Some Reactions of Cyameluric Chloride

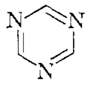
HANSJUERGEN SCHROEDER AND EHRENFRIED KOBER

The Organics Division, Olin Mathieson Chemical Corporation, New Haven, Connecticut

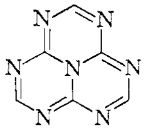
Received May 23, 1962

In contrast to the concept generally presented in the literature, cyameluric chloride was found to undergo nucleophilic displacement reactions readily, and therefore was utilized as the starting material for the synthesis of various tri-*s*-triazine derivatives. All three chlorine atoms can be easily replaced by means of sodium alkylates, phenols, or amines to give the respective trialkylcyamelurates, triarylcyamelurates, and melem (triaminotri-*s*-triazine) derivatives. Difficulties were encountered in the synthesis of unsymmetrical tri-*s*-triazines, since in most reactions cyameluric chloride trisubstitution predominated regardless of the ratio of the reactants. Only four unsymmetrical compounds could be obtained. A series of triaryltri-*s*-triazines was prepared by subjecting cyameluric chloride to a modified Friedel–Crafts reaction with benzene or alkylbenzenes. While *s*-triazine derivatives show their in-plane ring vibration in the region of 6.4–6.65 μ, the corresponding mode of the tri-*s*-triazines was found near 6.2 μ.

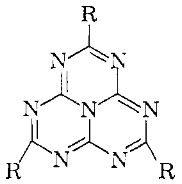
Certain heat-stable, insoluble, and chemically inactive compounds, such as melon, melem, and melonic acid, all of which contain the nucleus C_6N_7 (cyamelurine nucleus), have been known since 1835. Their mysterious structures made them the subject for many publications for approximately thirty years.[1,2] Then this area of chemical investigation lay dormant for almost a century, until Pauling and Sturdivant[3] established the structure of this nucleus by physical methods as a coplanar arrangement of three fused *s*-triazine rings. Chemical support was given to Pauling's formula with the synthesis of cyameluric chloride (I) from the polymeric melon through potassium melonate (II), potassium cyamelurate (III), and cyameluric acid (IV) by Redemann and Lucas.[4]



s-triazine



tri-*s*-triazine
(cyamelurine)



I. R = Cl
II. R = N(K)CN
III. R = OK
IV. R = OH

It could be expected that cyameluric chloride (I)[5] would be as reactive as cyanuric chloride, the analogous triazine compound, and would serve as the starting material for a great number of tri-*s*-triazine derivatives. But surprisingly, attempts to Redemann and Lucas[4] to convert compound I into the oxygen esters by reaction with sodium alkoxides failed. Amination attempts, by treating compound I with ammonia or ammonium hydroxide, gave only impure products. From this work two nitrogen substituted tri-*s*-triazine derivatives, 1,4,7-tribenzyl isocyamelurate and 1,4,7-trimethyl isocyamelurate obtained from III and IV, respectively, were the only well defined compounds, other than cyameluric chloride (I) which could be prepared.

The outstanding thermostability of compounds such as melem and cyameluric acid prompted us to undertake the preparation of a series of trisubstituted tri-*s*-triazine derivatives. Of the possible routes to the synthesis of these compounds, reactions of cyameluric chloride (I) with appropriate reagents, especially nucleophiles, appeared to be most suitable despite Redemann's and Lucas' results. Although it is not very readily available, compound I is such an outstanding member of the known derivatives of the tri-*s*-triazine with regard to reactivity that a more extensive study of typical replacement reactions seemed warranted.

In the search for improvement of the preparation of I, larger amounts of cyameluric chloride (I) became more easily available by simplifying the method of chlorination for the conversion of III into compound I.[6]

Since the reported unreactivity of I toward sodium methoxide and sodium phenoxide[4] was attributed to its insolubility in common organic solvents,[2] the solubility of I was reinvestigated. It was found that compound I is indeed insoluble in ether, ligroin, chloroform, and carbon tetrachloride, but if it is finely powdered or in a fine crystalline state, it will dissolve in ethyl acetate, acetone, dioxane, and ethanol, and can be recrystallized from benzene or xylene.

