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NUCLEOPHILIC SUBSTITUTION REACTIONS OF 2,4,6-TRIS(TRINITROMETHYL)-1,3,5-TRIAZINE.

2.* INTERACTION OF 2,4,6-TRIS(TRINITROMETHYL)-1,3,5-TRIAZINE WITH PRIMARY AMINES AND HEXAMETHYLDISILAZANE

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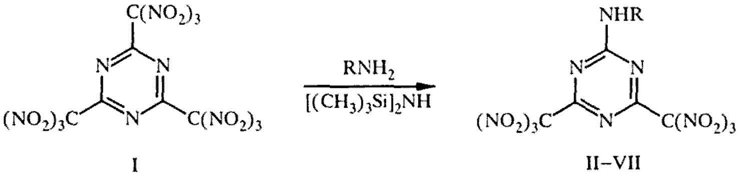
2-R-amino-4,6-bis(trinitromethyl)-1,3,5-triazines have been synthesized, and their structures have been established. Dynamic ^{13}C NMR spectroscopy has been used to measure the rotational barriers of the tert-butylamino group around the $C_{(2)}$—NHBu-t bond in 2-(tert-butylamino)-4,6-dichloro-1,3,5-triazine and 2-(tert-butylamino)-4,6-dimethoxy-1,3,5-triazine. X-ray diffraction was used to investigate the structure of 2-(tert-butylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine. From the results obtained in this work it has been concluded that the bond between the NHBu-t group and the triazine ring has a partial double-bond character.

We had previously reported on the synthesis of 2,4,6-tris(trinitromethyl)-1,3,5-triazine (I) [1, 2] and on its reactions with such nucleophiles as alcohols, diols, ammonia, and secondary amines [2]. We established that, depending on the conditions of the experiment, products of replacement of one, two, or three trinitromethyl groups may be obtained.

In the work reported here, we investigated the interaction of the triazine I with the primary amines methylamine, ethylamine, tert-butylamine, aniline, and ethanolamine, and also with hexamethyldisilazane, with equimolar reactant ratios. The products that were obtained, on the basis of elemental analyses, are identified as the corresponding mono-RNH-substituted 4,6-bis(trinitromethyl)-1,3,5-triazines (II-VII):



II R = CH_3; III R = C_2H_5; IV R = $t\text{-}C_4H_9$; V R = C_6H_5;
VI R = CH_2CH_2OH; VII R = $Si(CH_3)_3$

Further evidence in favor of replacement of only one trinitromethyl (TNM) group may be found in the chemical shifts of the signals from ^{14}N atoms of the remaining TNM groups (−38.6 to −39.6 ppm). The conclusion regarding monosubstitution follows from a comparison of these chemical shifts with those of analogous atoms in the previously obtained

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*For communication 1, see [2].

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TABLE 1. Data on ^1H, ^{13}C, and ^{14}N NMR Spectra of Compounds II-VII (Chemical Shifts, δ, ppm)

Compound	^1H	^{13}C					^{14}N, TNM group
		triazine ring			TNM group	other substituents	
		$C_{(2)}$	$C_{(4)}$	$C_{(6)}$			
II	3,1 (3H, d, CH_3), 6,6 (1H, m, NH)	165,0	162,8	161,9	122,3, 122,2	28,8 (CH_3)	-39,2
III	1,3 (3H, t, CH_3), 3,6 (2H, m, CH_2), 6,6 (1H, m, NH)	164,2	162,8	162,0	122,2, 122,1	37,7 (CH_2), 13,5 (CH_3)	-39,1, -39,3
IV	1,5 (9H, s, $3CH_3$), 6,6 (1H, s, NH)	163,4	162,3	161,8	122,2, 122,1	55,0 [$\underline{C}(CH_3)_3$], 27,9 [$C(\underline{C}H_3)_3$]	-39,2, -38,9
V	7,4...7,5 (5H, m, H_{Ph}), 8,2 (1H, s, NH)	162,6	162,2	162,3	121,4	133,7 (N–C_{Ph}), 129,9 (*o*-C_{Ph}), 127,8 (*m*-C_{Ph}), 121,5 (*p*-C_{Ph})	-39,4, -39,6
VI	3,7...3,8 (4H, m, $2CH_2$), 9,5 (2H, m, NH, OH)	171,1	165,7	163,6	122,4	60,0 (CH_2NH), 46,0 (CH_2OH)	-38,6
VII	0,4 (9H, s, $3CH_3$), 6,2 (1H, s, NH)	167,8	162,6	162,4	122,2	-1,5 (CH_3)	-39,1, -39,2

