

AD 285397

RESEARCH AND DEVELOPMENT DEPARTMENT
J. E. Wilson, Director

NavWeps Report 7109
Technical Report 116

11 May 1962

SYNTHESIS AND PROPERTIES OF
SOME CYANURIC CHLORIDE DERIVATIVES

By

M. S. Chang
A. J. Matuszko

U. S. NAVAL PROPELLANT PLANT
Indian Head, Maryland

O. A. WESCHE
Captain, USNavy
Commanding Officer

J. E. DODGEN
Commander, USNR
Technical Director

FOREWORD

This report combines a summary of significant accomplishments of foundational research task assignments of the Fundamental Processes Division during the period from September 1959 to September 1961.

This report is transmitted for information only. It does not represent the official views or final judgment of the Naval Propellant Plant. It represents information released at the working level that is still subject to modification and withdrawal.

The work was performed under Tasks NPP-00-213/32015/07041, R-360-FR109/RO1101/001, and R-360-FR109/RO1101/001/286/1, and data are recorded on laboratory notebook pages 71176-71250 and 61201-61275.

A. J. Matuszko

A. J. Matuszko
Head, Polymer Division

Approved by:

Bodo Bartocha

Bodo Bartocha
Associate Director for
Research

Released by:

O. A. Wesche

O. A. WESCHE
Captain, USNavy
Commanding Officer

NAVWEPS REPORT 7109

CONTENTS

<u>Heading:</u>	<u>Page no.</u>
Foreword _____	iii
Abstract _____	vi
Historical _____	1
Discussion _____	3
Experimental Details _____	10
References _____	19

ABSTRACT

Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Completely substituted reaction products were obtained with trifluoroethanol, tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol which has a tertiary nitro group, whereas alcohols with primary and secondary nitro groups did not react. The reaction with the potassium salt of nitroform gave a product which gradually decomposed on standing. The monoperchlorate salt of trihydrazino-s-triazine was obtained, but attempts at the preparation of perchlorate derivatives of amincazido-s-triazines were unsuccessful. Sensitivity and stability data are reported on some of the products.

SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES

A project involving the synthesis of cyanuric chloride derivatives was undertaken with the purpose of preparing heat-stable materials which might be useful as propellant ingredients. Because of certain similarities in structure between cyanuric chloride and trimeric phosphonitrilic chloride, an investigation of the reactions with these two compounds was undertaken concurrently. The study with trimeric phosphonitrilic chloride will appear in a later report.

Reactions of cyanuric chloride (2,4,6-trichloro-s-triazine) with hydroxyl compounds to give alkoxy-s-triazines and aryloxy-s-triazines have been studied extensively by F. C. Schaefer's group at American Cyanamid Company. (1,2) However, reactions with alcohols and alkanes containing nitroxy or nitro groups have not to our knowledge been reported. Therefore, as part of our study we undertook acquiring information on the reactivity of negatively substituted alcohols and alkanes with cyanuric chloride. Azido and hydrazino derivatives of cyanuric chloride proved of sufficient interest in gas-generator applications to warrant their inclusion in this investigation.

HISTORICAL

Cyanuric chloride has been known since 1827, (3) although for some time it was considered to be the trichloride of cyanogen. Liebig (4) determined its composition after preparing the compound by passing chlorine over dry potassium thiocyanate.

Impure cyanogen chloride was converted to cyanuric chloride with sunlight by Serullas. (3) However, the product was believed for many years to be an isomer rather than the trimer of cyanogen chloride. As late as 1867, (5) the trimer to monomer relationship of cyanuric chloride and cyanogen chloride was not clearly understood. Infrared and ultraviolet spectra (6) now support the triazine

NAVWEPS REPORT 7109

structure and indicate that the chlorines are located on the carbon atoms.

Cyanuric chloride is readily hydrolyzed by water vapor to cyanuric acid and hydrochloric acid. Treating cyanuric chloride with hot alcohols produces cyanuric acid⁽⁷⁾ and the corresponding alkyl halide with almost no esterification. Mono-, di-, and tri-alkyl esters of cyanuric acid have been made by reacting cyanuric chloride with alkaline earth alkoxides^(8,9) or with alcohols in the presence of basic acceptors.⁽⁹⁾ To carry out a stepwise substitution, the preferred base is either sodium carbonate or sodium hydroxide.⁽¹⁰⁾

Primary and secondary amines, hydrazines, and related compounds react with cyanuric chloride in three steps. The oversimplified rule of thumb, expressed frequently in the literature,⁽¹⁰⁻¹⁹⁾ that the first chlorine atom is replaced at 0° C, the second at 30°-50° C, and the third at 90°-100° C cannot be used generally. This rule applies only to water solutions and not to other solvents. Some amines react to replace all three chlorine atoms at 0° C; others do not react at all, or react with the replacement of only one of the chlorines even at 100° C.

Certain mercaptans or their alkali metal salts react with cyanuric chloride⁽²⁰⁾ indicating that the chlorine atoms are sufficiently active.

Cyanuric triazide is produced⁽²¹⁾ by the reaction of sodium azide and cyanuric chloride in aqueous acetone solution.

Cyanuric chloride has been reported⁽²²⁾ to react vigorously with silver nitrate in acetonitrile solution to form a trinitro-s-triazine which has not been well characterized.

Alkyl Grignard reagents react with one of the chlorine atoms of cyanuric chloride^(23,24), whereas, with some aryl Grignard reagents, two chlorine atoms^(24,25) undergo replacement. The products are 2-alkyl-4,6-dichloro-s-triazines and 2,4-diaryl-6-chloro-s-triazines, respectively.

Cyanuric chloride reacts⁽²⁶⁾ with iodo- or bromobenzene^(8,27) or with bromophenetole and sodium to give mixtures of di- and tri-aryl-s-triazines. A mixture of cyanuric iodide and 2-chloro-4,6-diiodo-s-triazine is produced when a cold 56% hydroiodic acid solution is mixed with cyanuric chloride.⁽⁷⁾ This again is

essentially a simple exchange reaction wherein iodine replaces chlorine on the triazine ring.

Tris-(hydroxyaryl)-s-triazines⁽¹⁰⁾ are formed by the reactions of phenols with cyanuric chloride in the presence of aluminum chloride catalyst. Cyanuric chloride reacts with sodium salts of organic carboxylic acids,⁽²⁸⁾ as well as with the free acids, to form sodium cyanurate and the corresponding acyl halides.

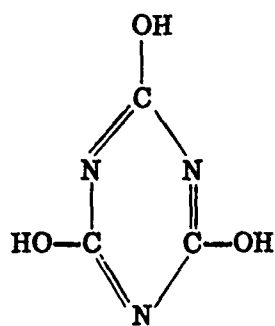
The active hydrogen of diethyl malonate reacts with one chlorine atom in cyanuric chloride⁽²⁹⁾ to form the (4,6-dichloro-s-triazinyl)-diethyl malonate. The primary reaction is base-catalyzed. In order to have a reaction with all three of the chlorines of cyanuric chloride at least three equivalents of sodium malonic ester and vigorous conditions are required.⁽²⁹⁾

When cyanuric chloride is heated with benzamide, the cyanuric chloride is hydrolyzed to cyanuric acid as benzamide is dehydrated to benzonitrile.⁽²⁸⁾

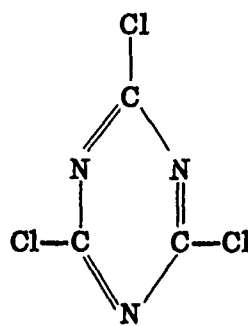
Cyanuric chloride is resistant to the action of most reducing agents. With lithium aluminum hydride in ether, Grundmann and Beyer⁽³⁰⁾ found only the inorganic products lithium chloride (LiCl), aluminum chloride (AlCl₃), and lithium aluminum cyanide (LiAl(CN)₄) in the reaction mixture; hydrogen was evolved during the reaction.

