,5	0,74 (b)	81 (58)
III c	$C_{21}H_{33}N_5OS$	50...52	0,32 (c)	73 (78)
III d	$C_{22}H_{35}N_5OS$	67...68	0,44 (c)	76
III e	$C_{25}H_{37}N_5O_3S$	175...177	0,38 (b)	79 (72)
III f	$C_{26}H_{39}N_5O_3S$	158...159	0,44 (b)	70
III g	$C_{27}H_{33}N_5O_3S$	147...148	0,54 (c)	68 (75)
III h	$C_{28}H_{35}N_5O_3S$	Oil	0,70 (c)	72
III i	$C_{38}H_{59}N_5O_2S$	180...182 (decomp.)	0,41 (a)	76
III j	$C_{44}H_{63}N_5O_2S$	103...105	0,54 (a)	64 (70)
III k	$C_{51}H_{77}N_5O_3S$	84...85	0,28 (b)	77 (65)
III *l*	$C_{52}H_{79}N_5O_3S$	Oil	0,37 (b)	67

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*Recrystallization of compounds: IIa, b, e, k, IIIe, k) from aqueous ethanol; IIc, d, g, IIIf, j) from a 10:1 toluene/2-propanol mixture; IIf, i, j) from aqueous dioxane; IIIa, b, g, i) from aqueous DMF; IIIc, d) from a 5:1 hexane/acetone mixture.

*2The yield of the compound prepared by an independently converging synthesis is given in parentheses.

In the spectra of compounds IIa, b and IIIa, b, the maximum absorption of variable intensity at 1675-1655 cm^{-1} belong to in-plane deformations of the N–H bonds in primary amine groups, and are characteristic of amino-*sym*-triazines [1, 5, 9, 15].

In the N–H stretching region in the spectra of *sym*-triazines IIg-*l* and IIIg-*l*, there are weak absorption bands in the 3365-3280 cm^{-1} range.

In the PMR spectra of the compounds synthesized (Table 2), the signals of the hydroxyl proton appear as singlets in the 4.86-5.15 ppm range, characteristic of screened phenols [13, 16]. The signals of the *tert*-butyl group protons are found as broadened singlets in the 1.52-1.73 ppm region. Singlets at 7.03-7.35 ppm correspond to the two magnetically equivalent protons of the hydroxyaryl groups [2-5, 16]. Signals of the primary amine group protons in the spectra of *sym*-triazines IIa, b and IIIa, b take the form of broadened singlets in the 5.80-6.32 range [1, 5, 17]. The signals of the secondary amine group protons in the spectra of compounds IIg-*l* and IIIg-*l* lie in the 5.52-5.72 ppm range, which is typical of amine derivatives of *sym*-triazines [2-5, 18].

EXPERIMENTAL

The IR spectra were taken on a Bruker IFS-48 instrument in KBr tablets, mineral oil suspension, or thin layer. The PMR spectra were recorded on a Bruker WP-100 SY (100 MHz) spectrometer, TMS internal standard. The course of the reactions and the purity of the compounds obtained were monitored by means of TLC on Al_2O_3 (III degree Brockman activity) in solvent systems of 15:1 benzene/methanol (a); 20:1 benzene/methanol (b); and 20:1 chloroform/acetone (c); developed with iodine vapor.

TABLE 2. PMR Spectral Parameters of N-Substituted 2-Amino-4-alkyl(aryl)thio- (II) and 2,4-Diamino-6-alkyl(aryl)thio-*sym*-triazines (III)

