

paration of compounds IIIa,b, the residue is distilled *in vacuo* in an inert gas atmosphere. In the preparation of compounds IIIc,d, the residue is chromatographed on a column with Al₂O₃ (3.5 × 50 cm) and eluted with 30:1 benzene-methanol mixture. After removal of the solvents, IIIc is obtained as a viscous light-yellow oil, and III d as an oil which crystallizes on keeping the material in cold.

2-(β-Cyanoethoxy)-4-trichloromethyl-6-n-decyl-sym-triazine (IIIe). A mixture of 3.2 g (7 mmoles) of triazine Ib, 0.5 g (7 mmoles) of ethylene cyanohydrin and 1.7 g (17 mmoles) of dry triethylamine in 20 ml of dry dioxane is boiled with stirring for 6 h, and then evaporated *in vacuo*. The residue is chromatographed on a column with Al₂O₃ (3.5 × 30 cm), and eluted by a 30:1 benzene-methanol mixture. After removal of the solvents, compound IIIe is obtained as a dark-yellow uncrystallizable oil.

2-(β-Nitroethoxy)-4-trichloromethyl-6-N-decyl-sym-triazine (III f) is obtained similarly as a viscous light-green oil.

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SYNTHESIS AND PROPERTIES OF sym-TRIAZINE DERIVATIVES.

2.* SYNTHESIS OF AMINO-sym-TRIAZINES CONTAINING FRAGMENTS OF STERICALLY HINDERED PHENOL

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The reaction of mono- and dichloro-sym-triazines with 4-hydroxy-3,5-di-tert-butyl-aniline was studied. N-substituted derivatives of 2,4,6-triamino-sym-triazine were synthesized, containing fragments of sterically hindered phenol.

In recent years, researchers are paying increasing attention to nitrogen containing derivatives of sterically hindered phenols, which are effective antioxidants for various materials, biologically active agents, and intermediates for their synthesis [2]. However, many compounds of this type have insufficient thermal stability and lose their effectiveness above 150°C [3, 4]. It would therefore be very interesting to try to increase the thermal stability of phenolic type antioxidants by using a sym-triazine ring as a thermostable binding unit, to which fragments of a sterically hindered phenol are attached, which impart antioxidizing properties to the entire molecule. In the literature [5-8] uncorrelated data are reported on the use of sym-triazine derivatives as antioxidants, thermo- and light stabilizers for polymeric materials and lubricants.

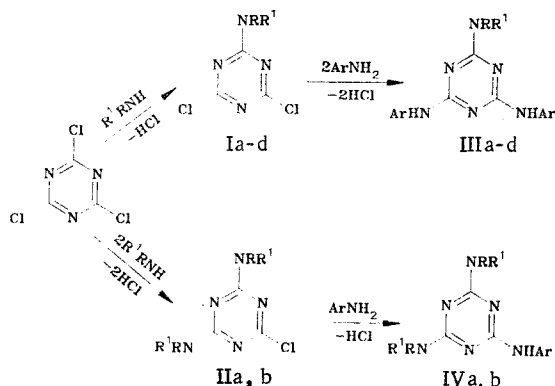
To search for new antioxidants in the above series of compounds, we carried out a synthesis of N-substituted derivatives of amino-sym-triazine, containing not only the fragments of the screened phenol, but also alkylamine and arylamine substituents (III, IV). As the starting material for the preparation of compounds of this type, we chose cyanuryl chloride (1,3,5-trichloro-sym-triazine).

The synthesis of the amino derivatives of sym-triazine (III, IV) was carried out in two stages. In the first stage, by reacting cyanuryl chloride with isobutylamine, N-methyl-N-

*For article 1, see [1].

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octadecylamine, and p-dodecylaniline, the corresponding N-substituted dichloroamino-sym-triazines Ia-d or chlorodiamino-sym-triazines IIa,b were obtained. The remaining chlorine atoms in these sym-triazine derivatives were then replaced by the residues of 4-hydroxy-3,5-di-tert-butylaniline.