DISCUSSION

Cyanuric chloride, the starting material in the synthesis of s-triazine derivatives, is the acid chloride of cyanuric acid.



Cyanuric Acid



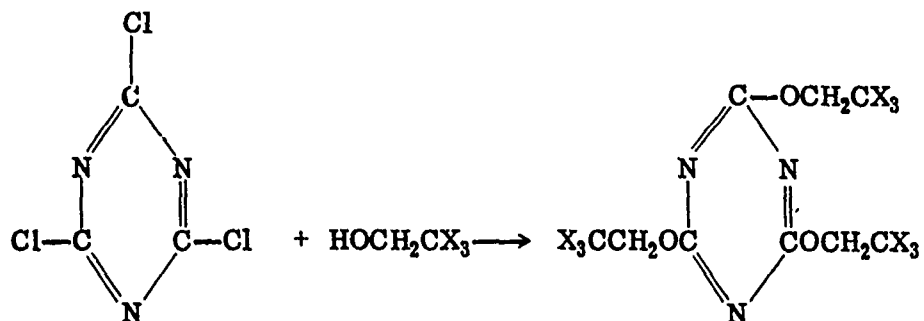
Cyanuric Chloride.

According to Pauling⁽³¹⁾ the s-triazine ring is stabilized by a resonance energy of 82.5 kcal/mole compared to 39 kcal/mole for benzene. The high resonance energy is probably due to the six nonbonding electrons on the three ring nitrogens which contribute to the resonating system. Because of the high stability of the ring, much of the chemistry of s-triazines is simply the chemistry of the substituent groups. The ring is not often involved in the reactions except for its effect on the charge distribution.

This study was initiated with the purpose of synthesizing and determining the properties of nitro and nitroxy derivatives having the s-triazine nucleus. It was hoped that the reactivity of the chlorines in cyanuric chloride together with the high ring stability would result in the preparation of highly stable products. Halogen derivatives were included in the study because of the electron withdrawing properties (electronegativities) of the halogens which are similar to those of the nitro and nitroxy groups. Hydrazino and azido compounds were synthesized as potential gas generator ingredients.

Reactions of Cyanuric Chloride with Polyhalogen Alcohols:

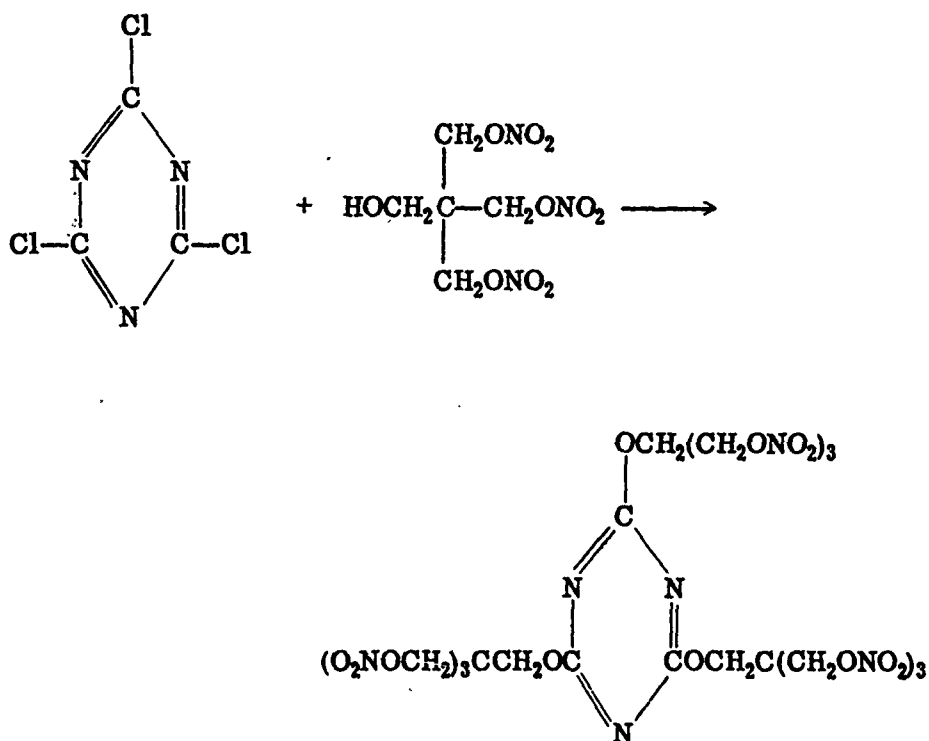
Trifluoroethanol and tribromoethanol were reacted with cyanuric chloride. These alcohols were used to determine whether electron withdrawing halogen substituents affected the reactivity of the alcohol with cyanuric chloride or the stability of the final product. Both reactions proceeded smoothly to form the corresponding esters in good yields indicating that the electronegative groups did not hinder ester formation. The products appeared to be thermally stable up to and above 190° C.



where X = F or Br.

Reactions of Cyanuric Chloride with Nitroxylalcohols:

Reactions were carried out to determine whether nitroxy groups affected esterification or the subsequent stability of the products. Pentaerythritol trinitrate (PETriN)¹ and pentaerythritol dinitrate² were the nitroxylalcohols used in these reactions. The cyanuric tri-ester was successfully obtained by the reaction of pentaerythritol trinitrate and cyanuric chloride in aqueous acetone solution with potassium hydroxide as the acid acceptor. This, to our knowledge, is the first nitrate ester reported in the s-triazine series.