Compound	Chemical shifts, δ, ppm				
	t-Bu (ex.b.s.)	OH (s)	H_{arom} (s)	NH_2, NH (b.s.)	Other protons
1	2	3	4	5	6
II a	1,58 (18H)	5,02 (1H)	7,24 (2H)	5,94 (2H)	–
II b	1,52 (18H)	4,90 (1H)	7,15 (2H)	5,80 (2H)	3,92 (2H, s, CH_2S)
II c	1,65 (18H)	4,88 (1H)	7,30 (2H)	–	3,12 (6H, b.s., Me_2N)
II d	1,60 (18H)	4,86 (1H)	7,22 (2H)	–	3,28 (6H, b.s., Me_2N), 3,88 (2H, s, CH_2S)
II e	1,55 (18H)	5,05 (1H)	7,18 (2H)	–	2,54...2,72 (4H, s, NCH_2), 3,58...3,73 (4H, m, OCH_2)
II f	1,68 (18H)	4,95 (1H)	7,34 (2H)	–	2,50...2,74 (4H, m, NCH_2), 3,42...3,60 (4H, m, OCH_2), 3,94 (2H, s, CH_2S)
II g	1,54 (18H)	5,10 1H)	7,25 (2H)	5,58 (1H)	3,35 (2H, d, CH_2, $J = 1{,}5$), 6,26 (1H, d.d., 3-H_{fur}, $J_{35} = 0{,}9$), 6,54 (1H, d.d., 4-H_{fur}, $J_{34} = 3{,}5$), 7,52 (1H, d.d., 5-H_{fur}, $J_{45} = 1{,}7$)
II h	1,50 (18H)	4,94 (1H)	7,26 (2H)	5,66 (1H)	3,28 (2H, d, CH_2, $J = 1{,}2$), 3,90 (2H, s, CH_2S), 6,18 (1H, d.d., 3-H_{fur}, $J_{35} = -0{,}8$), 6,62 (1H, d.d., 4-H_{fur}, $J_{34} = 3{,}3$), 7,45 (1H, d.d., 5-H_{fur}, $J_{45} = 1{,}8$)
II i	1,53 (18H)	5,00 (1H)	7,16 (2H)	5,54 (1H)	1,72...1,88 (4H, m, CH_2), 2,38 (3H, s, MeS), 3,25...3,33 (2H, m, $\underline{CH_2}NH$)
II j	1,58 (18H)	4,87 (1H)	7,22 (2H)	5,58 (1H)	1,70...2,10 (4H, m, CH_2), 3,43...3,62 (2H, m, $\underline{CH_2}NH$), 3,84 (2H, s, CH_2S), 6,80...7,03 (5H, m, Ph)
IIk	1,52 (18H), 1,68 (18H)	4,93 (1H), 5,08 (1H)	7,17 (2H), 7,30 (2H)	5,68 (1H)	1,80...2,16 (4H, m, CH_2), 3,48...3,65 (2H, m, CH_2NH)
II *l*	1,58 (18H), 1,73 (18H)	4,86 (1H), 5,12 (1H)	7,08 (2H), 7,32 (2H)	5,57 (1H)	1,85...2,24 (4H, m, CH_2), 3,28...3,50 (2H, m, $\underline{CH_2}NH$), 3,92 (2H, s, CH_2S)
III a	1,65 (18H)	4,94 (1H)	7,24 (2H)	6,32 (4H)	–

TABLE 2 (continued)

Compound	Chemical shifts, δ, ppm				
	t-Bu (ex.b.s.)	OH (s)	H_{arom} (s)	NH_2, NH (b.s.)	Other protons
1	2	3	4	5	6
III b	1,53 (18H)	5,15 (1H)	7,13 (2H)	6,14 (4H)	3,86 (2H, s, CH_2S)
III c	1,70 (18H)	4,98 (1H)	7,35 (2H)	–	3,35 (12H, b.s., Me_2N)
III d	1,58 (18H)	5,10 (1H)	7,21 (2H)	–	3,26 (12H, b.s., Me_2N), 3,95 (2H, s, CH_2S)
III e	1,63 (18H)	4,95 (1H)	7,33 (2H)	–	2,43...2,65 (8H, m, NCH_2), 3,43...3,72 (8H, m, OCH_2)
III f	1,54 (18H)	5,05 (1H)	7,18 (2H)	–	2,56...2,73 (8H, m, NCH_2), 3,28...3,52 (8H, m, OCH_2), 3,84 (2H, s, CH_2S)
III g	1,58 (18H)	4,90 (1H)	7,08 (2H)	5,60 (2H)	3,34 (4H, d, CH_2, $J = 1,1$), 6,34 (2H, d.d., 3-H_{fur}, $J_{35} = 0,8$), 6,58 (2H, d.d., 4-H_{fur}, $J_{34} = 3,6$), 7,37 (2H, d.d., 5-H_{fur}, $J_{45} = 1,8$)
III h	1,65 (18H)	5,11 (1H)	7,14 (2H)	5,55 (2H)	3,43 (4H, d, CH_2, $J = 1,3$), 3,96 (2H, s, CH_2S), 6,24 (2H, d.d., 3-H_{fur}, $J_{35} = 0,9$), 6,68 (2H, d.d., 4-H_{fur}, $J_{34} = 3,4$), 7,41 (2H, d.d., 5-H_{fur}, $J_{45} = 1,9$)
III i	1,72 (36H)	5,04 (2H)	7,03 (4H)	5,67 (2H)	1,82...2,14 (8H, m, CH_2), 2,45 (3H, s, MeS), 3,38...3,62 (4H, m, $\underline{CH_2}NH$)
III j	1,57 (36H)	4,87 (2H)	7,25 (4H)	5,52 (2H)	1,88...2.24 (8H, m, CH_2), 3,30...3,57 (4H, m, $\underline{CH_2}NH$), 3,77 (2H, s, CH_2S), 6,90...7,08 (5H, m, Ph)
III k	1,54...1,70 (54H)	4,89 (2H), 5,12 (1H)	7,10 (4H), 7,32 (2H)	5,60 (2H)	1,87...2,12 (8H, m, CH_2), 3,40...3,55 (4H, m, $\underline{CH_2}NH$)
III *l*	1,60...1,72 (54H)	4,93 (2H), 5,10 (1H)	7,15 (4H), 7,27 (2H)	5,72 (2H)	1,90...2,25 (8H, m, CH_2), 3,35...3,62 (4H, m, CH_2NH), 3,95 (2H, s, CH_2S)