TABLE 2. Data on ^{13}C NMR Spectra of Compounds XII-XIV

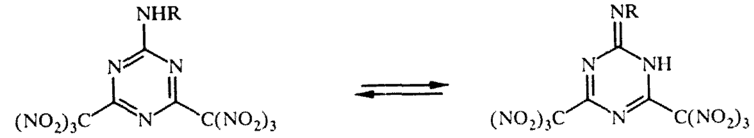
Compound	Spectrum recording temperature, °C	Chemical shifts, δ, ppm			
		triazine ring			substituent
XII	20	169,7	169,0	164,8	52,6 $[\underline{C}(CH_3)_3]$, 28,0 $[C(\underline{C}H_3)_3]$
XII	80		169,6	165,0	52,6 $[\underline{C}(CH_3)_3]$, 28,0 $[C(\underline{C}H_3)_3]$
XIII	20	171,3	171,0	166,8	53,7 (OCH_3), 53,3 (OCH_3), 50,6 $[\underline{C}(CH_3)_3]$, 28,0 $[C(\underline{C}H_3)_3]$
XIII	50		171,1	167,1	53,5 (OCH_3), 50,7 $[\underline{C}(CH_3)_3]$, 28,2 $[C(\underline{C}H_3)_3]$
XIV	20		165,2	164,8	49,9 $[\underline{C}(CH_3)_3]$, 35,5 $[N(CH_3)_2]$, 28,9 $[C(\underline{C}H_3)_3]$

monosubstituted product 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazine (VIII) and disubstituted product 2,4-diamino-6-trinitromethyl-1,3,5-triazine (IX): −39.8 and −35.6 ppm, respectively [2].

It should be noted that the ^{13}C NMR spectra of compounds II-VII exhibited three signals of ^{13}C nuclei of the triazine ring rather than two signals, as was observed previously for the amine VIII, its N,N-dimethyl derivative X and the diamine IX [2]. This indicates dissymetry of their molecules relative to the $C_{(2)}$—NHR bond. In such a case, the ^{13}C and ^{14}N atoms of the TNM groups of products II-VII should be represented by two signals in the corresponding NMR spectra. This is what was actually observed in the ^{13}C NMR spectra of the triazines II-IV and the ^{14}N NMR spectra of the triazines III-V and VII. In the other cases (compounds V-VII for the ^{13}C spectra and compounds II and IV for the ^{14}N spectra), we found only one signal for these atoms, possibly because of the very similar chemical shifts (Table 1).

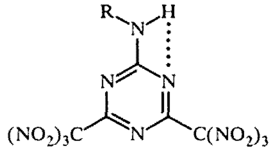
Possible reasons for the molecular dissymmetry of the triazines II-VII are as follows:

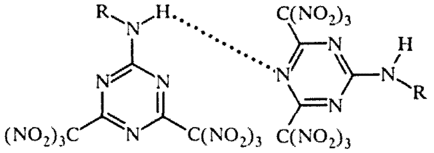
1) Existence of these compounds in the tautomeric form B:



A B

2) The presence of intermolecular or intramolecular hydrogen bonds in solution, for example:





3) Retarded rotation of the substituent around the $C_{(2)}$—NHR bond.

Evidence that the triazines II-VII exist in the tautomeric form A may be found in the significant differences between chemical shifts of the proton of the exocyclic NH group of II-VII (6.2-9.5 ppm) and that of the ring NH group in the 2,4,6-tris[di(alkoxycarbonyl)methylene]-1,3,5-hexahydrotriazines that we had synthesized previously [1] (12-14 ppm).

Attribution of the nonequivalence of the C and N atoms of the two TNM groups to intermolecular or intramolecular hydrogen bonds in solution can also be virtually ruled out. This conclusion is supported by ^{13}C NMR spectral data on 2-(methylphenylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine (XI), the substituents of which are incapable of forming hydrogen bonds: As expected, this spectrum contains three signals from the carbon atoms of the heterocycle and two from the carbon atoms of the TNM groups [2].

