Chemistry of Heterocyclic Compounds, Vol. 31, No. 1, 1995

SYNTHESIS AND PROPERTIES OF DERIVATIVES OF *sym*-TRIAZINES

14.* CYANOETHYLATION OF 4,6-DISUBSTITUTED 2-AMINO-*sym*-TRIAZINES

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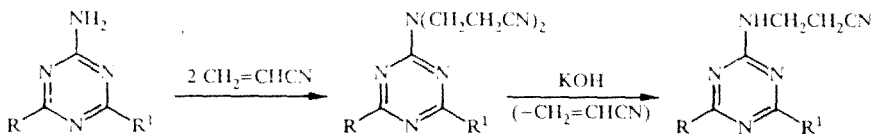
*The cyanoethylation of 4,6-disubstituted 2-amino-*sym*-triazines containing alkyl, trichloromethyl, and pyridyl groups was studied, and the corresponding dicyanoethyl derivatives were synthesized. It was shown that the yield of the latter and the duration of the reaction depend on the nature of the substituents in the ring of the initial amino-*sym*-triazines. A method of obtaining 2-(2-cyanoethyl)amino-*sym*-triazines is proposed based on the decyanoethylation and disproportionation of the dicyanoethyl derivatives as well as the trans-cyanoethylation.*

Derivatives of *sym*-triazines containing cyanoalkyl groups show high pharmacological activity [2, 3] as well as having herbicidal [4, 5] and fungicidal [6, 7] properties. In order to extend investigations in this direction, we have synthesized 2-cyanoethyl derivatives of a number of previously prepared amino-*sym*-triazines. Compounds of this type are of interest as potential biologically active substances, and also as intermediates for the preparation of *sym*-triazines with a functional group on a side chain.

Until now, the literature has had only limited information on the cyanoethylation of amines of the triazines series [3, 8-10]. In the present work we have studied the cyanoethylation of 2-amino-4,6-disubstituted (Ia-j) and 2-amino-4-dimethylamino-6-substituted (Ik-m) *sym*-triazines.

The cyanoethylation of these aminotriazines was carried out with an excess of acrylonitrile at a temperature of 55-60°C in the solvents usually used for this reaction [11] — dioxane, ethylene glycol, acetonitrile, *tert*-butyl alcohol, or DMF; the choice of solvent being dictated by the solubility in it of the initial amino-*sym*-triazine) — and in the presence of catalytic amounts of a 30% aqueous KOH solution. This procedure gave good yields of the corresponding 4,6-disubstituted 2-di(2-cyanoethyl)amino-*sym*-triazines (IIa-m).



Ia-m IIa-m IIIa-c, i, k-m

I—IIIa R = R^1 = C_5H_{11}, b R = R^1 = $C_{12}H_{25}$, c R = $C_{17}H_{35}$, R^1 = Ph, d R = C_5H_{11}, R^1 = furyl-2, e R = C_5H_{11}, R^1 = Cl_3C, f R = $C_{12}H_{25}$, R^1 = Cl_3C, g R = $C_{17}H_{35}$, R^1 = Cl_3C, h R = pyridyl-3, R^1 = Cl_3C, i R = R^1 = pyridyl-3, j R = pyridyl-3, R^1 = furyl-2, k R = C_5H_{11}, R^1 = Me_2N, l R = $C_{11}H_{23}$, R^1 = Me_2N, m R = pyridyl-3, R^1 = Me_2N

*For paper 12, see [1].

I. M. Gubkin State Petroleum and Gas Academy, Moscow 117917. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 111-119, January, 1995. Original article submitted November 2, 1994.

0009-3122/95/3101-0099$12.50

TABLE 1. Conditions of Preparation and Characterization of the Synthesized 2-Di(2-cyanoethyl)amino-*sym*-triazines