In view of these findings it appeared of interest to undertake the determination of the reactivity of the chlorine atoms of I by its reaction with sodium ethylate in ethanol. The main reaction product was the desired triethylcyamelurate (V); diethylcyamelurate (VI) was obtained as a by-product.

---

(1) For background see: C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, **61**, 3420 (1939).

(2) For summary see: E. M. Smolin and L. Rapoport, "s-Triazines and Derivatives," Interscience Publishers, Inc., New York, N. Y., 1959, chap. VIII.

(3) L. Pauling and J. H. Sturdivant, *Proc. Natl. Acad. Sci. U.S.*, **23**, 615 (1937).

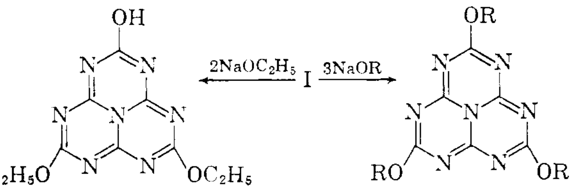
(4) C. E. Redemann and H. J. Lucas, *J. Am. Chem. Soc.*, **62**, 842 (1940).

(5) Current nomenclature for $C_6N_7H_3$ is tri-*s*-triazine (A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," American Chemical Society, 1960, p. 418). In this publication all compounds are named accordingly except for derivatives of cyameluric acid (2,5,8-trihydroxytri-*s*-triazine) and melem (2,5,8-triaminotri-*s*-triazine) where the trivial names are used as is common for the analogous *s*-triazine compounds.

(6) See Experimental.

Likewise, tri-*n*-butyl cyamelurate (VII) was obtained from I and sodium butylate.

These results prompted us to attempt the stepwise replacement of the chlorine atoms of I by alkoxy groups in order to obtain unsymmetrical tri-*s*-triazines. However, the reaction of compound I with two moles of sodium ethylate in ethanol did not give the desired diethyl chlorocyamelurate (VIII) but rather resulted in the formation of diethyl cyamelurate (VI). This indicates that either VIII is formed as an intermediate and further reacts with ethanol with the elimination of ethyl chloride, or that V might be first formed and then converted to VI by the attack of alcoholic hydrogen chloride.



VI

V. R = OC_2H_5
VII. R = OC_4H_9
IX. R = OCH_2CF_3
X. R = $OCH_2C_2F_5$
XI. R = $OCH_2C_3F_7$

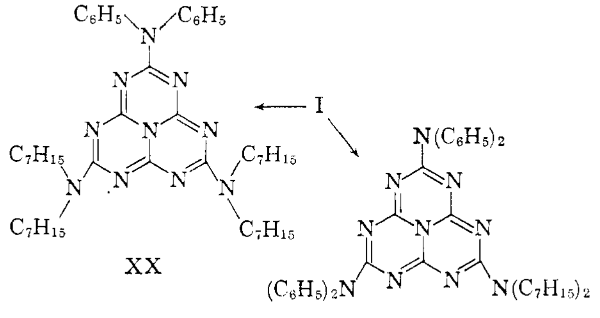
Compound I also reacted with the sodium salts of trifluoroethanol, pentafluoropropanol, and heptafluorobutanol in excess of the corresponding perfluorinated alcohol to give the desired compounds, tris(trifluoroethyl)cyamelurate (IX), tris(pentafluoropropyl) cyamelurate (X), and tris(heptafluorobutyl) cyamelurate (XI). Surprisingly, the fluorinated alkyl esters obtained had higher melting points than their unfluorinated homologs. All three compounds decomposed slowly on standing at room temperature, even when kept in sealed bottles.