Ar=4-HO-3,5-(tert-C₄H₉)₂C₆H₂; I-IV a R=(CH₃)₂CHCH₂, R¹=H; b R=CH₃, R¹=n-C₁₈H₃₇;
 I, III c R=4-C₁₂H₂₅C₆H₄, R¹=H; d R=Ar, R¹=H

N-Substituted 2,4-dichloro-6-amino-sym-triazines (Ia-d) were obtained by reacting equimolar amounts of the reagents in aqueous acetone at 0-5°C. N-Substituted 2-chloro-4,6-diamino-sym-triazines (IIa,b) were synthesized at room temperature and at a 1:2 molar ratio of cyanuryl chloride to the amine. The screened phenol fragments were introduced into the sym-triazine ring by replacing the chlorine atoms in compounds I, II with 4-hydroxy-3,5-di-tert-butylaniline residue at 65-70°C. In all cases an aqueous alkali solution was used as the hydrogen chloride acceptor.

The sym-triazine derivatives III, IV are stable crystalline compounds, and their composition and structure were confirmed by elemental analysis, IR, PMR, and mass spectra.

In the IR spectra of the above compounds, skeletal vibrations of the triazine ring are observed in the 1600-1400 cm⁻¹ region. The intense absorption maxima in the 1550-1530 and 1440-1430 cm⁻¹ regions should be attributed to stretching vibrations of the triazine ring of type E₁ (in-plane stretching vibrations, twice degenerated, of the benzenoid form of the ring) [9-11]. It should be noted that in the spectra of compounds I-IV, the first of the above bands are shifted somewhat toward the short wavelength region, compared with the initial cyanuryl chloride (1510 cm⁻¹) [9]. Medium intensity maxima in the 1120-1090 and 1020-1010 cm⁻¹ regions are due to ring "rocking" vibrations [10, 11]. The intense absorption bands at 810-805 cm⁻¹ are almost independent of the nature of the ring substituents, and are characteristic of extraplanar ring deformational vibrations; they can be attributed to the class of A₂ vibrations (antisymmetric vibrations with respect to the plane of the ring) [9]. The absorption frequencies in the 730-695 cm⁻¹ region correspond to the ring in-plane deformational vibrations and, like the absorption in the 1600-1400 cm⁻¹ region, belong to the type of E₁ vibrations.

In the IR spectra of the initial dichloro- and Ia-d and monochloro-sym-triazines IIa,b, several intense absorption maxima are observed at 1300, 1260-1255, 1160, and 850-845 cm⁻¹, attributed to the stretching vibrations of the C-Cl bonds and characteristic of chloro derivatives of sym-triazine [12]. These frequencies are absent in the IR spectra of compounds III, IV.

The spectra of N-substituted amino-sym-triazines I-IV (except for compounds Ib, IIb) contain two groups of absorption bands with a wide contour in the NH stretching vibrations region. One of these absorption bands is shifted to the long-wavelength region and appears in the 3250-3225 cm⁻¹ range (N-H symmetrical stretching vibration). The other band has a shorter wavelength and is observed in the 3450-3390 cm⁻¹ region (N-H antisymmetric stretching vibration). This position and the form of the doublet of the N-H stretching vibrations indicates the presence of a strong hydrogen bond in the crystalline state of these compounds [9]. The intense absorption maxima in the spectra of amino-sym-triazines I-IV (except for compounds Ib and IIb) in the 1650-1580 cm⁻¹ range belong to the deformational vibrations of the N-H bonds in secondary amino groups, which is characteristic of the amino derivatives of the sym-triazine [13]. Several medium intensity bands in the 1380-1000 cm⁻¹ region correspond to the stretching vibrations of the C-N bonds in compounds (I-IV). According to the data in [14],