In order to determine the influence on molecular dissymmetry from retarded rotation of the substituent around the $C_{(2)}$—NHR bond, we synthesized compounds with bulky tert-butyl substituents, namely 2-(tert-butylamino)-4,6-dichloro-1,3,5-triazine (XII) and 2-(tert-butylamino)-4,6-dimethoxy-1,3,5-triazine (XIII). The ^{13}C NMR spectra of these products indicate molecular dissymmetry. Thus, in the ^{13}C NMR spectra of the triazines XII and XIII, taken at 20°C, three signals of the triazine ring are observed, and in the case of compound XIII, two signals of the methoxy groups as well (Table 2). At the same time, the bis(trinitromethyl)triazines VIII and X, containing substituents such as an amino or dimethylamino group, manifest the properties of symmetric structures: two signals of the triazine ring in the ^{13}C NMR spectrum, and one signal of the TNM group in each of the ^{13}C and ^{14}N NMR spectra [2]. These differences are most likely related to hindered rotation of the RNH or RR'N group relative to the ring, such rotation presumably being facilitated by higher temperatures. In order to clarify this

TABLE 3. Activation Parameters of Process of Intramolecular Rotation around $C_{(2)}$—N Bonds in Compounds XII and XIII

Parameter	Compound	
	XII	XIII
E_a, kJ/mole	86,5 ± 0,9	54,6 ± 2,0
ΔG^*, kJ/mole	73,9 ± 0,9	67,7 ± 2,0
ΔS^*, $J \cdot mole \cdot K^{-1}$	28,5 ± 2,7	-52,3 ± 7,0
T, K	343	300

question, we observe the changes in ^{13}C NMR spectra of compounds XII and XIII at elevated temperatures. As noted above, the spectrum of compound XIII at 20°C contained two individual signals of carbon atoms of positions 4 and 6 of the triazine ring and two signals of methoxy groups; in contrast, when the specimen was heated, the signals gradually broadened and then merged in pairs, such that when the temperature had reached only 50°C, the observed spectrum corresponded to a symmetric compound: two signals of the ring and one of the methoxy groups. Analogous changes in the form of the spectra were observed for the triazine XII (see Table 2).

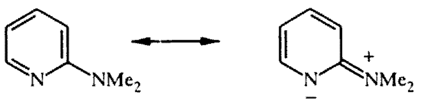
It is known that the NMR spectra of many compounds are temperature-dependent. For example, in a study of the spectrum of dimethylformamide [3], it was found that the spectrum taken at 40°C exhibited a doublet signal of the methyl-group protons, but at 160°C only a singlet.

A mathematical analysis of the temperature dependence of the complete form of the line for the signal of the exchanging pairs can provide a means for measuring the thermodynamic parameters of the exchange process. For this purpose, using a known equation of line form for a resonance signal of two exchanging nuclei [3, p. 256], we wrote an iteration program DYNNR. Calculated values for the barrier to rotation of the substituted amino group around the $C_{(2)}$—NHR bond in compounds XII and XIII are listed in Table 3.

It should be noted that the nature of the substituents in the triazine ring (with exactly the same substituent in the amino group) is the primary factor determining the magnitude of the rotational barrier. This influence can be followed in a series of disubstituted 2-(tert-butylamino)triazines containing, in positions 4 and 6, two TNM groups (IV), two chlorine atoms (XII), two methoxy groups (XIII), or two dimethylamino groups (XIV). In the case of compound IV, the NMR spectra did not change upon heating all the way up to 80°C; in the spectra of the triazine XII at 80°C and the triazine XIII at 50°C, we observed complete averaging of the signals of the unsymmetric carbon atoms, i.e., an overcoming of the rotational barrier; in contrast, the dimethylamino derivative XIV exhibited the properties of a symmetric compound even at room temperature, indicating a low barrier to rotation. The influence of the substituents in the triazine ring on the magnitude of the rotational barrier can also be seen from the quantitative data presented in Table 3.

In fundamental reviews devoted to 1,3,5-triazines [4, 5] and in original papers on the NMR spectroscopy of these compounds [6, 7], there is no information on hindered rotation around the N—C bond in substituted aminotriazines. We have found in the literature only an indirect indication of a possible influence of the triazine ring on the barrier to intramolecular rotation of a substituent RNH in our compounds. Thus, hindered rotation of amino groups in anilines containing electron-acceptor substituents in the benzene ring has been described by many investigators [8-11]. It was shown in those studies that the magnitude of the barrier increases with increasing electron-acceptor strength of the substituent; this correlates well with our observations for the series of 2-(tert-butylamino)-4,6-disubstituted triazines.