Whereas alcohols and I reacted at elevated temperatures to form cyameluric acid and alkyl chlorides,[4] and therefore the synthesis of alkyl cyamelurates required the use of the respective sodium alkylates, phenols and I reacted in the absence of alkali to form the desired aryl cyamelurates. Thus triphenyl cyamelurate (XII), tris(3,5-dimethylphenyl) cyamelurate (XIII), and tris(2,6-dimethylphenyl) cyamelurate (XIV) were prepared.

In order to extend our knowledge of the nucleophilic replacement of the chlorine atoms of I, an investigation of the action of amines on compound I was undertaken. Although melem (triaminotri-*s*-triazine) has been described in the literature,[7] none of the many possible derivatives were known. In a systematic study, compound I reacted with a variety of mostly secondary (both aliphatic and aromatic) amines to obtain in each case the expected melem derivative. Physical and analytical data for these and all other compounds prepared are listed in Table I. It appears of interest to note that hexaphenylmelem (XV) melts at 465° with only slight decomposition, and that the lowest melting compound prepared is hexaheptylmelem (XVI, m.p. 65–67°) which is the only derivative that was distilled (b.p. 335°/1 mm.). Some of the melems form a low melting, ether-soluble, as well as a higher melting, ether-insoluble, modification.

In an effort to prepare the unsymmetrical bis(dibutylamino)chlorotri-*s*-triazine by treating I and dibutylamine in a mole ratio 1:4, only the trisubstituted product, hexabutylmelem (XVII) was obtained besides unchanged I.

An unsymmetrically substituted melem was obtained, however, when I reacted with diphenylamine in a mole ratio 1:2 followed by treatment with di-*n*-heptylamine. The final product, N-diphenyl-N′,N″-tetraheptylmelem (XX), was obtained without isolation of the intermediate diphenylaminodichlorotri-*s*-triazine (XIX). By changing the ratio of the reactants as described in detail in the Experimental, N-diheptyl-N′,N″-tetraphenylmelem (XXI) was unexpectedly obtained. Pertinent to this discussion is the fact that when XX was treated with diphenylamine, no amine displacement occurred.



XX

XXI

Compound XX shows a pronounced gelatinizing effect upon aliphatic hydrocarbons. Hot solutions of 0.5% XX in aliphatic hydrocarbons solidified at room temperature to form stiff gels, which showed little or no change after standing for more than six months.[8] Compound XXI, dissolved in hot aliphatic hydrocarbons, formed gels upon rapid cooling, but these gels liquefied at room temperature within three hours in contrast to the stable gels obtained from XX. Compound XXI as well as compound XX form two crystalline modifications which are also described in the Experimental.

The surprising behavior of cyameluric chloride (I) toward nucleophilic substitution in contrast to other aza-aromatic systems, was again verified in the reaction of I with one mole of sodium ethylate followed by treatment with di-*n*-heptylamine. Not the desired bis(diheptylamino)ethoxytri-*s*-triazine (XXII), but hexaheptylmelem (XVI),

---

(7) J. v. Liebig, *Ann.*, **10**, 10 (1834).

(8) H. Schroeder, U.S. Patent, Ser. no. 90970 (1962).

triethyl cyamelurate (V), and a small amount of diethyl cyamelurate (VI) were isolated.

Substitution as expected was found to occur with a very weak base, di-α-pyridylamine. Refluxing this amine with I in xylene led to the replacement of two chlorine atoms with the formation of bis(di-α-pyridylamino)chlorotri-*s*-triazine (XXIII). The monochloro compound was finally converted into hexa-α-pyridylmelem (XXIV) by treatment with di-α-pyridylamine in refluxing decaline.

A particular objective of this investigation was the direct attachment of alkyl, phenyl, and substituted phenyl groups to the tri-*s*-triazine nucleus. A possible method of achieving this goal appeared to be the reaction of cyameluric chloride (I) with Grignard compounds in accordance with the corresponding reaction of cyanuric chloride.[9] The reaction of I, however, with phenyl- or propylmagnesium bromide failed to give the desired reaction products. Likewise, attempts to achieve a Wurtz–Fittig reaction by refluxing I and *n*-butyl bromide in ether or xylene in the presence of sodium dust were unsuccessful, compound I being recovered almost quantitatively in each experiment.