Compound	Molecular Formula	T_{mp}, °C	Rf*2	Reaction Conditions		Yield, %
				Solvent	Reaction Time, h	
IIa	$C_{19}H_{30}N_6$	66...67	0,54 (a)	DMF	16,0	71
IIb	$C_{33}H_{58}N_6$	137...138	0,64 (b)	DMF	22,0	74
IIc	$C_{32}H_{48}N_6$	94...95	0,68 (a)	Dioxane	10,0	84
IId	$C_{18}H_{22}N_6O$	230...232 (decomp.)	0,58 (c)	DMF	12,0	68
IIe	$C_{15}H_{19}Cl_3N_6$	112...113	0,72 (a)	Dioxane	6,0	86
IIf	$C_{22}H_{33}Cl_3N_6$	128...129	0,85 (b)	MeCN	6,0	90
IIg	$C_{27}H_{43}Cl_3N_6$	150...151,5	0,80 (c)	Dioxane	6,0	88
IIh	$C_{15}H_{12}Cl_3N_7$	154...155	0,54 (c)	MeCN	5,0	85
IIi	$C_{19}H_{16}N_8$	270...272	0,65 (c)	*t*-BuOH	12,0	78
IIj	$C_{18}H_{15}N_7O$	109...110,5	0,43 (a)	*t*-BuOH	12,0	75
IIk	$C_{16}H_{25}N_7$	118...120	0,74 (c)	DMF	36,0	63
IIl	$C_{22}H_{37}N_7$	142...143	0,56 (b)	Ethylene Glycol	33,0	67
IIm	$C_{16}H_{18}N_8$	158...159,5	0,52 (a)	DMF	35,0	62

*Solvent for recrystallization: 5:1 ethanol:CCl_4 (IIa-j); aqueous DMF (IIb); aqueous ethanol (IIc, h, k); acetone (IId); aqueous acetone (IIf); 1:2 ethanol–hexane (IIg); ethanol (IIm).

*2The system solvent is indicated in parentheses (see experimental section).

TABLE 2. Effect of Catalysts and Solvents on the Cyanoethylation of 2-Amino-4-pentyl-6-trichloromethyl-*sym*-triazine (Ie)

Catalyst	Solvent	Reaction temperature, °C	Reaction time, h	Yield of Triazine Ie %
30 % KOH	Dioxane	50...55	5,0	75,5
30 % KOH	Dioxane	60	2,6	86
KOH	Dioxane	60...65	6,0	83
EtONa	Dioxane	50...55	6,0	70
KF · $2H_2O$	BuOH	60...65	8,0	68
Rodion's Catalyst*	MeCN	55...60	6,0	72
30% KOH	DMF	70...75	3,0	75
30 % KOH	Dioxane:water (7:1)	60	5,0	64
30% KOH + 0 mole % NH_4Cl	Dioxane	60	5,0	52,5
Na_2CO_3 (10 mole %)	Dioxane	60	8,0	25
AB-17 (15 mass %)	Dioxane	55...60	8,0	63
AB-17 (15 mass %)	Dioxane	70...75	8,0	50,5
KU-2 (15 mass %)	MeCN	50...55	14,0	0

*35% solution of ethoxytrimethylphenylammonia in absolute ethanol.

The reaction time and yield of products IIa-m were found to depend on the nature of the substituent in the initial amino-*sym*-triazine. Reacting the most readily and with the highest yields were 2-amino-4-trichloromethyl-6-substituted Ie-h. The corresponding bisadducts, IIe-h, were formed in yields of 85-90% after heating in acetonitrile or dioxane for 5-6 h. Amino-*sym*-triazines Ic, d, i, j are cyanoethylated at a somewhat lower rate. In the case of compounds Ik-m, the presence of the electron donating dimethylamino group leads to a sharp decrease in the reaction rate; the corresponding products, IIk-m, were obtained in 62-67% yields only after 33-36 h. It should be noted that when the reaction temperature was increased to 75-80°C, tar formation was observed in the reaction mixtures, and the yields of the desired dicyanoethyl derivatives were lowered considerably.

TABLE 3. Characteristics of the 2-(2-Cyanoethyl)amino-*sym*-triazines III Synthesized

Compound	Molecular Formula	T_{mp}, °C	R_f *2	Yield, % (preparative method)
IIIa	$C_{16}H_{27}N_5$	105...106	0,64 (c)	72 (A)
IIIb	$C_{30}H_{55}N_5$	130...131	0,41 (b)	60 (A), 58 (C)
IIIc	$C_{29}H_{45}N_5$	112...114	0,52 (b)	74 (A), 65 (C)
IIIe	$C_{12}H_{16}Cl_3N_5$	128...129	0,84 (c)	56 (B), 64 (C)
IIIf	$C_{19}H_{30}Cl_3N_5$	154...155,5	0,67 (b)	62 (B), 70 (C)
IIIg	$C_{24}H_{40}Cl_3N_5$	142...144	0,60 (b)	65 (B), 68 (C)
IIIh	$C_{12}H_9Cl_3N_6$	167...168 (decomp.)	0,75 (a)	60 (B), 67 (C)
IIIi	$C_{16}H_{13}N_7$	195...197	0,58 (a)	73 (A), 70 (C)
IIIk	$C_{13}H_{22}N_6$	138...139	0,50 (c)	63 (A), 72 (C)
IIIl	$C_{19}H_{34}N_6$	161...162,5	0,33 (c)	74 (A)
IIIm	$C_{13}H_{15}N_7$	179...181	0,45 (b)	66 (A)