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*The spectra of compounds IIa-d, h-j, IIIc-f were recorded in CD_3OD; of compounds IIe, f, IIIk, *l*, in acetone-D_6; of compounds IIg, j, *l*, IIIa, b, g-j, in DMSO-D_6.

The elementary analyses of the compounds synthesized for C, H, N and S agreed with the calculated values.

The starting 6-methythio-2,4-bis(trichloromethyl)- (Ia) [19], 6-benzylthio-2,4-bis(trichloromethyl)- (Ib) [19], 6-(3,5-di-*tert*-butyl-4-hydroxyphenol)-2,4-bis(trichloromethyl)- (Ic) [20], and 6-(3, 5-di-*tert*-butyl-4-hydroxybenzylthio)-2,4-bis(trichloromethyl)-*sym*-triazine (Id) [20], 3,5-di-*tert*-butyl-4-hydroxyphenylthiocyanate (IVa) [21], 3,5-di-*tert*-butyl-4-hydroxybenzylthiocyanate (IVb) [22], N-(trichloroacetyl)guanidine (V) [23], as well as 2,4-bis(dimethylamino)-6-chloro-(VIa) [24], 2,4-dimorpholino-6-chloro- (VIb) [24], and 2,4-difurfurylamino-6-chloro-*sym*-triazine (VIc) [25] were prepared by methods given in the papers cited above.

2-Amino-6-arylthio-4-trichloromethyl-*sym*-triazines (IIa, b). A suspension of 15 mmoles of *sym*-triazine Ic, d in 30 ml of 28% aqueous ammonia is stirred for 3 h at 30-35°C. The solid material is filtered off, washed on the filter with water, dried, and crystallized from aqueous ethanol.

6-Arylthio-2-dimethylamino-4-trichloromethyl-*sym*-triazines (IIc, d) are prepared in a manner analogous to compounds IIa, b from 15 mmoles of *sym*-triazine Ic, d in 30 ml of a 33% solution of dimethylamine.

2-Amino-6-(3,5-di-tert-butyl-4-hydroxyphenylthio)-4-trichloromethyl-*sym*-triazine (IIa). A mixture of 2.63 g (10 mmoles) of thiocyanate IVa and 2.04 g (10 mmoles) of guanidine V in 75 ml of ethanol is boiled for 5 h with stirring. The reaction mass is evaporated to dryness under reduced pressure. The residue is washed with ether and crystallized from aqueous ethanol to obtain 3.6 g of *sym*-triazine IIa.

sym-Triazine IIb is synthesized in analogous manner from thiocyanate IVb.

N-Substituted 6-Alkyl(aryl)thio-2-amino-4-trichloromethyl-*sym*-triazines (IIe-*l*). A mixture of 15 mmoles of *sym*-triazine Ia-d, 16.5 mmoles of the corresponding amine, and 1.66 g (16.5 mmoles) of triethylamine in 50 ml of anhydrous dioxane or benzene is stirred for 4 h at 30-35°C. The reaction mass is evaporated to dryness under reduced pressure. The residue is washed with ether (2 × 20 ml) and crystallized from the appropriate solvent (in the case of compounds IIe-g, i-*l*, see Table 1). In the preparation of IIh, the residue is chromatographed on an Al_2O_3 column with a 15:1 benzene/methanol mixture as eluant. After removal of the solvent the *sym*-triazine IIh is obtained as a viscous, dark-yellow oil that cannot be crystallized.