Nitrogen-containing heterocycles are known electron acceptors owing to the presence of the nitrogen atoms in the ring, leading to an increase in magnitude of the rotational barrier in comparison with the anilines. The electronic effect can be explained by additional stabilization of a structure containing an exocyclic double bond and a localized negative charge on the nitrogen atom of the ring.



A comparative study of the barriers to rotation in dimethylamino-substituted nitropyridines and pyrimidines was reported in [12, 13].

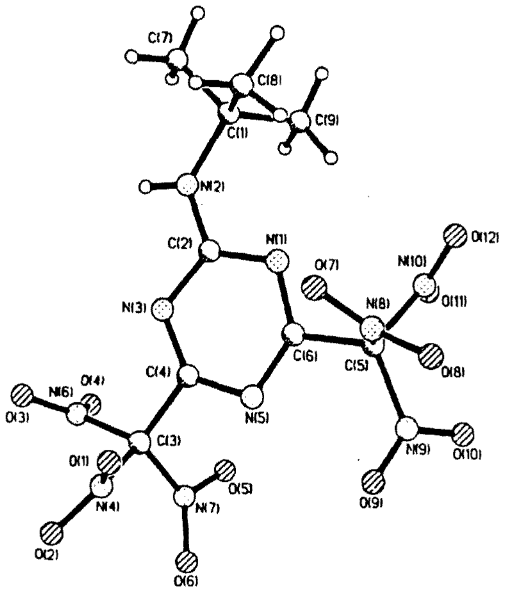
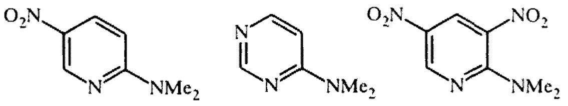


Fig. 1. Structure of molecule of 2-(tert-butylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine (IV).



ΔG# (kJ/mole)	51,5	51,1	41,5

On the basis of the data obtained in those studies, the investigators concluded that the influence of one or several nitrogen atoms on the electron-acceptor properties of the heterocyclic ring is comparable to the effect of replacing a nitro group at the corresponding position of a carbon ring.

Thus, by analogy with compounds XII and XIII, we can conclude that all of our synthesized triazines have a high barrier to rotation of the RNH substituent (or the NMePh substituent) around the $C_{(2)}$—NR bond, which bond apparently has a partial double-bond character as a consequence of the acceptor properties of the triazine ring.

For the 2-(tert-butylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine IV, we determined the molecular structure by means of electron diffraction. This structure is shown in Fig. 1. The coordinates of the atoms and their temperature factors are listed in Table 4, and the bond lengths and angles in Tables 5 and 6, respectively.

The triazine ring in the molecule of compound IV is planar; the mean square deviation of the atoms from the average plane is 0.006 Å, and the $N_{(2)}$ nitrogen atom in the NHR group deviates by 0.021 Å. All of the nitro groups depart from the plane of the heteroring by rotation around the $C_{(2)}$—$N_{(2)}$ bond by 55-90°. The bond lengths and angles in the triazine ring are in good agreement with the analogous values found for previously studied derivatives of 1,3,5-triazine, for example 6-methoxy-2-chloro-4-cyclohexylamino-1,3,5-triazine [14]. The $N_{(2)}$ atom has a plane-trigonal coordination of the bonds. The length of the $C_{(2)}$—$N_{(2)}$ bond is 1.325(5) Å, i.e., appreciably shorter than the analogous single bond in aromatic amines, for example in the molecule of N,N-dimethylaniline 1.43(2) Å [15], and very close to the average value of the length of the C—N bonds (1.336 Å) in six-membered nitrogen-containing aromatic rings [16]. This is evidence of significant conjugation of the unshared electron pair of the $N_{(2)}$ atom and the π-system of the 1,3,5-triazine ring, i.e., evidence of partial double-bond character.