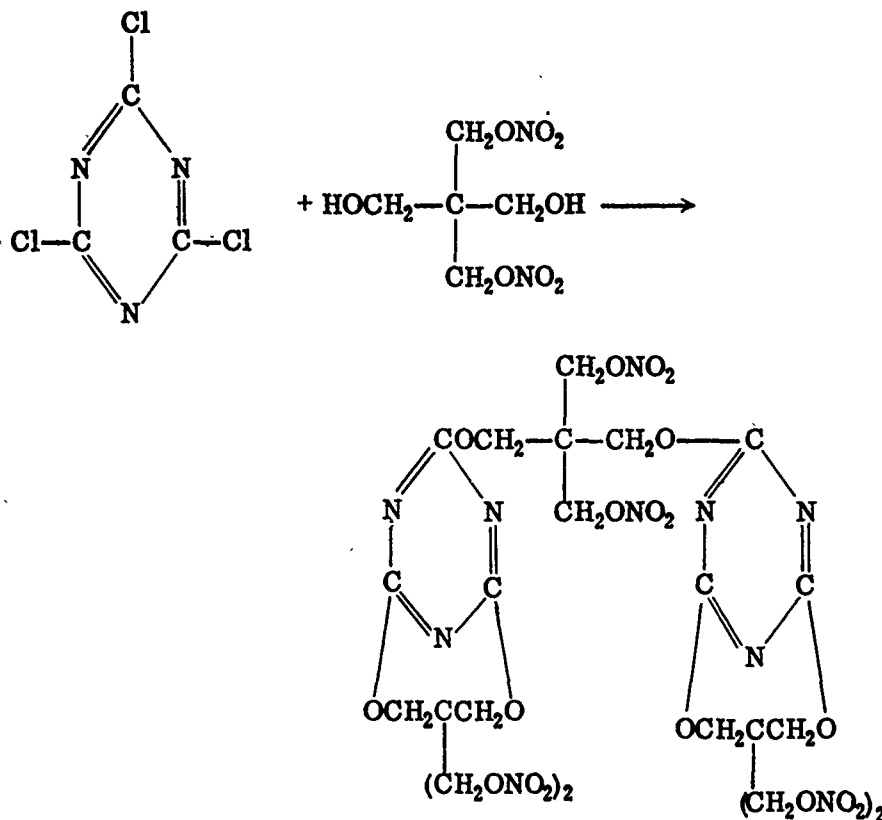


Pentaerythritol dinitrate was reacted as above to form the corresponding tri-ester. The second hydroxyl group of pentaerythritol dinitrate underwent esterification as did the first hydroxyl group. Elemental analyses and molecular weight data indicate a reaction between two molecules of cyanuric chloride and three

¹ 2,2-Bis(nitroxymethyl)-3-nitroxy-1-propanol.

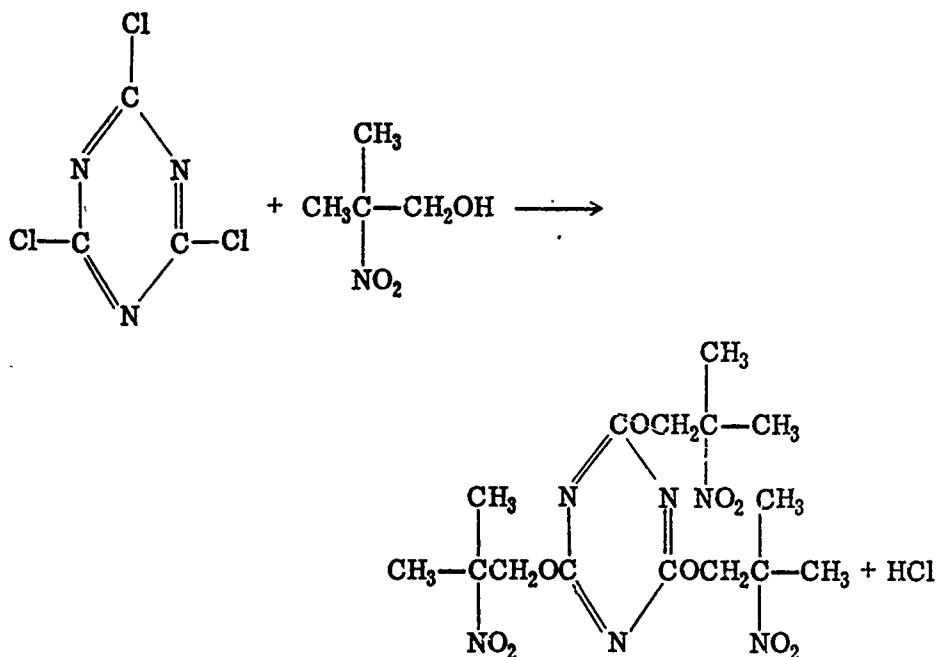
² 2,2-Bis(nitroxymethyl)-1,3-propanediol.

molecules of pentaerythritol dinitrate. A possible structure for the product is shown below.

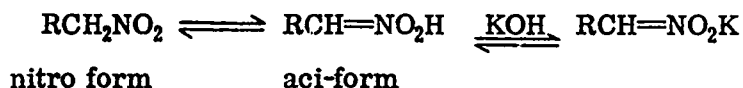


Reactions of Cyanuric Chloride with Mononitroalcohols and with Trinitroethanol:

Reactions with Mononitroalcohols: Reactions of cyanuric chloride with nitroethanol, 2-nitro-1-butanol, and 2-methyl-2-nitro-1-propanol were tried. Corresponding esters were not obtained by attempted reactions of nitroethanol (and 2-nitro-1-butanol) with cyanuric chloride, (1) in aqueous solution with an acid acceptor, (2) by suspension of potassium hydroxide in the nitroethanol with slow addition of cyanuric chloride, or (3) by fusion of nitroethanol and cyanuric chloride. However, 2-methyl-2-nitro-1-propanol did react in aqueous alkali solution to give the di- and the tri-esters in low yields.



The above may be at least partially explained on the basis of a tautomeric shift to the aci-form of primary and secondary nitro compounds. Nitroethanol with a primary nitro group and 2-nitro-1-butanol with a secondary nitro group can exist in both tautomeric forms. In basic solution the equilibrium shifts in the direction of the aci-form.



Under the reaction conditions used, the cyanuric chloride probably reacted with the aci-forms in these two instances to form the corresponding nitronic esters which then decomposed on attempted isolation. A tertiary nitro compound, such as 2-methyl-2-nitro-1-propanol, has no hydrogen alpha to the nitro group and, therefore, can have no aci-form. The reaction with cyanuric chloride would result in esterification through the alcohol group of the nitroalcohol.

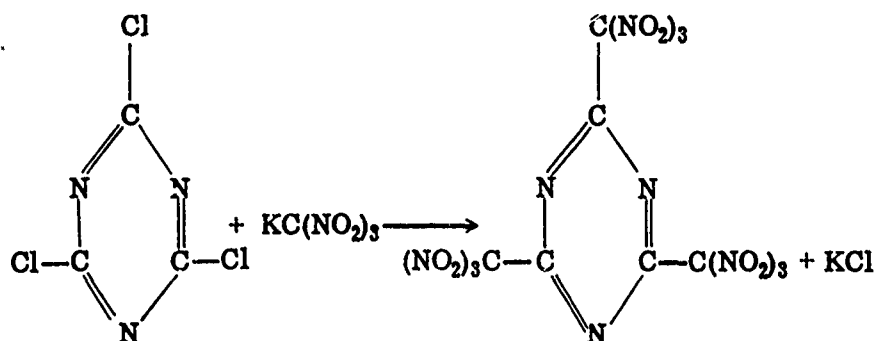
Reaction with Trinitroethanol: Methods of carrying out the reaction of cyanuric chloride with trinitroethanol were limited because

of the decomposition of trinitroethanol in basic solution as well as at high temperatures. Hence, it was not possible to fuse the two components at elevated temperatures. Attempted fusion at a relatively low temperature yielded an oil which was probably a mixture of di- and tri-substituted derivatives. When ferric chloride (or aluminum chloride) was used as a catalyst in carbon tetrachloride solution, the main product was trinitroethylorthocarbonate (TNEOC).

Reactions with Nitroalkanes:

Reactions with Nitromethane: The reactions were tried (1) in aqueous alkali solution, (2) in suspension of potassium hydroxide in nitromethane with addition of cyanuric chloride, and (3) in a refluxing mixture of cyanuric chloride and nitromethane. However, no expected product was obtained. Nitromethane, compared to other nitroparaffins, is uniquely sensitive to the action of alkali.⁽³¹⁾ Also, as in the case of the nitroalcohols, the formation of an unstable nitronic ester may have taken place when the reaction was carried out in alkaline solution. When cyanuric chloride was refluxed in nitromethane, the starting material was recovered almost quantitatively.