TABLE 1. Characteristics of Synthesized Compounds I-IV

Compound	Mp, °C*	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
IIa	224-225	51,6	8,0	27,1	C ₁₁ H ₂₀ ClN ₅	51,4	7,8	27,2	68
IIb	63-65	73,0	12,0	10,0	C ₄₁ H ₈₀ ClN ₅	72,6	11,8	10,3	62
Ia	93-94	38,6	5,0	25,7	C ₇ H ₁₀ ClN ₄	38,1	4,6	25,3	67
Ib	49-52	61,3	13,2	9,5	C ₂₂ H ₄₀ Cl ₂ N ₄	61,1	12,9	9,3	65
Ic	97-98	61,8	7,4	13,6	C ₂₁ H ₃₀ Cl ₂ N ₄	61,7	7,3	13,7	76
Id	144-145	55,2	6,2	15,3	C ₁₇ H ₂₂ Cl ₂ N ₄ O	55,3	6,0	15,2	54
IVa	218-219	68,0	9,7	18,8	C ₂₅ H ₄₂ N ₆ O	67,9	9,6	19,0	67
IVb	173-174	76,8	11,7	9,6	C ₃₅ H ₁₀₂ N ₆ O	76,6	11,8	9,7	66
IIIa	212-213	71,3	9,4	14,0	C ₃₅ H ₅₄ N ₆ O ₂	71,2	9,2	14,2	51
IIIb	146-147	74,9	10,4	10,5	C ₅₀ H ₈₄ N ₆ O ₂	75,0	10,5	10,5	59
IIIc	160-161	75,7	9,6	10,7	C ₄₉ H ₇₄ N ₆ O ₂	75,6	9,5	10,8	74
IIId	306-307	72,9	9,0	11,3	C ₄₅ H ₆₆ N ₆ O ₃	73,1	8,9	11,4	67

*The compounds were crystallized: IIa, IIIa-d, IVa,b - from a 1:1 toluene-hexane mixture; IIb - from hexane; Ia from aqueous alcohol; Ib,c from acetone; Id from a 2:1 toluene-hexane mixture.

the absorption maxima in the 1380-1345 cm⁻¹ range should be attributed of the N-ring bond stretching vibrations, while the absorption frequencies at 1240-1230, 1185-1175, 1135-1130, and 1065-1050 cm⁻¹ should be attributed to the vibrations of the N-alkyl (aryl) bonds. It must be noted that in the presence of electronegative chlorine atoms in the sym triazine ring (Ia-d, IIa,b) noticeable shift is observed in the IR spectra (compared with compounds III, IV) of the absorption bands characteristic of both stretching and deformational N-H vibrations toward the lower frequency region of the spectrum. In the IR spectra of N-substituted 2,4,6-triamino-sym-triazines (III, IV) containing fragments of sterically hindered phenol, there is a characteristic absorption band of the OH group appearing as a narrow band in the 3650-3640 cm⁻¹ region [2]. Moreover, the comparison of the IR spectra of these compounds showed that they contain several common absorption bands characteristic of 4-substituted 2,6-di-tert-butylphenols [15, 16] (3010, 2960, 2920, 1490, 1460, 1390, 1295, 1240, 1200, 1120, 1090, 930, 880, 740, and 625 cm⁻¹).

The PMR spectra of sym-triazines I-IV measured in CCl₄ or DMSO-D₆ also confirm well the above proposed structure. The signals were assigned taking into account the data on the proton spectra of sterically hindered phenols [2] and sym-triazine derivatives [17]. In the PMR spectra of N-substituted 2,4,6-triamino-sym-triazines III, IV, the proton signals of the hydroxyl groups appear as singlets in the 6.68-6.72 ppm region, which is characteristic of screened phenols [18]. The proton signals of tert-butyl radicals are observed as broadened singlets in the range of 1.58-1.84 ppm. The multiplet signals with an intensity of two (Id, IVa,b), four (IIIa-c), or six (IIId) proton units at 7.10-7.34 ppm correspond to aromatic protons of the hydroxyaryl fragments. All the signals of the NH groups were represented as broadened singlets in the range of 5.76-6.12 ppm.

EXPERIMENTAL

The IR spectra were run on the UR-20 spectrophotometer in KBr tablets, and the PMR spectra on the Tesla BS-487C spectrometer with a working frequency of 80 MHz on the δ scale in CCl₄ or DMSO-D₆ with HMDS as internal standard. The mass spectra were recorded on the Varian MAT-212 and Finninga-4000 mass spectrometers with direct introduction of the sample to the ionic source (ionization energies of electrons 70 eV). The composition of the reaction mixtures and the purity of the compounds obtained were determined by TLC on Al₂O₃ activity grade II according to Brockman, in a 10:1 benzene-ethanol system of solvents; the development was carried out with iodine vapors.