EXPERIMENTAL

The IR spectra of the substances we synthesized were obtained in a Specord IR-75 instrument in KBr tablets. The ^1H, ^{13}C, and ^{14}N NMR spectra were recorded in a Bruker AM-300 instrument at respective working frequencies of 300, 75.5, and

TABLE 4. Coordinates of C, O, and N Atoms ($\times 10^4$) and H Atoms ($\times 10^3$) and Their Equivalent Isotropic Temperature Factors ($U_{eq} \times 10^3$) in Molecule of 2-(tert-Butylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine (IV)

Atom	x	y	z	U_{eq}
$O_{(1)}$	5440(3)	4807(5)	3611(2)	45(1)
$O_{(2)}$	6299(4)	6779(8)	4414(3)	79(2)
$O_{(3)}$	5694(4)	8981(7)	3194(3)	69(2)
$O_{(4)}$	4647(4)	10653(5)	3493(3)	72(2)
$O_{(5)}$	3474(4)	8588(8)	4196(3)	68(2)
$O_{(6)}$	4722(5)	7037(9)	4935(3)	89(3)
$O_{(7)}$	2635(4)	1562(5)	1984(3)	53(2)
$O_{(8)}$	1865(3)	14(4)	2607(2)	39(1)
$O_{(9)}$	2684(3)	2330(5)	3893(2)	52(1)
$O_{(10)}$	1108(4)	3064(6)	3627(2)	57(2)
$O_{(11)}$	377(3)	4961(6)	2310(3)	64(2)
$O_{(12)}$	357(3)	2485(6)	1667(2)	63(2)
$N_{(1)}$	2173(3)	5495(4)	1901(2)	20(1)
$N_{(2)}$	2549(3)	7705(4)	1143(2)	22(1)
$N_{(3)}$	3571(3)	7561(4)	2380(2)	20(1)
$N_{(4)}$	5489(4)	6158(5)	3952(2)	42(1)
$N_{(5)}$	3230(3)	5361(4)	3200(2)	21(1)
$N_{(6)}$	5053(3)	9223(5)	3460(2)	33(1)
$N_{(7)}$	4261(4)	7942(8)	4347(2)	46(2)
$N_{(8)}$	2149(3)	1412(5)	2398(2)	28(1)
$N_{(9)}$	1877(4)	2823(5)	3473(2)	36(1)
$N_{(10)}$	745(3)	3561(6)	2170(3)	38(1)
$C_{(1)}$	1677(3)	7328(5)	435(2)	29(1)
$C_{(2)}$	2755(3)	6897(4)	1807(2)	18(1)
$C_{(3)}$	4610(3)	7495(5)	3686(2)	23(1)
$C_{(4)}$	3733(3)	6761(5)	3029(2)	20(1)
$C_{(5)}$	1819(3)	3208(5)	2667(2)	20(1)
$C_{(6)}$	2472(3)	4836(4)	2599(2)	19(1)
$C_{(7)}$	1804(5)	8760(8)	-127(3)	39(2)
$C_{(8)}$	1752(5)	5404(6)	153(3)	37(2)
$C_{(9)}$	684(4)	7652(7)	570(3)	37(2)
$H_{(2)}$	297(4)	857(8)	115(3)	80

21.6 MHz in the Fourier mode, in $(CD_3)_2SO$. The purity of the compounds was checked by means of TLC on Silufol UV-254 plates, with CH_2Cl_2 or $CHCl_3$ as the solvent. The melting points were determined on a Boetius heating stage.

The temperature dependence of the form of the ^{13}C NMR spectra of the triazines XII and XIII was investigated by means of a JEOL-FX90Q instrument (frequency 22.55 MHz for ^{13}C). For the compound XII, 7 measurements were made in the temperature interval from +40° to +100°C; for the XIII, 11 measurements were made at temperatures from −10° to +50°C. The error in measuring the temperature was no greater than ±1°C. The rate constants of the intramolecular exchange process were determined separately at each temperature by analyzing the complete form of the line corresponding to the NMR signal. For the best approximation of the form of the experimental spectra, the DYNNMR iteration program was used. The thermodynamic characteristics of the transition state were determined from the temperature dependence of the rate constant by use of the Arrhenius equation; here, the respective coefficients of correlation for XII and XIII were 0.9942 and 0.9738.