Reactions with Potassium Nitroform: An attempt was made to react potassium nitroform with cyanuric chloride according to the following reaction:

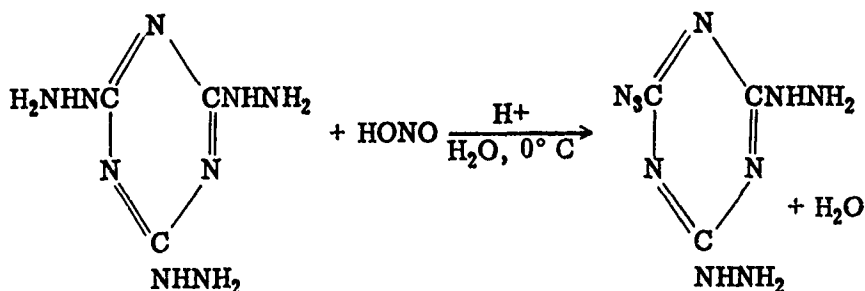


Based on the quantitative yield of KCl obtained, the reaction appeared to have proceeded smoothly. However, an accurate microanalysis was not obtained, probably due to instability of the product formed. Once again, the instability may be due to the formation of the nitronic ester which gradually decomposed following isolation.

On the other hand, if the reaction proceeded as given above, the instability of the product could be due to the electropositive nature of the ring carbon as well as the carbon with the three electron withdrawing nitro groups resulting in weak C-C linkages. Attempts at removing residual quantities of solvent from the n-hexane soluble portion of the reaction mixture proved difficult. Gradual decomposition was apparent from changing microanalysis on standing.

Reactions with Trihydrazino-s-triazine:

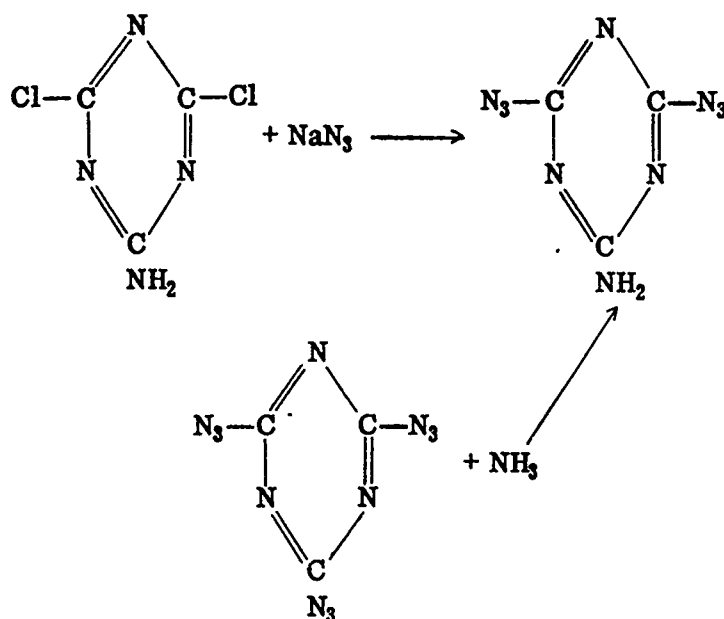
The trihydrazino-s-triazine was made with the hope that the triperchlorate could be prepared. However, the experimental results indicate that only the monoperchlorate was obtained. Trihydrazino-s-triazine did react with 3 moles of acetone to give the corresponding hydrazone derivative. Apparently, the trihydrazino-s-triazine was not basic enough to form the stable triperchlorate. Upon diazotization of trihydrazino-s-triazine, 2-azido-4,6-dihydrazino-s-triazine was isolated. ⁽²¹⁾



This compound decomposed upon addition of perchloric acid and therefore no perchlorate was obtained.

Reaction of Cyanuric Chloride with Ammonia Followed by Sodium Azide:

Cyanuric chloride was reacted with ammonia to give 2-amino-4,6-dichloro- and 2-chloro-4,6-diamino-s-triazine by varying the conditions according to Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen. ⁽³³⁾ Treating sodium azide with 2-amino-4,6-dichloro-s-triazine produced 2-amino-4,6-diazido-s-triazine which was identical with an authentic sample synthesized by another route (passing ammonia gas into an ether solution of cyanuric triazide).



This former route for making 2-amino-4,6-diazo-*s*-triazine was less hazardous than the latter. Attempts at making the perchlorate of the 2-amino-4,6-diazo-*s*-triazine were unsuccessful and only starting material was recovered in all cases. Treatment of 2-chloro-4,6-diamino-*s*-triazine with sodium azide gave none of the corresponding azide. The limited solubility of the 2-chloro-4,6-diamino-*s*-triazine in common organic solvents might explain this.

EXPERIMENTAL DETAILS¹

2,4,6-Tris(trifluoroethoxy)-*s*-triazine:

A suspension of 0.85 g (0.015 mole) of potassium hydroxide in 10 ml of trifluoroethanol was stirred at room temperature while 0.9 g (0.005 mole) of cyanuric chloride was added gradually; the reaction temperature was held at 30°-35° C. After all the cyanuric chloride was added, the mixture was refluxed for 5 hours. A solid (potassium chloride) was separated by filtration. The filtrate was washed with water, and the excess trifluoroethanol removed by distillation. The residue was washed with water and then dried. Recrystallizations from petroleum ether gave colorless crystals; mp 45°-46° C; yield 1.2 g (64%).

¹All melting points are uncorrected.

NAVWEPS REPORT 7109

Anal for $C_9H_6F_3N_3O_3$:

	<u>C</u>	<u>H</u>	<u>F</u>	<u>N</u>
Calcd	28.80	1.60	45.60	11.20
Found	28.96	1.54	45.67	11.60

Ignition temperature: 325°+ (slight fuming 192°-290° C).

2,4,6-Tris(tribromoethoxy)-s-triazine:

A solution of 0.9 g (0.005 mole) of cyanuric chloride in 15 ml of acetone was mixed with 4.4 g (0.015 mole) of tribromoethanol in 15 ml of acetone. A solution of 0.85 g (0.015 mole) of potassium hydroxide in 10 ml water was then added slowly in order to keep the reaction temperature around 45° C. After all the solution was added, the mixture was stirred for 20 min. The solid was separated by filtration and washed with water, alcohol, and then acetone. Repeated recrystallizations from methylene chloride and n-hexane yielded the pure product weighing 4.0 g (86%); mp 280°-281° C (d).

Anal for $C_9H_3Br_3N_3O_3$:

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Br</u>
Calcd	11.70	0.65	4.56	77.89
Found	11.57	0.57	4.64	78.38

Triphenyl cyanurate (or 2,4,6-tris [2,2,2-tris (nitroxymethyl) ethoxy] -s-triazine):

A solution of 3.0 g (0.011 mole) of PETriN in 5 ml of acetone and 10 ml of 5% potassium hydroxide solution was stirred at room temperature. The mixture was added to a solution of 0.7 g (0.00379 mole) of cyanuric chloride in 10 ml of acetone. There was an immediate rise in temperature up to 45° C. Stirring was continued for 20 min. The mixture was then placed under an air stream to evaporate the acetone. Upon removal of the acetone the aqueous solution was decanted. The residue was washed with portions of water, alcohol, and benzene, and then recrystallized from acetone and alcohol to form small needles; mp 131°-132° C; yield 3.0 g (0.00337 mole, 88%).