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

N-Substituted 2,4-Dichloro-6-amino-sym-triazines (Ia-d). A solution of 0.1 mole of the corresponding amine in 50 ml of acetone is added dropwise, with stirring, to a suspension of 18.45 g (0.1 mole) of cyanuryl chloride in 225 ml of a 2:1 mixture of water and acetone. The reaction mixture is stirred for 1 h at 0°C, neutralized by adding dropwise a 10% aqueous

NaOH solution to pH 7.5-8.0, and then held for 1 h at 20°C. The precipitate is filtered off, washed on the filter with water, and dried *in vacuo* over P₂O₅. PMR spectrum (CCl₄): Ib: 1.24 (3H, t, CH₃); 1.38-2.06 (32H, m CH₂); 3.14 (3H, s, N-CH₃); 3.35 ppm (2H, q, N-CH₂); Ic: 1.18 (3H, t, CH₃); 1.34-1.86 (20H, m, CH₂); 2.68 (2H, t, CH₂C₆H₄); 5.88 (1H, br, NH); 6.74-7.08 ppm (4H, m, arom.). Mass spectrum, m/z (relative intensity, %)*: Ib: M⁺ 430 (6), 397 (14), 396 (10), 395 (35), 195 (10), 194 (22), 193 (59), 192 (35), 191 (100), 179 (8). Ia: M⁺ 220 (12.5), 180 (11.8), 179 (66.5), 177 (100), 165 (27.4), 62 (25.4), 57 (31.2), 55 (54.8), 43 (74.2).

N-Substituted 2-Chloro-4,6-diamino-sym-triazines (IIa,b). A solution of 0.2 g of the corresponding amine in 75 ml of acetone is added dropwise at 20°C to a stirred suspension of 18.45 g (0.1 mole) of cyanuryl chloride in 225 ml of a 2:1 water and acetone mixture. The reaction mixture is neutralized, and after a 10% aqueous NaOH solution has been added dropwise to pH 7.5-8.0, it is stirred for 1 h at 40-45°C. The precipitate is filtered off, washed on the filter, and dried *in vacuo* over P₂O₅. PMR spectrum of IIb (DMSO-D₆): 1.26 (6H, t, CH₃); 1.30-2.20 (64H, m, CH₂); 3.22 (6H, s, N-CH₃); 3.54 ppm (4H, m, N-CH₂). Mass spectrum of IIa: M⁺ 257 (29.0), 242 (18.2), 214 (100), 158 (43.0), 146 (23.8), 68 (17.1), 54 (19.7), 55 (24.1), 43 (25.6), 41 (32.4).

N-Substituted 2-Amino-4,6-bis(4-hydroxy-3,5-di-tert-butylamino)-sym-triazines (IIIa-d). A solution of 4.42 g (0.02 mole) of 4-hydroxy-3,5-di-tert-butylaniline in 30 ml of acetone is added dropwise to a stirred solution of 0.01 mole of dichloro-sym-triazine Ia-d in 50 ml of acetone. The reaction mixture is heated to boiling, and after a solution of 0.8 g (0.02 mole) of NaOH in 5 ml of water has been added, it is boiled with stirring for 6 h. The mixture is cooled to 20°C, and poured into 300 ml of ice water. The dark amorphous precipitate is filtered off, dried, and washed with hot hexane (3 × 30 ml). PMR spectrum of IIIc (DMSO-D₆): 1.10 (3H, t, CH₃); 1.58-1.64 (36H, br.s, tert-C₄H₉); 1.88-2.10 (20H, m, CH₂); 2.78 (2H, t, CH₂-C₆H₄); 5.84-5.90 (3H, br.s, NH); 6.68-6.70 (2H, s, HO); 6.98-7.22 ppm (8H, m, arom.). Mass spectrum of IIIc: M⁺ 778 (100), 763 (5.2), 721 (4.3), 637 (6.2), 610 (5.2), 389 (4.5), 57 (5.0), 43 (8.3).

N-Substituted 2,4-Diamino-6-(4-hydroxy-3,5-di-tert-butylanilino)-sym-triazines (IVa,b) are obtained similarly from 0.01 mole of chloro-sym-triazine IIa,b, 0.01 mole of 4-hydroxy-3,5-di-tertbutylaniline, and 0.01 mole of NaOH. PMR spectrum of IVb (DMSO-D₆): 1.18 (6H, t, CH₃); 1.60-1.64 (18H, br.s, tert-C₄H₉); 1.84-2.36 (64H, m, CH₂); 3.38 (6H, s, N-CH₃); 3.58 (4H, m, N-CH₂); 5.80 (1H, s, NH); 6.76 (1H, s, HO); 7.50-7.88 ppm (2H, m, arom.).