X-ray Structure Analysis of Compound IV. The analysis was performed at 178 K in a Syntex $P2_1$ diffractometer (λ MoKα, graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max} = 48°$). Crystals of IV ($C_9H_{10}N_{10}O_{12}$, M 450.2) were grown from hexane and were found to be monoclinic: $a = 14.086(7)$, b = 7.331(3), c = 18.892(9) Å, $\beta = 110.29(4)°$, V = 1829.8(15) Å^3, Z = 4, space group $P2_1/c$.

The structure was deciphered by the direct method and refined by the full-matrix least squares method in the anisotropic approximation for the nonhydrogen atoms. The hydrogen atom of the amino group was localized from a difference synthesis; the coordinates of the hydrogen atoms of the t-Bu group were calculated geometrically. The hydrogen atoms of the t-Bu group were refined in the rider model. All of the hydrogen atoms were refined isotropically with fixed temperature factors ($U_{iso} = 0.08$ Å^2). The final values of the divergence factor were R = 0.085 and $R_w = 0.11$ on the basis of 2462 independent

TABLE 5. Bond Lengths d (Å) in Molecule of Compound IV

Bond	d	Bond	d
$O_{(1)}$—$N_{(4)}$	1,171(6)	$O_{(2)}$—$N_{(4)}$	1,256(6)
$O_{(3)}$—$N_{(6)}$	1,189(8)	$O_{(4)}$—$N_{(6)}$	1,207(6)
$O_{(5)}$—$N_{(7)}$	1,147(8)	$O_{(6)}$—$N_{(7)}$	1,263(7)
$O_{(7)}$—$N_{(8)}$	1,209(7)	$O_{(8)}$—$N_{(8)}$	1,215(5)
$O_{(9)}$—$N_{(9)}$	1,195(6)	$O_{(10)}$—$N_{(9)}$	1,226(8)
$O_{(11)}$—$N_{(10)}$	1,219(7)	$O_{(12)}$—$N_{(10)}$	1,210(6)
$N_{(1)}$—$C_{(2)}$	1,364(5)	$N_{(1)}$—$C_{(6)}$	1,327(5)
$N_{(2)}$—$C_{(1)}$	1,495(5)	$N_{(2)}$—$C_{(2)}$	1,325(5)
$N_{(3)}$—$C_{(2)}$	1,367(4)	$N_{(3)}$—$C_{(4)}$	1,306(5)
$N_{(4)}$—$C_{(3)}$	1,521(6)	$N_{(5)}$—$C_{(4)}$	1,348(5)
$N_{(5)}$—$C_{(6)}$	1,319(4)	$N_{(6)}$—$C_{(3)}$	1,537(6)
$N_{(7)}$—$C_{(3)}$	1,527(7)	$N_{(8)}$—$C_{(5)}$	1,541(5)
$N_{(9)}$—$C_{(5)}$	1,523(6)	$N_{(10)}$—$C_{(5)}$	1,501(5)
$C_{(1)}$—$C_{(7)}$	1,546(7)	$C_{(1)}$—$C_{(8)}$	1,524(6)
$C_{(1)}$—$C_{(9)}$	1,525(8)	$C_{(3)}$—$C_{(4)}$	1,515(5)
$C_{(5)}$—$C_{(6)}$	1,540(6)	$N_{(2)}$—$H_{(2)}$	0,87(5)