*Solvent for recrystallization: aqueous ethanol (IIIa-c, h, l), 5:1 chloroform–ether (IIIe), aqueous dioxane (IIIf, g, k), methyl cellosolve (IIIi), 2-propanol (IIIm).

*2Solvent system shown in parentheses (see experimental section).

The effect of different catalysis, additives, and solvents commonly used for the cyanoethylation of aromatic and heteroaromatic amines [11-14] on the yield of bisadduct IIe was studied for the reaction of 2-amino-4-pentyl-4-trichloromethyl-*sym*-triazine, Id. The reactions were carried out with a Id:acrylonitrile mole ratio of 1:4 in the presence of 3-5 mole % of catalyst (Table 2).

It is known [13] that aromatic amines are cyanoethylated in good yield in the presence of water. However, the addition of water to the reaction mixture lowered the rate of reaction in the case of amino-*sym*-triazine Id (Table 2) and, in the case of compounds Ia and Ik, the presence of water (10-15 vol. %) stopped the reaction completely. We also note that cationite KU-2 does not catalyze the reaction under discussion, although the literature contains data on the use of cationites in the cyanoethylation of aromatic amines [12, 13].

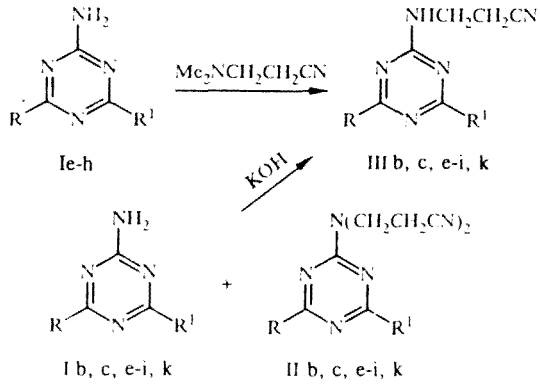
We did not succeed in synthesizing the monocyanoethylated derivatives by the reaction of amino-*sym*-triazines Ia-i with acrylonitrile. When the starting compounds were heated with an equimolar amount of acrylonitrile, only the starting amine was isolated from the reaction mixture, and with an excess of acrylonitrile, the sole reaction products were bisadducts IIa-m. In the present work, we used the partial decyanoethylation of the bisadducts to obtain the 2-(2-cyanoethyl)amino-*sym*-triazines [15].

It was established that on brief heating with an alcoholic solution of KOH (II:KOH mole ratio of 1:15), compounds IIa-c, i, m are partially decyanoethylated, being converted in good yield (Table 3) to the 4,6-disubstituted 2-(2-cyanoethyl)amino-*sym*-triazines, IIIa-c, i, k-m (method A). However, under the same conditions with bisadducts IIe-h, which contain labile, trichloromethyl groups, there was extensive tar formation in the the reaction mixture, from which, by means of preparative TLC, we isolate 2-(2-cyanoethyl)amino-4-trichloromethyl-6-substituted *sym*-triazines (IIIe-h) in 21-30% yield along with the products of the complete decyanoethylation of amino-*sym*-triazines Ie-h (18-23% yield).

For the synthesis of monoadducts IIIe-h we used the transcyanoethylation reaction [15]:these compounds were obtained in yields of 56-60% when 6-substituted 2-amino-4-trichloromethyl-*sym*-triazines Ie-h were heated with β-dimethylaminopropionitrile (molar ratio 1:5.5) in DMF (Table 3, method B). It must be noted that compounds Ia-d, i-m did not give the corresponding monocyanoethyl derivatives under analogous conditions.