Anal for $C_{18}H_{24}N_{12}O_{30}$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	24.32	2.71	18.91
Found	24.30	2.89	18.79

NAVWEPS REPORT 7109

Ignition temperature: 175° C

Vacuum stability: 0.34 cc gas at 100° C for 40 hours

Heat of combustion at constant volume at 25° C: 2437 cal/g

Reaction of cyanuric chloride with pentaerythritol dinitrate:

A solution of 0.9 g (0.005 mole) of cyanuric chloride in 20 ml of acetone and 3.4 g (0.015 mole) of pentaerythritol dinitrate was stirred at room temperature. A solution of 0.9 g of potassium hydroxide in 10 ml of water was added dropwise to the mixture while keeping the temperature at approximately 45° C. When all the aqueous solution had been added the mixture was continuously stirred at 45° C for 30 minutes and then at room temperature for 15 minutes. After evaporating the solvent, the oily residue was washed with water several times and then evaporated to dryness. The oily material was crystallized from n-butanol; yield 1.1 g (0.0011 mole, 22%); mp 94°-95° C. The crystallized material was assumed to have 1 mole of residual butanol.

Anal for $C_{21}H_{24}N_{12}O_{24} \cdot C_4H_{10}O$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	33.25	3.77	17.51
Found	32.88	3.98	17.52

Recrystallization from dioxane and methanol yielded a white solid in which a mole of methanol was retained; mp 185°-186° C (d).

Anal for $C_{21}H_{24}N_{12}O_{24} \cdot CH_4O$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	30.69	3.25	19.53
Found	31.05	3.62	19.14

The pentaerythritol dinitrate was made by conversion of pentaerythritol dibromide to the dinitrate according to Cragle and Pistera. (34)

Reactions of cyanuric chloride with 2-methyl-2-nitro-1-propanol:

A solution of 1.8 g (0.01 mole) of cyanuric chloride and 3.7 g (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml of acetone was

NAVWEPS REPORT 7109

slowly added to a solution of 1.7 g of KOH in 15 ml of water keeping the temperature at approximately 45° C. After the addition was completed, the mixture was stirred continuously for 30 minutes. Evaporation of the acetone yielded a solid which was recrystallized from methanol-water mixture; mp 103°-104° C. Analysis indicated that 2 moles of the alcohol reacted with 1 mole of cyanuric chloride to form the disubstitution product, 2-chloro-4,6-di(2-methyl-2-nitropropoxy)-s-triazine, yield 0.6 g (0.0017 mole, 17%).

Anal for $C_{11}H_{16}N_5O_6Cl$:

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Cl</u>
Calcd	37.76	4.57	20.28	10.15
Found	38.16	5.27	20.33	10.52

A solution of 1.8 g (0.01 mole) of cyanuric chloride and 3.7 g (0.03 mole) of 2-methyl-2-nitro-1-propanol in 30 ml of acetone was added to a solution of 1.7 g of KOH in 15 ml of water. The temperature rose immediately to 55° C, and then the mixture was allowed to reflux for 1-1/2 hours. Evaporation of the acetone gave a white solid which was recrystallized from nitromethane-methanol mixture; mp 248°-249° C. Analysis indicated the formation of the triester, 2,4,6-tris (2-methyl-2-nitropropoxy)-s-triazine, yield 0.7 g (0.0015 mole, 16%).

Anal for $C_{15}H_{24}N_6O_9$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	41.64	5.55	19.44
Found	41.98	5.65	19.85

Attempted reactions of cyanuric chloride with nitroethanol and 2-nitro-1-butanol:

The attempted reactions of cyanuric chloride with nitroethanol and 2-nitro-1-butanol were carried out as above. Cyanuric acid was the only product isolated.

Attempted reactions of cyanuric chloride and trinitroethanol:

- (a) A mixture of 0.7 g of cyanuric chloride and 2.2 g of trinitroethanol was placed in a flask and allowed to stand at room temperature for 3 days. When the trinitroethanol was extracted with water cyanuric chloride was recovered almost quantitatively.

NAVWEPS REPORT 7109

(b) To a solution of 0.5 g of cyanuric chloride in 10 ml of acetone was added 2.0 g of trinitroethanol and 10 ml of 10% K_2CO_3 . After stirring at 30°-35° C for 20 minutes the mixture was evaporated to dryness and the residue extracted with ethyl acetate. The ethyl acetate insoluble material was a mixture of potassium nitroform and potassium chloride. When the ethyl acetate solution was added to p-ether, a yellow solid was obtained which decomposed upon standing. An accurate analysis on this material was not obtained.

(c) When a mixture of 1.0 g of trinitroethanol and 0.3 g of cyanuric chloride was heated slowly in an oil bath at 130°-135° C, the evolution of brown fumes was observed. After heating for 1 hour, cyanuric acid was the only product isolated.

(d) A mixture of 4.5 g of trinitroethanol and 0.9 g of cyanuric chloride and 0.45 g of anhydrous ferric chloride was heated to 75°-80° C for 13 hours followed by 85°-90° C for 1 hour, 95°-100° C for 2 hours, and finally 95°-100° C for an additional 8 hours. The mixture was cooled and washed with dilute HCl and then with H_2O . Only a yellow oil was obtained. Attempts at crystallization were not successful. The crude oil was washed with H_2O until the yellow color disappeared. It was then dried in a vacuum desiccator. Assuming a mononitroform adduct to cyanuric acid, the following analysis was obtained:

Anal for $C_4H_4H_6O_9$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	18.46	1.54	24.61
Found	18.47	1.72	24.56

(e) To a suspension of 0.9 g of cyanuric chloride and 2.8 g of trinitroethanol in 30 ml of CCl_4 was added 0.3 g of anhydrous $FeCl_3$. The mixture was heated in an oil bath at 75°-80° C for 20 hours. Upon cooling, a solid separated. The solid was washed with dilute HCl and H_2O and then recrystallized from aqueous alcohol. The major product was identified as TNEOC by a mixed melting point with an authentic sample.

2,4,6-Tris-(trinitromethyl)-s-triazine:

A solution of 1.84 g (0.01 mole) of cyanuric chloride and 5.7 g (0.03 mole) of freshly made potassium nitroform, prepared according to MacBeth and Orr (35) in 50 ml of acetonitrile, was heated gently for about 30 minutes and then allowed to cool to room temperature.

The suspended insoluble material (KCl) was separated by filtration, 1.69 g (0.0262 mole, 87%). The filtrate was evaporated under vacuum. The residue was extracted with n-hexane and dried with anhydrous sodium sulfate. The n-hexane solution was allowed to stand in a dry ice acetone bath overnight. A solid separated; mp 75°-89° C. After recrystallization from n-hexane the product was immediately sent for microanalysis without trying to remove residual n-hexane.

Anal for $C_6N_{12}O_{18}$:

	<u>C</u>	<u>N</u>
Calcd	13.64	31.81

Anal for $C_6N_{12}O_{18} \cdot 1/2 C_6H_{14}$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	18.91	1.22	29.42
Found	19.43	1.23	28.10

Analysis after drying in a vacuum desiccator for 2 hours gave the following results: C, 19.78; H, 1.39.