TABLE 6. Bond Angles ω in Molecule of Compound IV

Angle	ω	Angle	ω
$C_{(2)}$—$N_{(1)}$—$C_{(6)}$	114,0(3)	$C_{(1)}$—$N_{(2)}$—$C_{(2)}$	127,4(4)
$C_{(2)}$—$N_{(3)}$—$C_{(4)}$	114,2(3)	$O_{(1)}$—$N_{(4)}$—$O_{(2)}$	123,7(5)
$O_{(1)}$—$N_{(4)}$—$C_{(3)}$	118,5(4)	$O_{(2)}$—$N_{(4)}$—$C_{(3)}$	115,8(4)
$C_{(4)}$—$N_{(5)}$—$C_{(6)}$	110,5(3)	$O_{(3)}$—$N_{(6)}$—$O_{(4)}$	126,5(5)
$O_{(3)}$—$N_{(6)}$—$C_{(3)}$	115,8(4)	$O_{(4)}$—$N_{(6)}$—$C_{(3)}$	117,1(5)
$O_{(5)}$—$N_{(7)}$—$O_{(6)}$	126,4(7)	$O_{(5)}$—$N_{(7)}$—$C_{(3)}$	116,3(4)
$O_{(6)}$—$N_{(7)}$—$C_{(3)}$	113,2(5)	$O_{(7)}$—$N_{(8)}$—$O_{(8)}$	127,7(4)
$O_{(7)}$—$N_{(8)}$—$C_{(5)}$	116,0(3)	$O_{(8)}$—$N_{(8)}$—$C_{(5)}$	116,2(4)
$O_{(9)}$—$N_{(9)}$—$O_{(10)}$	127,0(5)	$O_{(9)}$—$N_{(9)}$—$C_{(5)}$	115,3(5)
$O_{(10)}$—$N_{(9)}$—$C_{(5)}$	117,6(4)	$O_{(11)}$—$N_{(10)}$—$O_{(12)}$	127,5(4)
$O_{(11)}$—$N_{(10)}$—$C_{(5)}$	115,0(4)	$O_{(12)}$—$N_{(10)}$—$C_{(5)}$	117,5(4)
$N_{(2)}$—$C_{(1)}$—$C_{(7)}$	103,6(4)	$N_{(2)}$—$C_{(1)}$—$C_{(8)}$	110,4(3)
$C_{(7)}$—$C_{(1)}$—$C_{(8)}$	110,5(4)	$N_{(2)}$—$C_{(1)}$—$C_{(9)}$	109,7(4)
$C_{(7)}$—$C_{(1)}$—$C_{(9)}$	109,9(4)	$C_{(8)}$—$C_{(1)}$—$C_{(9)}$	112,4(4)
$N_{(1)}$—$C_{(2)}$—$N_{(2)}$	121,1(3)	$N_{(1)}$—$C_{(2)}$—$N_{(3)}$	122,9(3)
$N_{(2)}$—$C_{(2)}$—$N_{(3)}$	116,0(3)	$N_{(4)}$—$C_{(3)}$—$N_{(6)}$	105,1(4)
$N_{(4)}$—$C_{(3)}$—$N_{(7)}$	108,9(3)	$N_{(6)}$—$C_{(3)}$—$N_{(7)}$	109,1(3)
$N_{(4)}$—$C_{(3)}$—$C_{(4)}$	112,4(3)	$N_{(6)}$—$C_{(3)}$—$C_{(4)}$	111,0(3)
$N_{(7)}$—$C_{(3)}$—$C_{(4)}$	110,1(4)	$N_{(3)}$—$C_{(4)}$—$N_{(5)}$	129,2(3)
$N_{(3)}$—$C_{(4)}$—$C_{(3)}$	116,0(3)	$N_{(5)}$—$C_{(4)}$—$C_{(3)}$	114,8(3)
$N_{(8)}$—$C_{(5)}$—$N_{(9)}$	104,7(3)	$N_{(8)}$—$C_{(5)}$—$N_{(10)}$	107,2(3)
$N_{(9)}$—$C_{(5)}$—$N_{(10)}$	110,5(4)	$N_{(8)}$—$C_{(5)}$—$C_{(6)}$	112,1(4)
$N_{(9)}$—$C_{(5)}$—$C_{(6)}$	113,7(3)	$N_{(10)}$—$C_{(5)}$—$C_{(6)}$	108,4(3)
$N_{(1)}$—$C_{(6)}$—$N_{(5)}$	129,2(4)	$N_{(1)}$—$C_{(6)}$—$C_{(5)}$	111,9(3)
$N_{(5)}$—$C_{(6)}$—$C_{(5)}$	118,9(3)	$C_{(2)}$—$N_{(2)}$—$H_{(2)}$	113(4)
		$C_{(1)}$—$N_{(2)}$—$H_{(2)}$	120(4)

reflections [$I \geq 3\delta(I)$]. The high R-factor can be explained by the imperfection of the crystal, apparently attributable to the nature of the substance. All of the calculations were performed in an IBM PC/AT using SHELXTL PLUS programs [17].

The syntheses of 2,4,6-tris(trinitromethyl)-1,3,5-triazine (I) and 2-(methylphenylamino)-4,6-bis(trinitromethyl)-1,3,5-triazine (XI) were described in [2].

2-(tert-Butylamino)-4,6-dichloro-1,3,5-triazine (XII) was synthesized by a method described in [18]. Yield 93%, mp 131.5-132°C. Literature value mp 130.5-131.5.