It is known that monocyanoethylated amides and arylsulfamides can be obtained through the disproportionation of their dicyanoethyl derivatives in the presence of base [16]. In the present work, we have extended this method to the preparation of monocyanoethyl derivatives in the amino-*sym*-triazine series. Thus, by heating equimolar amounts of 2-amino-*sym*-triazines Ib, c, e-i, k and IIb, c, e-i, in ethanol in the presence of 30% KOH as a catalyst, we synthesized the corresponding products, IIIb, c, e-i, k in good yield (method C).

The structure of synthesized bisadducts IIa-i and monoadducts IIIa-c, e-i, k-m were confirmed by IR, PMR, and mass spectral data.



In the IR spectra of compounds IIa-m there are no absorption bands due to the stretching and bending vibrations of N–H bonds in primary amine groups present in the 3400-3100 and 1670-1645 cm^{-1} regions. The spectra of compounds IIIa-c, e-i, k-m contain a single band of average intensity at 3370 ≥ 3300 cm^{-1}, characteristic of the N–H stretch in N-substituted amino-*sym*-triazines [17], and also an absorption band a 1525-1510 cm^{-1} related to the N–H bending vibrations of secondary amine groups [18]. The presence of the C≡N group is confirmed by the occurrence in the spectra of all of the synthesized compounds of an intense absorption band in the 2240-2225 cm^{-1} region, characteristic of the spectra of aliphatic nitriles [18].

In the PMR spectra of bisadducts IIa-m (Table 4), the protons of the 2-cyanoethyl groups give two groups of signals in the form of triplets at 2.72-2.96 and 3.38-3.82 ppm. Signals at a weaker field must be assigned to the resonance of protons of methylene groups bonded to a nitrogen atom [3]. In the spectra of the monoadducts, the signals of these last have the form of unsymmetrical multiplets in the 3.22-3.66 ppm range. The signals of the secondary amine group protons are seen as broadened singlets at 5.65-6.02 ppm (see also [17, 18]).

In the mass spectra of cyanoethyl derivatives II and III (Table 5) there are present peaks of molecular ions $M^{+\bullet}$ with intensities of 12-37% of the maximum. In these spectra one finds competing processes of fragmentation of the di- and monocyanoethyl groupings. One of the fragmentation paths of these groupings in the mass spectra of bisadducts IIa-m, is the sequential elimination of two acrylonitrile molecules from ion $M^{+\bullet}$ with the formation of fragment ions $[M\text{-}C_3H_3N]^{+\bullet}$ (Φ_1) and $[M\text{-}2C_3H_3N]^{+\bullet}$ (Φ_2). Along with these processes the elimination of $C_2H_2N^{\bullet}$ and $C_3H_4N^{\bullet}$ radicals from the molecular ions, M^+ occurs, leading to the formation of ions Φ_3 and Φ_4, with the intensity of the Φ_3 peak usually the maximum in the spectra of compounds IIa-m. Analogous processes also occur in ion Φ_1, as shown by the presence of appreciable peaks of ions Φ_5 and Φ_6 in the mass spectra of all of the compounds under consideration.