Analysis after storing in an ice box for 1 week gave the following results: C, 20.57; H, 1.49; N, 30.53.

2,4,6-Trihydrazino-s-triazine perchlorate:

To a solution of 1.7 g (0.01 mole of trihydrazino-s-triazine in 15 ml of acetic acid was slowly added 1N perchloric acid. After standing at room temperature for a few minutes, the mixture upon addition of ether gave a white solid which was recrystallized from alcohol and dried in a desiccator: mp 170°-175° C (d). The analytical results suggest that only the monoperchlorate was formed.

Anal for $C_3H_9N_9O_4Cl$:

	<u>C</u>	<u>H</u>	<u>N</u>	<u>Cl</u>
Calcd	13.26	3.68	46.40	12.70
Found	13.23	4.20	45.99	13.13

Attempted preparation of the triperchlorate by using 70% perchloric acid or by prolonged standing of the mixture was unsuccessful.

NAVWEPS REPORT 7109

Reaction of 2,4,6-trihydrazino-s-triazine with acetone:

A solution of 1.7 g (0.01 mole) of trihydrazino-s-triazine and 17.4 g (0.3 mole) acetone in 7 ml of acetic acid was heated gently for 15 minutes. Upon cooling to room temperature a solid separated which was filtered and recrystallized from methanol; mp 163°-164° C.

Anal for $C_{12}H_{21}N_9 \cdot 2H_2O$:

	<u>C</u>	<u>H</u>	<u>N</u>
Calcd	44.03	7.67	38.53
Found	44.35	6.75	38.82

Diazotization of 2,4,6-trihydrazino-s-triazine:

The diazotization of 2,4,6-trihydrazino-s-triazine was carried out according to Ott and Ohse.⁽²¹⁾

2-Amino-4,6-dichloro-s-triazine and 2-chloro-4,6-diamino-s-triazine:

These compounds were made according to Thurston, Dudley, Kaiser, Hechenbleikner, Schaefer, and Holm-Hansen. (33)

2-Amino-4,6-diazido-s-triazine:

A solution of 0.7 g (0.002 mole) of 2-amino-4,6-dichloro-s-triazine in 10 ml of acetone was added to a solution of 0.2 g (0.003 mole) of sodium azide in 5 ml of water. The mixture was stirred for 30 minutes at room temperature. Evaporation of the acetone yielded a white solid which gave the same physical properties as the product prepared from the treatment of cyanuric triazide with ammonia.

Attempted synthesis of 2-amino-4,6-diazido-s-triazine perchlorate:

A suspension of 0.36 g (0.002 mole) of 2-amino-4,6-diazido-s-triazine in alcohol was added to 1N perchloric acid at 0° C. No reaction was observed. The mixture was allowed to stand at room temperature for several hours, but still no reaction was observed. Upon evaporation of the solvent the starting material was recovered. When acetic acid was used instead of alcohol as a solvent, no perchlorate was obtained.

Attempted synthesis of 2-azido-4,6-diamino-s-triazine:

A suspension of 2.9 g (0.02 mole) of 2-chloro-4,6-diamino-s-triazine and 1.95 g (0.03 mole) of sodium azide in 100 ml of dioxane

was heated to reflux for 3 hours. No 2-azido-4,6-diamino-s-triazine was obtained. The solvent was changed from dioxane to o-xylene, but still no azide was formed.

Cyanuric triazide:

Cyanuric triazide was made according to Ott and Ohse. (21)

Ignition temperature: 182° C.

Vacuum stability at 80° C for 24 hours: 0.57 cc gas

40 hours: 0.58 cc gas.

REFERENCES

- (1) James R. Dudley, et al, J. Am. Chem. Soc., 73: 2986-90 (1951).
- (2) Frederic C. Schaefer, et al, J. Am. Chem. Soc., 73: 2990-2 (1951).
- (3) Serullas, Ann. chim. et phys., (2), 43: 76 (1828).
- (4) J. Liebig, Pogg. Ann., 15: 359, 622 (1829).
- (5) A. Gautier, Ann., 141: 122 (1867).
- (6) Irving M. Klotz and Themis Askounis, J. Am. Chem. Soc., 69: 801-3 (1947).
- (7) P. Klason, J. prakt. Chem., (2), 34: 152 (1886).
- (8) O. Diels and M. Liebermann, Ber., 36: 3191 (1903).
- (9) A. Hofmann, Ber., 19: 2061 (1886).
- (10) H. E. Fierz-David and M. Matter, J. Soc. Dyers Colourists, 53: 424-36 (1937).
- (11) H. Fries, Ber., 19: 2056 (1886).
- (12) C. K. Banks, et al, J. Am. Chem. Soc., 66: 1771-5 (1944).
- (13) W. W. Cuthbertson and S. S. Moffatt, J. Chem. Soc., 561-4 (1948).
- (14) E. A. H. Friedheim, J. Am. Chem. Soc., 66: 1775-8 (1944).
- (15) Ernest A. H. Friedheim, U. S. Patent 2,295,574 (1942), through Chem. Abstract 37: 1228 (1943); U. S. Patent 2,390,092 (1945), through Chem. Abstract 41: 160-2 (1947); U. S. Patent 2,390,090 (1945), through Chem. Abstract 41: 160-2 (1947).
- (16) Ernest A. H. Friedheim, U. S. Patent 2,390,529 (1945), through Chem. Abstract 40: 5070 (1946).
- (17) Ernest A. H. Friedheim, U. S. Patent 2,422,724 (1947), through Chem. Abstract 41: 6900 (1947).
- (18) H. Fries, Ber., 19: 242 (1886).
- (19) H. Fritzsche, et al, U. S. Patent 1,625,530 (1927), through Chem. Abstract 21: 2193 (1927).

NAVWEPS REPORT 7109

- (20) A. Hofmann, Ber., 18: 2196 (1885).
- (21) E. Ott and E. Ohse, Ber., 54B: 179-86 (1921).
- (22) H. Finger, J. Pr. Chem. 75: 103-4 (1907).
- (23) Winfrid Hentrich and Max Hardtmann, U. S. Patent 1,911,689 (1933), through Chem. Abstract 27: 3952 (1933).
- (24) R. Hirt, et al, Helv. Chem. Acta., 33: 1365-9 (1950).
- (25) A. Ostrogovich, Chem. Ztg., 36: 738-9 (1912).
- (26) F. Kraftt, Ber., 22: 1759 (1889).
- (27) P. Klason, J. prakt. Chem., 35: 82 (1887).
- (28) A. Senier, Ber., 19: 311 (1886).
- (29) W. Kolb, J. prakt. Chem., (2) 49: 90 (1894).
- (30) Christoph Grundmann and Elfriede Bleyer, J. Am. Chem. Soc., 76: 1948-9 (1954).
- (31) Linus Pauling and J. H. Sturdivant, Proc. Natl. Acad. Sci., 23: 615-20 (1937).
- (32) H. B. Hass and Elizabeth F. Riley, Chem. Review, 32-34: 373-430 (1943).
- (33) Jack T. Thurston, et al, J. Am. Chem. Soc., 73: 2981-3 (1951).
- (34) Picatinny Arsenal. "Preparation and Analysis of the Di-, Tri-, and Tetranitrates of Pentaerythritol", by Delbert J. Cragle and Frank Pristera, Progress Report for Feltman Research and Engineering Laboratories, (1960).
- (35) Alexander K. Macbeth and W. B. Orr, J. Chem. Soc., 534-43 (1932).