Our goal was partially attained, however, by the alternate method of utilizing a modified Friedel-Crafts reaction. Compound I reacted with benzene or alkyl-substituted benzenes such as mesitylene and durene in the presence of aluminum chloride to form in good yields the expected triaryltri-*s*-triazines, namely triphenyltri-*s*-triazine (XXV, decomp. > 450°), tris(2,4,6-trimethylphenyl)tri-*s*-triazine (XXVI), and tris(2,3,5,6-tetramethylphenyl)tri-*s*-triazine (XXVII). When monosubstituted, disubstituted, and trisubstituted alkylbenzenes other than mesitylene, were employed for this reaction, in each case a mixture of isomers of the respective tris(polyalkyphenyl)tri-*s*-triazine was obtained. This method, unfortunately, was not applicable to the preparation of the desired trialkyltri-*s*-triazines.

s-Triazine derivatives show a major absorption near 6.5 μ which has been assigned to a C=N stretching mode (in-plane vibration of the triazine ring).[10] During a study of the shift of this band with respect to various substituents attached to the *s*-triazine ring, this band was found to appear between 6.4 and 6.64 μ (1563–1506 cm.$^{-1}$).[11] The tri-*s*-triazine derivatives prepared in this investigation show their strongest absorption in the region of 6.1 to 6.3 μ (1640–1589 cm.$^{-1}$). All the compounds of which infrared spectra were taken had sharp and very strong maxima (see Table I) and it is assumed that this characteristic frequency represents the in-plane vibration of the tri-*s*-triazine ring system.

Experimental[11]

Cyameluric Chloride (I).—The conversion of cyameluric acid (IV) or its potassium salt (III) into compound I had been reported as an operation in a closed system using phosphorus pentachloride as chlorinating agent.[4] Repeated release of pressure upon changing to higher temperature baths made the procedure rather tedious. Our attempts to replace phosphorus pentachloride by $C_6H_5PCl_4$—in order to bypass the closed system—were unsuccessful. But it has been found in this investigation that the chlorination of I with phosphorus pentachloride can be conducted rather simply as follows.

A mixture of anhydrous potassium cyamelurate (III, 25 g.) and phosphorus pentachloride (60 g.) was heated in a sealed bomb tube at 230° for 12 hr. No pressure was observed when opening the tube at room temperature. The reaction products were added, with stirring, to ice water keeping the temperature below 10°. The undissolved cyameluric chloride (I) was filtered *by suction*, placed *rapidly* into a desiccator, and dried over phosphorus pentoxide *in vacuo* to give 19.0 g. of product (92% yield), m.p. 405° dec.[13]; further purification is not necessary.

Anal. Calcd. for $C_6H_7Cl_3$: Cl, 38.47. Found: Cl, 38.42.

Alkoxylation of Cyameluric Chloride (I). Triethyl Cyamelurate (V) and Diethyl Cyamelurate (VI).—Cyameluric chloride (I, 5.55 g., 0.02 mole) was added, with stirring, in small portions within 5 min. to a solution of sodium (1.38 g., 0.06 g.-atom) in absolute ethanol (60 ml.) at 20° with external cooling. After the addition was complete, the cooling bath was removed and the temperature rose to 35°. Afterwards, the mixture was refluxed and became neutral after 5 min. The ethanol was evaporated *in vacuo* and the residue, containing sodium chloride, extracted with 80 ml. of acetone. The filtered solution was evaporated to dryness and the residue was dissolved in hot benzene. Upon cooling, *diethyl cyamelurate* (VI) separated, m.p. 192–196°; yield 0.515 g. (9.5%). Petroleum ether was added to the filtrate to precipitate the triethyl cyamelurate (V), m.p. 172–174°; yield 4.1 g. (64%).