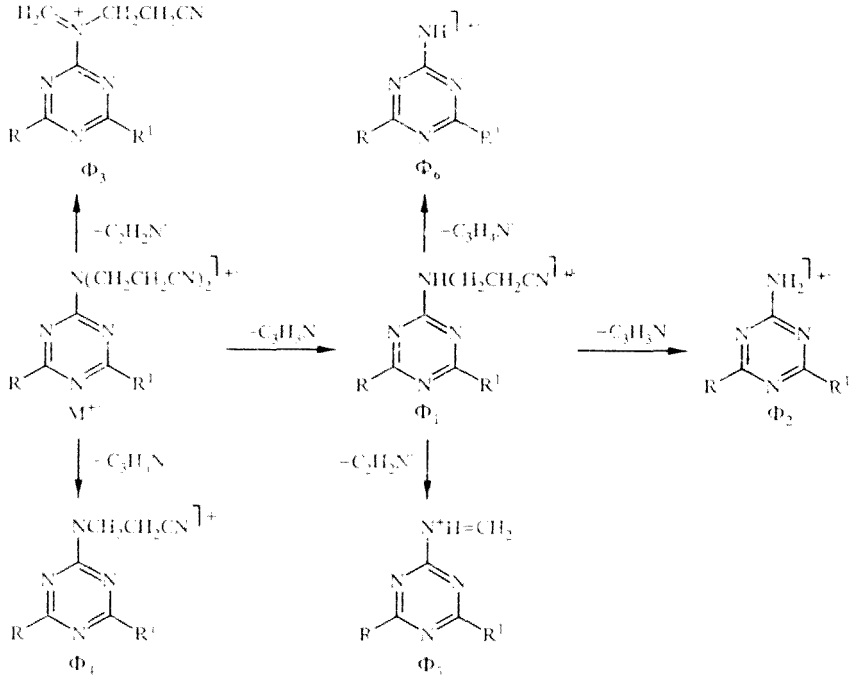


TABLE 4. PMR Spectral Data for the Compounds Synthesized

Compound	Proton chemical shift, d, ppm*, SSCC (J), Hz			
	$NC-CH_2-$	$N-CH_2$	NH (1H, ex.b.s.)	R, R^1
IIa	2,78 (4H)	3,58 (4H, t)	—	1,12 (6H, t, Me), 1,25...1,38 (12H,m, CH_2), 3,15 (4H, t, CH_2)
IIb	2,72 (4H)	3,44 (4H, t)	—	1,16 (6H, t, Me), 1,26...1,84 (4 OH, m, CH_2), 3,10 (4H, t, CH_2)
IIc	2,80 (4H)	3,74 (4H, t)	—	1,08 (3H, t, Me), 1,22...1,68 (3 OH, m, CH_2), 3,21 (2H, t, CH_2), 6,82...7,10 (5H,m, H_{Ph})
IId	2,83 (4H)	3,38 (4H, t)	—	1,15 (3H, t, Me), 1,30...1,56 (6H,m, CH_2), 3,05 (2H, t, CH_2), 6,12 (1H, d.d, 4-H_{Fur}*2, J_{34} = 3,5), 6,32 (1H, d.d, 3-H_{Fur}, J_{35} = 0,8), 7,14 (1H, d.d, 5-H_{Fur}, J_{45} = 1,8)
IIe	2,88 (4H)	3,48 (4H, t)	—	1,18 (3H, t, Me), 1,32...1,65 (6H,m, CH_2), 3,14 (2H, t, CH_2)
IIf	2,90 (4H)	3,64 (4H, t)	—	1,10 (3H, t, Me), 1,28...1,74 (2 OH, m, CH_2), 3,20 (2H, t, CH_2)
IIg	2,78 (4H)	3,82 (4H, t)	—	1,14 (3H, t, Me), 1,30...1,92 (3 OH, m, CH_2), 2,95 (2H, t, CH_2)
IIh	2,96 (4H)	3,70 (4H, t)	—	7,36...7,65 (4H,m, H_{Py})
IIi	2,82 (4H)	3,54 (4H, t)	—	7,42...7,83 (8H,m, H_{Py})
IIj	2,90 (4H)	3,80 (4H, t)	—	6,34 (1H, d.d, 3-H_{Fur}, J_{35} = 0,9), 6,68 (1H, d.d, 4-H_{Fur}, J_{34} = 3,5), 7,08 (1H, d.d, 5-H_{Fur}, J_{45} = 1,8), 7,32...7,75 (4H,m, H_{Py})
IIk	2,85 (4H)	3,78 (4H, t)	—	1,08 (3H, t, Me), 1,28...1,60 (6H,m, CH_2), 3,07 (2H, t, CH_2), 3,22 (6H, ex.b.s, N—Me)