2-(tert-Butylamino)-4,6-dimethoxy-1,3,5-triazine (XIII) was synthesized from the triazine XII and sodium methylate by a procedure given in [5, p. 274]. Yield 86%; oily liquid. Found, %: C 50.85, H 7.71, N 26.53. $C_9H_{16}N_4O_2$. Calculated, %: C 50.92, H 7.59, N 26.39.

TABLE 7. Characteristics of Compounds II-VII

Compound	Empirical formula	Found, % / calculated, %			mp, °C	IR spectrum, ν, cm^{-1}	Yield, %*
		C	H	N			
II	$C_6H_4N_{10}O_{12}$	17,78 17,65	1,03 0,99	34,73 34,32	103...104	3425, 1630, 1590, 1535, 1430, 1385, 1350, 1290, 1215, 1150, 1100, 1050, 990, 860, 840, 815, 800, 790, 786	70
III	$C_7H_6N_{10}O_{12}$	20,00 19,91	1,55 1,43	33,16 33,18	88	3420, 2970, 2850, 1620, 1580, 1530, 1270, 1080, 1020, 950, 780, 580	70
IV	$C_9H_{10}N_{10}O_{12}$	23,84 24,00	2,24 2,22	30,84 31,11	146	3400, 3000, 1590, 1530, 1280, 1200, 1100, 1000, 800	55...60
V	$C_{11}H_6N_{10}O_{12}$	28,11 28,09	1,50 1,28	29,83 29,79	146,5	3370, 2980, 1620, 1600, 1510, 1500, 1460, 1420, 1380, 1290, 1100, 990, 840, 790	60...65
VI	$C_7H_6N_{10}O_{13}$	19,30 19,18	1,49 1,38	32,21 31,96	146...148	3610, 3270, 3200, 3150, 3050, 2960, 2910, 2590, 2290, 1600, 1550, 1450, 1290, 1200, 1160, 1140, 1070, 990, 870, 860, 790	57
VII*²	$C_8H_{10}N_{10}O_{12}Si$				102...103	3250, 2900, 1580, 1560, 1500, 1420, 1400, 1360, 1250, 1200, 800	70...80

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*Product yield values refer to recrystallized sample, calculated on hexahydrotriazine XV.

*²Compound VII was not subjected to elemental analysis, since the product was converted quantitatively to a compound we had described previously [2], 2-amino-4,6-bis(trinitromethyl)-1,3,5-triazine, by treatment with a solution of methanol or ethanol in CCl_4.

2-(tert-Butylamino)-4,6-bis(dimethylamino)-1,3,5-triazine (XIV) was obtained from the triazine XII and dimethylamine by a known method [19]. Yield 90%, mp 105°C sublimes at 100°C. Found, %: C 55.60, H 9.23, N 35.40. $C_{11}H_{22}N_6$. Calculated, %: C 55.42, H 9.30, N 35.21.

2-R-amino-4,6-bis(trinitromethyl)-1,3,5-triazines (II-VII) (general procedure). To a solution of the triazine I, obtained from 4 mmoles of 2,4,6-tris[di(tert-butoxycarbonyl)methylene]-1,3,5-hexahydrotriazine XV in 100 ml of absolute CCl_4, at 0-5°C with stirring, a solution of the appropriate amine or hexamethyldisilazane in CCl_4 was added until disappearance of the TLC spot corresponding to the original triazine I on the start and "tail" of nitroform. The subsequent treatment of the reaction mixture was carried out in accordance with method A or B. *A*) The precipitated nitroform salt of the amine was filtered off and washed with CCl, the wash liquid being combined with the original filtrate. The solvent was driven off, and the residue was recrystallized from hexane or a minimum quantity of CCl_4. ***B***) The contents of the flask were washed with water until a colorless water layer was obtained. The organic layer was separated off and dried with calcined $MgSO_4$, the solvent was driven off, and the residue was recrystallized in the same manner as in method A.

In case of interaction of the triazine I with hexamethyldisilazane, in order to decompose the trimethylsilyl ester of nitroform that was formed in the course of the reaction, the reaction mixture was washed with a minimum quantity of water (10 × 3 ml), so as to avoid hydrolysis of the final product. Subsequent treatment followed method B.

The characteristics of the synthesized compounds are listed in Table 7.

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