2,4,6-Tris-(4-hydroxy-3,5-di-tert-butylanilino)-sym-triazine (IIIId). A solution of 33.15 g (0.15 mole) of 4-hydroxy-3,5-di-tert-butylaniline in 50 ml of acetone is added dropwise at 20°C to a vigorously stirred suspension of 9.2 g (0.05 mole) of cyanuryl chloride in 120 ml of a 2:1 water-acetone mixture. The reaction mixture is boiled with stirring for 2 h, and after a solution of 6.0 g (0.15 mole) of NaOH in 75 ml of water has been added, it is boiled for another 2 h. The reaction mixture is treated as described above. Samples of IIIId prepared by various methods give no depression of their mixed melting point, and their IR spectra are identical. PMR spectrum of IIIId (DMSO-D₆): 1.68-1.84 (54H, br. signal, tert-C₄H₉); 5.78-5.82 (3H, br, NH); 6.68 (3H, s, OH); 7.54-8.02 ppm (6H, m, arom.).

All the synthesized N-substituted sym-triazines III, IV are soluble in toluene, DMFA, and DMSO, and on heating, in acetone, alcohol, and dioxane; they are insoluble in hexane, ether, and CCl₄.

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SYNTHESIS AND PROPERTIES OF 1,5-DIAMINOTETRAZOLE

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An effective method was developed for preparation of 1,5-diamino tetrazole from thiosemicarbazide and sodium azide in the presence of lead(II) oxide and ammonium chloride in DMFA. Its physical properties and certain reactions were studied.

1,5-Diaminotetrazole (DAT) is a convenient reagent for a directed synthesis of tetrazole-containing compounds, which find application in certain branches of national economy [1]. However, until now DAT is difficultly accessible. Two synthetic methods for the preparation of DAT have been described: 1) based on the reaction of 5-aminotetrazole with hydroxylamine-O-sulfonic acid, DAT is formed in a low (8.5%) yield in a mixture with the 2,5-diaminotetrazole isomer [2]; 2) based on the reaction of more simple and available compounds — thiosemicarbazide, lead (II) oxide and sodium azide in ethanol in a CO₂ atmosphere [3]. The latter reaction has, however, been practically not studied. The authors do not even report the yield of the product. The stage of isolation of DAT as hydrochloride is labor consuming.

In the present work, we tried to find the optimal parameters of this synthetic path. On reproducing the conditions of [3] it was found that the reaction proceeds incompletely and the unreacted thiosemicarbazide contaminates the desired product by reacting with benzaldehyde, which is used to purify DAT. The end product, DAT hydrochloride, is obtained in a 35-40% yield, and its melting point corresponded to the literature data after multiple recrystallizations. We found that the stage of DAT purification via the benzylidene derivative can be eliminated, and the yield of the desired product could thus be increased to 45-50%, if DAT is isolated by recrystallization from water. By using ammonium azide, passage of carbon dioxide is unnecessary, and the course of the reaction is well controlled, as can be inferred from the evolution of ammonia. However, unreacted ammonium azide interferes with the purification of the product, and the yield of DAT is 34-37%. A mixture of equimolar amounts of sodium azide and ammonium chloride in boiling ethanol behaves similarly, but the yield of DAT is still lower (15-20%). The best results were obtained by using a small excess of this mixture in DMFA, and the yield of DAT thus reaches 60%. The improved method of synthesis makes it possible to obtain DAT easily and rapidly in a good yield.

Little is known of the properties of DAT. Triacetyl [2] and benzylidene [3] derivatives have been described. The IR [4] and PMR spectra [2] of DAT have reported. The PMR spectrum of DAT shows a singlet at normal temperature. At -50°C, two resolved singlets are observed spaced 28 Hz apart. The two amino groups of DAT also differ little with respect to the position in the IR spectrum of the absorption bands of the stretching (3305 and 3215 cm⁻¹) and deformational (1624 cm⁻¹) vibrations both in the crystal (KBr tablet) and in solution (DMSO).

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