DISTRIBUTION LIST

<u>Addressee</u>	<u>Copy no.</u>
Naval Propellant Plant (Archives copy)	1
U. S. Department of the Interior Bureau of Mines 4800 Forbes Street Pittsburgh 13, Pennsylvania Attn: M. P. Benoy, Reports Librarian Explosives Research Lab.	2
National Aeronautics and Space Administration Washington 25, D. C. Attn: Office of Technical Information and Educational Programs Code: ETL	3-9
Headquarters 6593rd Test Group (Dev) Air Force Systems Command United States Air Force Edwards Air Force Base, California Attn: DGS	10
Air Proving Ground Center Eglin Air Force Base Florida Attn: PGAPI	11
Headquarters, Space Systems Division Air Force Systems Command P. O. Box 262, Air Force Unit Post Office Los Angeles 45, California Attn: TDC	12
Commander Armed Services Tech. Info. Agency Arlington Hall Station Arlington 12, Virginia Attn: TIPCR	13-22

Commander
Air Force Flight Test Center
Edwards Air Force Base, California
Attn: FTRP 23

Commander
Aeronautical Systems Division
Wright-Patterson Air Force Base, Ohio
Attn: ASRCNP 24

Commander
Air Force Missile Development Center
Holloman Air Force Base
New Mexico
Attn: MDGRTL, Technical Library 25

Commanding General
Aberdeen Proving Ground
Maryland
Attn: Ballistic Research Laboratories
ORDBG-BLI 26-27

Commanding General
USA Ordnance Arsenal, Frankford
Philadelphia 37, Pennsylvania
Attn: Propellant and Explosives
Section, 1331 28

Commanding Officer
Ordnance Office
Duke Station
Durham, North Carolina 29

Commanding Officer
Picatinny Arsenal
Dover, New Jersey
Attn: Library 30-31

Commander
Army Rocket and Guided Missile Agency
Redstone Arsenal, Alabama
Attn: Technical Library
ORDXR-OTL 32-35

Commanding General
White Sands Missile Range
New Mexico
Attn: ORDBS-OM-TL 36-38

Commanding Officer
Radford Ordnance Plant
Radford, Virginia 39

Commanding General
Ordnance Ammunition Command
Joliet, Illinois
Attn: ORDLY-AREL, Emgr. Library 40

Commanding Officer
Diamond Ordnance Fuze Laboratories
Washington 25, D. C.
Attn: ORDTL (012) 41

Commander
Army Ballistic Missile Agency
Redstone Arsenal, Alabama
Attn: ORDAB-HSI 42

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: NPP Representative
Room 3115 43

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: DLI-3 44-45

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: RMMP-2 46

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: RMMP-331 47

Commander
U. S. Naval Weapons Laboratory
Dahlgren, Virginia
Attn: Technical Library 48

Commander
U. S. Naval Ordnance Laboratory
White Oak
Silver Spring, Maryland
Attn: Library 49-50

Commander
U. S. Naval Ordnance Test Station
China Lake, California
Attn: Technical Library Branch 51-53

Director
U. S. Naval Research Laboratory
Washington 20, D. C.
Attn: Chemistry Division, Code 6130
R. R. Miller 54

Department of the Navy
Office of Naval Research
Washington 25, D. C.
Attn: Code 429 55

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: CS 56

Commanding Officer
Office of Naval Research
1030 E. Green Street
Pasadena 1, California 57

Director
Special Projects Office
Department of the Navy
Washington 25, D. C. 58

U. S. Naval Ordnance Laboratory
Corona, California
Attn: Code 44

59

Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: RRRE-6

60

Superintendent
U. S. Naval Weapons Plant (Code 752)
Washington 25, D. C.

61-63

Aerojet-General Corporation
P. O. Box 296
Azusa, California
Attn: Librarian

64-65

Hercules Powder Company
Allegany Ballistics Laboratory
P. O. Box 210
Cumberland, Maryland
Attn: Library

66-67

Armour Research Foundation
of Illinois Institute of Technology
Technology Center
Chicago 16, Illinois
Attn: Fluid Dynamics and Propulsion
Research, Department D

68

Atlantic Research Corporation
Shirley Highway and Edsall Road
Alexandria, Virginia

69-70

Explosives Department
Hercules Powder Company
Delaware Trust Building
Wilmington 99, Delaware
Attn: A. M. Ball

71

Jet Propulsion Laboratory
4800 Oak Grove Drive
Pasadena 3, California
Attn: L. E. Newlan
Chief, Reports Group

72

Arthur D. Little, Inc.
35 Acorn Park
Cambridge 40, Massachusetts
Attn: W. H. Varley

73

The Martin Company
Baltimore 3, Maryland
Attn: T. W. Woodard

74

Midwest Research Institute
425 Volker Boulevard
Kansas City 10, Missouri
Attn: Librarian

75

Forrestal Research Center
Princeton University
Princeton, New Jersey
Attn: Librarian

76

Purdue University
Department of Chemistry
Lafayette, Indiana
Attn: Dr. Henry Feur

77

Rohm and Haas Company
Redstone Arsenal Research Division
Huntsville, Alabama
Attn: Librarian

78

Solid Propellant Information Agency
Applied Physics Laboratory
The Johns Hopkins University
Silver Spring, Maryland

79-81

Thiokol Chemical Corporation
Redstone Division
Huntsville, Alabama
Attn: Technical Director

82-83

Thiokol Chemical Corporation
Elkton Division
Elkton, Maryland
Attn: Librarian

84

Olin Mathieson Chemical Corporation
Marion, Illinois
Attn: Research Library
Box 508

85

Reaction Motors Division
Thiokol Chemical Corporation
Denville, New Jersey
Attn: Librarian

86

Rocketdyne, A Division of
North American Aviation, Inc.
Solid Propulsion Operations
P. O. Box 548, McGregor, Texas
Attn: Library

87

B. F. Goodrich Aviation Products
P. O. Box 395
Rialto, California
Attn: Mr. A. B. Japs, Manager
Rocket Motor Development

88

American Machine and Foundry Co.
Mechanics Research Department
7501 North Natchez Avenue
Niles 48, Illinois
Attn: Phil Rosenberg

89

Southwest Research Institute
Department of Chemistry and
Chemical Engineering
8500 Culebra Road
San Antonio 6, Texas
Attn: Dr. Robert C. Dehart

90

Rocketdyne
6633 Canoga Avenue
Canoga Park, California
Attn: Library, Dept. 596-306

91-93

Lockheed Propulsion Company
P. O. Box 111
Redlands, California
Attn: Miss Belle Berlad, Librarian 94-96

Wyandotte Chemicals Corporation
Wyandotte, Michigan
Attn: R. A. Graham
Department of Contract Research
Research and Development Division 97

Aerojet-General Corporation
Box 1947
Sacramento, California
Attn: Technical Information Office 98-100

Thiokol Chemical Corporation
Wasatch Division
Box 524
Brigham City, Utah
Attn: Library Section 101-102