2,4-Diamino-6-arylthio-*sym*-triazines (IIIa, b). Dry ammonia is passed into a stirred solution of 10 mmoles of *sym*-triazines Ic, d in 30 ml of anhydrous DMF at 150-155°C for 2 h. The reaction mixture is cooled to 20°C and poured into 150 ml of water. The precipitate is filtered off, washed on the filter with water, dried, and crystallized.

6-Arylthio-2,4-bis(dimethylamino)-*sym*-triazines IIIc, d are synthesized in analogous manner to compounds IIIa, b from 10 mmoles of *sym*-triazine Ic, d and gaseous dimethylamine.

2,4-Diamino-6-(3,5-di-*tert*-butyl-4-hydroxyphenylthio)-*sym*-triazine (IIIa). A mixture of 2.63 g (10 mmoles) of thiocyanate IVa, 0.84 g (10 mmoles) of dicyanidiamide, and 0.3 ml of piperidine in 60 ml of methanol is boiled with stirring for 5 h. The reaction mixture is cooled to 20°C and poured into 200 ml of water. The precipitate that forms is filtered off, washed on the filter with water, dried, and crystallized to obtain 2.25 g of *sym*-triazine IIIa.

sym-Triazine IIIb is synthesized in analogous manner from thiocyanate IVb.

N-Substituted 2,4-Diamino-*sym*-triazines (IIIe-*l*). A mixture of 8 mmoles of *sym*-triazine Ia-d, 16.8 mmoles of the corresponding amine, and 1.7 g (16.8 mmoles) of triethylamine in 35 ml of anhydrous dioxane or toluene is held for 5 h at 120-130°C in a sealed ampule. After having cooled to 20°C the content of the ampule is evaporated to dryness under educed pressure. The residue is washed with hexane (2 × 20 ml) and chromatographed on an Al_2O_3 column (90 × 5.0 cm) with a 10:1 chloroform/acetone mixture as eluant. The solvents are removed under reduced pressure and the compounds obtained purified by recrystallization from the appropriate solvents (*sym*-triazines IIIe, f, g, i, j, k). Products IIIh, *l*, however, are chromatographed a second time on an Al_2O_3 column (*sym*-triazines IIIh, *l*), with a 10:1 benzene/methanol mixture as eluant. After the solvent is removed, compound IIIh, *l* is obtained as a viscous, colored oil that cannot be crystallized.

2,4-bis[γ-(3,5-Di-*tert*-butyl-1-4-hydroxyphenyl)propylamino-6-chloro-*sym*-triazine (VId, $C_{37}H_{56}ClN_5O_2$). A solution of 5.26 g (20 mmoles) of γ-(4-hydroxy-3,5-di-*tert*-butylphenyl)propylamine in 30 ml of acetone is added dropwise to a stirred suspension of 1.84 g (10 mmoles) of cyanuric chloride in 30 ml of a 1:1 acetone/water mixture at 0-5°C. The reaction mixture is stirred for 1 h at 30-35°C, neutralized by the dropwise addition of 10% NaOH to a pH of 7.5-8.0, and stirred for 0.5 h at 40°C. The precipitate forming is filtered off, washed on the filter with water, dried in vacuum over P_2O_5, and crystallized from a 1:1 toluene/heptane mixture to obtain 4.33 g (63%) of *sym*-triazine VId, T_{mp} 204-205°C, R_f 0.64 (a). PMR spectrum in DMSO-D_6: 1.52 (36 H, ex.b.s. [exchange broadened singlet], *t*-Bu), 1.88-2.16 (8H, m, CH_2), 3.45-3.67 (4H, m, CH_2NH), 5.14 (2H, s, OH), 5.68 (2H, b.s., NH), 7.13 ppm (2H, s, H_{arom}).

2,4-bis(Dimethylamino)-6-(3,5-di-*tert*-Butyl-4-hydroxyphenyl-thio)-*sym*-triazine (IIIc). A solution of the K mercaptide obtained from 1.67 g (7 mmoles) of 3,5-di-*tert*-butyl-4-hydroxythiophenol and 0.42 g (7.5 mmoles) of KOH in 15 ml of absolute ethanol is added dropwise to a stirred solution of 1.4 g (7 mmoles) of chloro-*sym*-triazine VIa in 30 ml of absolute ethanol. The reaction mixture is boiled with stirring for 1.5 h, cooled to 20°C, and poured into 150 ml of water. The precipitate forming is filtered off, dried, and crystallized to obtain 2.2 g of product IIIc.

sym-Triazines IIIe, g, j, k are synthesized in analogous manner from the chloro-*sym*-triazines VIb-d and the corresponding K mercaptides.

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