IIl	2,92 (4H)	3,68 (4H, t)	—	1,15 (3H, t, Me), 1,33...1,74 (18H,m, CH_2), 3,12 (2H, t, CH_2), 3,32 (6H, ex.b.s, N—Me)
IIm	2,75 (4H)	3,58 (4H, t)	—	3,18 (6H, ex.b.s, N—Me), 7,21...7,63 (4H,m, H_{Py})
IIIa	2,84 (2H)	3,22...3,43 (2H, m)	5,92	1,16 (6H, t, Me), 1,28...1,54 (12H,m, CH_2), 2,58 (4H, t, CH_2)
IIIb	2,80 (2H)	3,25...3,47 (2H, m)	5,65	1,10 (6H, t, Me), 1,20...1,76 (4 OH, m, CH_2), 2,93 (4H, t, CH_2)
IIIc	2,76 (2H)	3,28...3,50 (2H, m)	6,02	1,06 (3H, t, Me), 1,22...1,65 (3 OH, m, CH_2), 3,14 (2H, t, CH_2), 6,74...7,15 (5H,m, H_{Ph})
IIIe	2,72 (2H)	3,32...3,54 (2H, m)	5,83	1,14 (3H, t, Me), 1,32...1,63 (6H,m, CH_2), 2,88 (2H, t, CH_2)
IIIf	2,92 (2H)	3,25...3,48 (2H, m)	5,78	1,18 (3H, t, Me), 1,35...1,78 (2 OH, m, CH_2), 2,80 (2H, t, CH_2)
IIIg	2,85 (2H)	3,22...3,57 (2H, m)	5,97	1,12 (3H, t, Me), 1,24...1,83 (3 OH, m, CH_2), 3,15 (2H, t, CH_2)
IIIh	2,90 (2H)	3,30...3,65 (2H, m)	5,70	7,38...7,87 (4H,m, H_{Py})
IIIi	2,88 (2H)	3,38...3,66 (2H, m)	5,86	7,32...7,94 (8H,m, H_{Py})
IIIk	2,80 (2H)	3,42...3,64 (2H, m)	5,92	1,14 (3H, t, Me), 1,25...1,57 (6H, m, CH_2), 2,62 (2H, t, CH_2), 3,12 (6H, ex.b.s, N—Me)
IIIl	2,78 (2H)	3,22...3,36 (2H, m)	5,82	1,08 (3H, t, Me), 1,28...1,78 (18H,m, CH_2), 3,04 (2H, t, CH_2), 3,12 (6H, ex.b.s, N—Me)
IIIm	2,95 (2H)	3,42...3,64 (2H, m)	5,95	3,24 (6H, ex.b.s, N—Me), 7,24...7,68 (4H, m, H_{Py})