Tributyl cyamelurate (VII) and tris(trifluoroethyl) cyamelurate (IX) were prepared accordingly and recrystallized from petroleum ether and dioxane (or chloroform), respectively. **Tris(pentafluoropropyl) cyamelurate (X)** and **tris(heptafluorobutyl) cyamelurate (XI)** were purified by reprecipitation from ether or ethyl acetate with petroleum ether.

Triphenyl Cyamelurate (XII).—A mixture of cyameluric chloride (I, 5.55 g., 0.02 mole) and phenol (7.9 g., 0.08 mole) was heated. The reaction started at an oil bath temperature of 120° with the evolution of hydrogen chloride. After 20 min. the mixture turned solid and was kept at 150° for one additional hour, then melted with an open flame for 2 min. After recrystallization from xylene the yield of XII was 7.4 g. (82.4%); m.p. 285–287°.

Tris(3,5-dimethylphenyl) cyamelurate (XIII) and tris-(2,6-dimethylphenyl) cyamelurate (XIV) were prepared by the same procedure as for XII except for substitution of 3,5-dimethylphenol and 2,6-dimethylphenol, respectively, for phenol. The former compound XIII was recrystallized from acetone, while compound XIV was purified by dissolving in carbon tetrachloride and subsequent precipitation with petroleum ether.

The following procedure is representative of the syntheses performed.

Hexaheptylmelem (XVI).—Cyameluric chloride (I, 11 g., 0.04 mole) was added, with stirring, in small portions

---

[9] R. Hirt, H. Niedecker, and R. Bechthold, *Helv. Chim. Acta*, **33**, 1365 (1950).

[10] W. M. Padgett, II, and W. F. Hammer, *J. Am. Chem. Soc.*, **80**, 803 (1958).

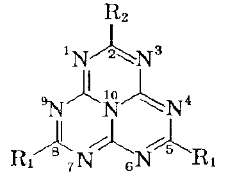
[11] H. Schroeder, *ibid.*, **81**, 5658 (1959).

[12] Melting points are uncorrected; those reported below 330° were determined on a Fisher–Johns apparatus, and those above 330° in a capillary tube (Mel-Temp apparatus). Analyses were by R. Rittner, F. O. Geenty, and D. E. Aylwin of the Olin Mathieson Microchemical Section.

[13] Previously unreported.