Olin Mathieson Chemical Corporation
Research Library 1-K-3
275 Winchester Avenue
New Haven, Connecticut
Attn: Mail Control Room
Miss Laura M. Kajut 103-104

Shell Development Company
4560 Horton Street
Emeryville 8, California 105

Hughes Tool Company
Aircraft Division
Culver City, California 106

U. S. Borax Research Corporation
412 Crescent Way
Anaheim, California 107

Ethyl Corporation P. O. Box 3091, Istrouma Branch Baton Rouge, Louisiana	108
Peninsular Chemical Research Incorporated 1103-5 N. W. 5th Avenue P. O. Box 3597, University Station Gainesville, Florida	109
E. I. duPont deNemours and Company Eastern Laboratory Gibbstown, New Jersey Attn: Mrs. Alice R. Steward	110
Ethyl Corporation Research Laboratories 1600 West Eight Mile Road Ferndale, Michigan Attn: E. B. Rifkin, Assistant Director, Chemical Research	111
The Dow Chemical Company Security Section Box 31 Midland, Michigan Attn: Dr. R. S. Karpulk 1710 Building	112
Minnesota Mining and Manufacturing Co. 900 Bush Avenue St. Paul 6, Minnesota Attn: Dr. William S. Friedlander VIA: Mr. H. G. Zeman Security Administrator	113-114
Esso Research and Engineering Co. Chemicals Research Division P. O. Box 51 Linden, New Jersey Attn: Dr. J. P. Longwell VIA: Chief, New York Ordnance District U. S. Army 770 Broadway, New York 3, New York Attn: Facilities and Resources Branch	115

American Cyanamid Company 1937 W. Main Street Stamford, Connecticut Attn: Dr. A. L. Pieker	116
Hercules Powder Company Bacchus Works Magna, Utah Attn: Librarian	117
Monsanto Chemical Company Boston Laboratories Everett, Massachusetts Attn: Library	118
Allied Chemical Corporation General Chemical Division Research Laboratory, P. O. Box 405 Morristown, New Jersey Attn: L. J. Wiltrakis, Security Office	119
National Cash Register Co. Dayton 9, Ohio Attn: Mr. B. Treadwell	120
Callery Chemical Company Research and Development Callery, Pennsylvania Attn: Document Control	121
The B. F. Goodrich Company Research Center Brecksville, Ohio Attn: Charles H. Stockman	122
Pennsalt Chemicals Corporation Box 4388 Philadelphia 18, Pennsylvania Attn: Dr. G. Barth-Wehrenalp	123
Dr. Charles S. Waring Asst. Technical Director of Research U. S. Naval Ordnance Test Station China Lake, California	124

Space Technology Laboratory, Inc.
5730 Arbor-Vitae Street
Los Angeles 45, California
Attn: Mr. Robert C. Anderson 125

Aeroprojects, Inc.
310 East Rosedale Avenue
West Chester, Pennsylvania
Attn: C. D. McKinney 126

United Technology Corp.
P. O. Box 358
Sunnyvale, California
Attn: Librarian 127

Aerojet-General Corporation
11711 South Woodruff Avenue
Downey, California
Attn: Florence Walsh
Librarian 128

Rocket Power/Talco
Research Laboratories
3016 East Foothill Boulevard
Pasadena, California
Attn: Dr. Milton Farber 129

Aerospace Corporation
P. O. Box 95085
Los Angeles 45, California
Attn: Library - Documents 130-131

Thiokol Chemical Corp.
Rocket Operations Center
P. O. Box 1640
Ogden, Utah
Attn: Librarian 132

British Defence Staff
British Embassy
3100 Massachusetts Avenue
Washington, D. C.
Attn: Scientific Information Officer
VIA: Chief, Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: DSC-3 133-136

Defence Research Member
Canadian Joint Staff(W)
2450 Massachusetts Avenue, N. W.
Washington 8, D. C.
VIA: Chief, Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.
Attn: DSC-3

137-140

Polaris Project Management Office, NPP

141

Quality Assurance Department, NPP

142

Production Department

143

Technical Library, NPP

144-145

Research and Development Department, NPP

146-162

Naval Propellant Plant Files

163-167

Naval Propellant Plant, Indian Head, Maryland (NAVWEPS REPORT 7109) SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES (U). By M. S. Chang and A. J. Matuszko. 11 May 1962 20 p. (TR 116) UNCLASSIFIED Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Trifluoroethanol, (over)	1. S-triazines 2. 2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine 3. 2,4,6-Trihydrazino-s-triazine perchlorate 4. 2,4,6-Tris(trifluoroethoxy)-s-triazine 5. 2,4,6-Tris(tribromoethoxy)-s-triazine	Naval Propellant Plant, Indian Head, Maryland (NAVWEPS REPORT 7109) SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES (U). By M. S. Chang and A. J. Matuszko. 11 May 1962 20 p. (TR 116) UNCLASSIFIED Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Trifluoroethanol, (over)	1. S-triazines 2. 2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine 3. 2,4,6-Trihydrazino-s-triazine perchlorate 4. 2,4,6-Tris(trifluoroethoxy)-s-triazine 5. 2,4,6-Tris(tribromoethoxy)-s-triazine
Naval Propellant Plant, Indian Head, Maryland (NAVWEPS REPORT 7109) SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES (U). By M. S. Chang and A. J. Matuszko. 11 May 1962 20 p. (TR 116) UNCLASSIFIED Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Trifluoroethanol, (over)	1. S-triazines 2. 2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine 3. 2,4,6-Trihydrazino-s-triazine perchlorate 4. 2,4,6-Tris(trifluoroethoxy)-s-triazine 5. 2,4,6-Tris(tribromoethoxy)-s-triazine	Naval Propellant Plant, Indian Head, Maryland (NAVWEPS REPORT 7109) SYNTHESIS AND PROPERTIES OF SOME CYANURIC CHLORIDE DERIVATIVES (U). By M. S. Chang and A. J. Matuszko. 11 May 1962 20 p. (TR 116) UNCLASSIFIED Cyanuric chloride was reacted with several negatively substituted primary alcohols with fluoro, bromo, nitro, or nitroxy groups as electronegative substituents. Trifluoroethanol, (over)	1. S-triazines 2. 2,4,6-Tris[2,2,2-tris(nitroxymethyl)ethoxy]-s-triazine 3. 2,4,6-Trihydrazino-s-triazine perchlorate 4. 2,4,6-Tris(trifluoroethoxy)-s-triazine 5. 2,4,6-Tris(tribromoethoxy)-s-triazine

tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.	tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.	tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.
tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.	tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.	tribromoethanol, pentaerythritol trinitrate, and pentaerythritol dinitrate produced completely substituted reaction products. Di- and tri-substituted products were obtained with 2-methyl-2-nitro-1-propanol with its tertiary nitro group, but none from alcohols with primary and secondary nitro groups. The product from the reaction with the potassium salt of nitroform gradually decomposed. The monoperochlorate salt of trihydrazino-s-triazine was obtained, but no perchlorate derivatives of aminoazido-s-triazines.	6. 2, 4, 6-Tris [2, 2, 2-tris(nitroxymethyl)ethoxy]-s-triazine 7. 2-Chloro-4, 6-bis(2-methyl-2-nitropoxy)-s-triazine 8. 2, 4, 6-Tris(2-methyl-2-nitropoxy)-s-triazine I. Chang, M. S. II. Matuszko, A. J.