*Spectra of compounds IIa-c, i, j, IIIa-c, i, e-m were taken in DMSO-D_6, of IId-h, IIIe-h, in acetone-D_6; of IIk-m, in CD_3OD.

*2H_{Fur} = furan proton.

Note also that, in parallel with the destruction of the cyanoethyl groupings, and finds in the mass spectra of bis- and monoadducts II and III processes involving the splitting of substituents of the *sym*-triazine ring and which occur by paths typical of the fragmentation of molecular ions in the spectra of amino derivatives of *sym*-triazines containing alkyl [20, 21], trichloromethyl [21, 22], or pyridyl [23] groups.

TABLE 5. Mass Spectral Data for the Compounds Synthesized

Compound	m/z (relative intensity of the ion peaks, % of the maximum*)
IIa	342 (M^+, 12), 302 (Φ_3, 78), 299 (26), 289 (Φ_1, 39), 288 (Φ_4, 23), 284 (100), 249 (Φ_5, 12), 247 (5), 244 (5), 241 (8), 236 (Φ_2, 7), 235 (Φ_6, 19), 230 (20), 226 (8), 194 (5), 178 (6), 173 (9), 120 (42)
IIb	538 (M^+, 14), 498 (Φ_3, 100), 485 (Φ_1, 18), 484 (Φ_4, 27), 445 (Φ_5, 10), 432 (Φ_2, 15), 431 (Φ_6, 8), 414 (37), 384 (53), 374 (5), 361 (6), 360 (11), 344 (7), 331 (15), 330 (5), 291 (25), 278 (62), 243 (12), 230 (14), 137 (10), 124 (6), 97 (33), 96 (9)
IIc	516 (M^+, 27), 476 (Φ_3, 100), 463 (Φ_1, 21), 462 (Φ_4, 14), 423 (Φ_5, 8), 410 (Φ_2, 26), 409 (Φ_6, 5), 305 (72), 292 (43), 265 (53), 252 (10), 251 (17), 239 (7), 238 (13), 199 (5), 189 (16), 186 (32), 104 (22), 103 (8), 83 (25), 82 (5)
IIf*2	486 (M^+, 15,5), 451 (24), 446 (Φ_3, 58), 433 (Φ_1, 22), 432 (Φ_4, 10), 416 (M—Cl_2, 100), 393 (Φ_5, 6), 381 (20), 380 (Φ_2, 11), 379 (Φ_6, 7), 369 (5), 345 (35), 332 (52), 310 (6), 297 (18), 292 (7), 279 (17), 278 (8), 275 (5), 262 (33), 239 (44), 226 (5), 225 (7), 191 (25), 156 (11), 121 (7), 117 (15), 109 (10), 108 (13)
IIh*2	395 (M^+, 18), 360 (30), 355 (Φ_3, 72), 342 (Φ_1, 13), 341 (Φ_4, 5), 325 (M—Cl_2, 100), 321 (6), 307 (38), 306 (11), 301 (Φ_5, 22), 290 (7), 289 (Φ_2, 14), 288 (Φ_6, 11), 278 (43), 272 (10), 237 (24), 174 (7), 117 (8), 105 (27), 104 (6)
IIi	356 (M^+, 37), 316 (Φ_3, 100), 303 (Φ_1, 45), 302 (Φ_4, 15), 263 (Φ_5, 17), 250 (Φ_2, 37), 249 (Φ_6, 10), 198 (16), 197 (5), 145 (57), 116 (10), 105 (24), 104 (11), 78 (6), 40 (32)
IIj	345 (M^+, 18), 303 (Φ_3, 100), 292 (Φ_1, 27), 291 (Φ_4, 8), 250 (Φ_5, 36), 239 (Φ_2, 21), 238 (Φ_6, 5), 144 (12), 117 (12), 105 (54), 104 (6), 94 (21), 93 (7), 78 (18), 77 (6)
IIk	315 (M^+, 25), 273 (Φ_3, 100), 272 (20), 262 (Φ_1, 32), 261 (Φ_4, 13), 257 (52), 230 (5), 220 (Φ_5, 17), 219 (8), 218 (6), 209 (Φ_2, 42), 208 (Φ_6, 11), 204 (6), 203 (5), 166 (18), 157 (7), 151 (9), 117 (14), 78 (6), 64 (15)
III	399 (M^+, 21), 370 (6), 359 (Φ_3, 100), 346 (Φ_1, 17), 345 (Φ_4, 8), 306 (Φ_5, 24), 293 (Φ_2, 14), 292 (Φ_6, 10), 272 (26), 259 (57), 232 (5), 230 (15), 219 (43), 218 (5), 206 (22), 205 (8), 166 (17), 153 (7), 117 (9)
IIIe*2	335 (M^+, 13), 300 (6), 293 (Φ_5, 86), 292 (23), 282 (Φ_2, 5), 281 (Φ_6, 12), 279 (34), 265 (M—Cl_2, 100), 244 (5), 239 (7), 238 (11), 237 (5), 230 (24), 226 (29), 225 (10), 223 (6), 222 (11), 212 (7), 209 (34), 187 (5), 177 (8), 174 (13), 117 (21)
IIIg*2	503 (M^+, 13,5), 468 (27), 463 (Φ_5, 72), 450 (Φ_2, 36), 449 (Φ_6, 11), 433 (M—Cl_2, 100), 415 (6), 398 (17), 386 (7), 380 (15), 345 (8), 292 (16), 279 (43), 257 (5), 244 (13), 239 (10), 226 (33), 225 (7), 222 (15), 209 (8), 187 (27), 175 (12), 174 (37), 162 (16), 117 (5), 109 (16), 108 (5)
IIIh*2	342 (M+·, 27), 307 (14), 302 (Φ_5, 64), 289 (Φ_2, 22), 288 (Φ_6, 19), 272 (M—Cl_2, 100), 254 (17), 253 (6), 237 (11), 225 (14), 219 (5), 218 (31), 198 (13), 184 (26), 183 (6), 117 (7), 105 (24), 104 (5)
IIIk	262 (M^+, 31), 261 (6), 222 (Φ_5, 100), 219 (6), 209 (Φ_2, 37), 208 (Φ_6, 9), 206 (37), 177 (25), 166 (48), 165 (12), 164 (5), 153 (15), 152 (7), 71 (18)
IIIl	346 (M^+, 23), 345 (5), 317 (9), 306 (Φ_5, 100), 293 (Φ_2, 16), 292 (Φ_6, 13), 219 (33), 206 (77), 179 (43), 177 (13), 166 (8), 165 (26), 153 (31), 152 (11), 71 (12)

*Showing peaks with an intensity of ≥ 5% of the maximum.

*2The *m/z* values of the molecular ions calculated for the ^{35}Cl isotope.