TABLE I

DERIVATIVES OF TRI-*s*-TRIAZINE FROM CYAMELURIC CHLORIDE



	R₁	R₂	M.p., °C.	Yield, %	Formula	Mol. wt.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found	In-plane vibr. cm.⁻¹
V	OC_2H_5	$\equiv R_1$	172–174	64	$C_{12}H_{15}N_7O_3$	305.3	47.21	47.29	4.95	4.90	32.12	32.27			
VII	OC_4H_9	$\equiv R_1$	116–118	89	$C_{18}H_{27}N_7O_3$	389.5	55.51	55.33	6.99	7.08	25.18	25.29			
VIII	OC_2H_5	OH	192–196	59	$C_{10}H_{11}N_7O_3$	277.2	43.32	43.66	4.00	4.51	35.37	34.41			
IX	OCH_2CF_3	$\equiv R_1$	216–225	42	$C_{12}H_6F_9N_7O_3$	467.2	30.85	31.45	1.29	1.41	20.99	21.22	F, 36.60	35.80	
X	$OCH_2CF_2CF_3$	$\equiv R_1$	141–145	58	$C_{15}H_6F_{15}N_7O_3$	617.3	29.18	30.07	0.98	1.21	15.88	14.78	F, 46.17	45.22	
XI	$OCH_2CF_2CF_2CF_3$	$\equiv R_1$	114–127	45	$C_{19}H_6F_{21}N_7O_3$	767.3	28.17	29.19	0.79	0.92	12.78	13.14	F, 41.99	49.90	
XII	OC_6H_5	$\equiv R_1$	285–287	82.4	$C_{24}H_{15}N_7O_3$	449.4	64.14	64.19	3.36	3.17	21.82	21.42			1631
XIII	$OC_6H_3(CH_3)_2$ (3,5)	$\equiv R_1$	314	71	$C_{30}H_{27}N_7O_3$	533.6	67.52	66.78	5.10	5.35	18.38	17.49			1640
XIV	$OC_6H_3(CH_3)_2$ (2,6)	$\equiv R_1$	304	76	$C_{30}H_{27}N_7O_3$	533.6	67.52	67.62	5.10	5.26	18.38	18.48			1642
XV	$N(C_6H_5)_2$	$\equiv R_1$	465	86	$C_{42}H_{30}N_{10}$	674.7	74.76	74.45	4.48	4.54	20.76	21.09			
XVI	$N(n\text{-}C_7H_{15})_2$	$\equiv R_1$	65–67[a]	91	$C_{48}H_{90}N_{10}$	807.3	71.41	71.18	11.24	11.26	17.63	17.25			1634
XVII	$N(n\text{-}C_4H_9)_2$	$\equiv R_1$	137–139	88	$C_{30}H_{54}N_{10}$	554.8[d]	64.94	65.24	9.81	9.93	25.25	25.21			
XX	$N(n\text{-}C_7H_{15})_2$	$N(C_6H_5)_2$	160–162 (137)[b]	48	$C_{46}H_{70}N_{10}$	763.1	72.40	73.43	9.25	7.59	18.36	18.17			
XXI	$N(C_6H_5)_2$	$N(n\text{-}C_7H_{15})_2$	193 (178)[b]	32	$C_{44}H_{50}N_{10}$	718.9	73.50	73.43	7.01	6.81	19.49	19.37			1631
XXIII	$N(\alpha\text{-}C_5H_4N)_2$	Cl	>400 dec.	85[c]	$C_{26}H_{16}ClN_{13}$	545.9	57.20	58.10	2.95	2.45	33.36	31.55	Cl, 6.49	7.94	
XXIV	$N(\alpha\text{-}C_5H_4N)_2$	$\equiv R_1$	456–462 dec.	70[c]	$C_{36}H_{64}N_{16}$	680.7	63.52	63.44	3.55	3.55	32.93	32.81			1634
XXVIII	$N(CH_2C_6H_5)$	$\equiv R_1$	242	78.5	$C_{48}H_{42}N_{10}$	758.9	75.96	75.52	5.58	5.79	18.46	17.10			
XXIX	$N(\text{cyclo-}C_6H_{11})_2$	$\equiv R_1$	342–345	76	$C_{42}H_{66}N_{10}$	711.0	70.94	72.13	9.36	9.70	19.70	19.25			
XXX	$N(C_6H_5)(CH_3)$	$\equiv R_1$	280 (161–165)[b]	84	$C_{27}H_{24}N_{10}$	488.5	66.38	65.34	4.95	5.45	28.67	26.46			1638
XXXI	NHC_6H_5	$\equiv R_1$	372–374	88.5	$C_{24}H_{18}N_{10}$	446.5	64.56	64.35	4.06	4.15	31.38	30.89			1640
XXV	C_6H_5	$\equiv R_1$	450 dec.	74[c]	$C_{24}H_{15}N_7$	401.4	71.80	71.63	3.77	3.81	24.43	24.33			1620/1592[e]
XXVI	2,4,6-$(CH_3)_3C_6H_2$	$\equiv R_1$	326	63	$C_{33}H_{33}N_7$	527.7	75.11	75.17	6.30	6.56	18.58	18.48			1600
XXVII	2,3,5,6-$(CH_3)_4C_6H$	$\equiv R_1$	330	68	$C_{36}H_{39}N_7$	567.7	75.80	75.63	6.92	7.04	17.27	17.37			1594
XXXII	x-$CH_3C_6H_4$	$\equiv R_1$	>300	62[c]	$C_{27}H_{21}N_7$	443.5	73.12	72.97	4.77	4.68	22.11	21.88			
XXXIII	x,x′-$(CH_3)_2C_6H_3$	$\equiv R_1$	300–311	64[c]	$C_{30}H_{27}N_7$	485.6	74.20	74.17	5.61	5.88	20.19	19.96			1589
XXXIV	x,x′,x″-$(CH_3)_3C_6H_2$	$\equiv R_1$	308–318	68.5[c]	$C_{33}H_{33}N_7$	527.7	75.11	75.31	6.30	6.40	18.58	18.66			1594
XXXV	x-$C_2H_5C_6H_4$	$\equiv R_1$	160–175	46	$C_{30}H_{27}N_7$	485.6	74.20	74.25	5.61	5.75	20.19	19.55			
XXXVI	x,x′-$(C_2H_5)_2C_6H_3$	$\equiv R_1$	133–135	70.5[c]	$C_{36}H_{39}N_7$	567.7	75.80	75.64	6.92	7.17	17.27	17.10			
XXXVII	x,x′,x″-$(C_2H_5)_3C_6H_2$	$\equiv R_1$	96–114	54.5	$C_{42}H_{51}N_7$	653.9	77.14	76.19	7.86	7.96	15.00	13.58			