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS-48 instrument in KBr tablets. The PMR spectra were taken on a Bruker WP-100SY spectrometer, internal standard TMS. The mass spectra were obtained on an LKB-2091 instrument using direct introduction of the sample into the ion source (energy of the ionizing electrons, 70 eV; emission current 25 μA; temperature of ion source, 200°C) with vaporization of the samples at 130-150°C. The course of the reactions and purity of the products obtained were monitored by mean of TLC on Al_2O_3 of III degree activity (Brockman) in solvent systems of 15:1 chloroform–acetone (a), 15:1 benzene–methanol (b), and 10:1 benzene–methanol (c); development with iodine vapor.

The elementary analyses for C, H, and N agree with the calculated values.

The initial 2-amino-4,6-dipentyl- (Ia) [21], 2-amino-4,6-didodecyl- (b) [21], 2-amino-4-heptadecyl- (Ic) [24], 2-amino-4-pentyl-6(2-furyl)- (Id) [21], 2-amino-4-pentyl-6-trichloromethyl- (Ie) [21], 2-amino-4-dodecyl-6-trichloromethyl- (If) [25], 2-amino-4-heptadecyl-6-trichloromethyl- (Ig) [25], 2-amino-4-(3-pyridyl)-6-trichloromethyl- (Ih) [23], 2-amino-4,6-di(3-pyridyl)- (h) [23], 2-amino-4-(3-pyridyl)-6-(2-furyl)- (Ij) [26], 2-amino-4-dimethylamino-6-pentyl- (Ik) [27], 2-amino-4-dimethylamino-6-

undecyl- (Ii) [20], and 2-amino-4-dimethylamino-6-(3-pyridyl)-*sym*-triazine (Im) [23], were prepared by the methods in the papers cited above.

4,6-Disubstituted 2-Di(2-cyanoethyl)amino-*sym*-triazines (IIa-m). To a stirred solution of 20 mmoles of amino-*sym*-triazines Ia-m in 60-75 ml of solvent (Table 1) is added 1.5 ml of 30% aqueous KOH and then, dropwise, 4.32 g (80 mmoles) of freshly distilled acrylonitrile. The reaction mixture is stirred for 5-36 h at 55-60°C, then cooled to 20°C, neutralized with 5% HCl, and poured into 250 ml of cold water. The precipitate that forms is filtered off, washed on the filter with water, dried in vacuum over P_2O_5, and crystallized from the appropriate solvent (see Table 1).

2-(2-Cyanoethyl)amino-4,6-dipentyl-*sym*-triazine (IIIa). A. To a stirred solution of 1.0 g (18 mmoles) of KOH in 70 ml of absolute ethanol is added 4.10 g (12 mmoles) of bisadduct IIa. The reaction mixture is then stirred for 1.5 h at 40-45°C, cooled to 20°C, neutralized with 5% HCl, and poured into 250 ml of cold water. The precipitate of product IIIa that forms is filtered off, washed on the filter with water, dried, and crystallized from aqueous ethanol.

In analogous fashion, monoadducts IIIb, c, i, k-m are synthesized from bisadducts IIb, c, i, k-m, respectively.

2-(2-Cyanoethyl)amino-4-pentyl-6-trichloromethyl-*sym*-triazine (IIIe). B. A mixture of 2.83 g (10 mmoles) of amino-*sym*-triazine Ie and 1.47 g (15 mmoles) of β-dimethylaminopropionitrile in 30 ml of anhydrous DMF is stirred 8-10 h at 130-135°C. The reaction mixture is cooled to 20°C and poured into 150 ml of cold water. The precipitate of product IIIe that forms is filtered off, washed on the filter with water, dried in vacuum over P_2O_5, and crystallized from a 5:1 chloroform–acetone mixture.

In analogous fashion, monocyanoethyl derivatives IIIe-h are synthesized from amino-*sym*-triazines Ie-h, respectively.

2-(2-Cyanoethyl)amino-4,6-di(3-pyridyl)-*sym*-triazine (IIIi). C. A mixture of 2.5 g (10 mmoles) of amino-*sym*-triazine Ii, 3.56 (10 mmoles) of bisadduct IIi, and 0.5 ml of 30% aqueous KOH in 75 ml of ethanol is stirred for 5 h at 50-55°C. The reaction mixture is cooled to 20°C, neutralized with 5% HCl, and poured into 250 ml of cold water. The precipitate of product IIIi that forms is filtered off, washed on the filter with water, dried, and crystallized from methyl cellosolve.

In analogous fashion, derivatives IIIb, c, e-h, k are synthesized from compounds Ib, c, e-h, respectively.

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