[a] B.p. 335° (1 mm.). [b] Melting point of the low melting modification. [c] Crude product. [d] Mol. wt. found by ebullioscopic determination: 560. [e] Doublet.

within 10 min. to a solution of di-*n*-heptylamine (60 g., 0.28 mole) in toluene (80 ml.), maintaining the temperature below 40°. The mixture was kept at 100° for 20 min., then cooled, and filtered by suction. The filtrate was evaporated and the residue was recrystallized from ethanol resulting in 29.3 g. of XVI (91%); m.p. 65–67°; b.p. 335° (1 mm.).

Hexabutylmelem (**XVII**) was recrystallized from alcohols or from acetone. **Hexabenzylmelem** (**XXVIII**) and **hexacyclohexylmelem** (**XXIX**) were prepared in xylene and recrystallized from benzene. **Hexaphenylmelem** (**XV**), **N,-N′,N″-triphenyl-N,N′,N″-trimethylmelem** (**XXX**), and **N,N′,N″-triphenylmelem** (**XXXI**) were also prepared in xylene, but because of their insolubility in the reaction medium they separated together with the respective amine hydrochlorides. After filtration the filter cakes were washed with water and ethanol to remove the respective salts, and the remaining crude melem derivatives were recrystallized, XV from nitromethane, XXX from dioxane, and XXXI from a mixture of pyridine and benzene.

N-Diphenyl-N′,N″-tetraheptylmelem (**XX**).—A solution of diphenylamine (10.2 g., 0.06 mole) in toluene (50 ml.) was added at 20°, with stirring, to a suspension of cyameluric chloride (I, 8.3 g., 0.03 mole) in toluene (50 ml.); then the mixture was kept at 80° for 1 hr. After cooling to 30° a solution of di-*n*-heptylamine (25.6 g., 0.12 mole) in toluene (50 ml.) was added and the mixture was then refluxed for 1 hr. After cooling and filtration, the filtrate was evaporated and the residue was first washed with ligroin to remove hexaheptylmelem (XVI), then recrystallized from ethanol. Compound XX melts at 137°, forming then a white nontransparent solid which melts at 160–162°.

N-Diheptyl-N′,N″-tetraphenylmelem (**XXI**).—A solution of diphenylamine (5.1 g., 0.03 mole) in toluene (50 ml.) was added at 20°, with stirring, to a suspension of cyameluric chloride (I, 8.3 g., 0.03 mole) in toluene (50 ml.); then the mixture was kept at 80° for 1 hr. After cooling to 30°, a solution of di-*n*-heptylamine (25.6 g., 0.12 mole) in toluene (50 ml.) was added. The mixture was refluxed for 1 hr., cooled, and filtered, whereupon a small amount of hexaphenylmelem (XV) precipitated. The filtrate was evaporated and the viscous residue dissolved in hot ligroin. Upon cooling with ice–water, a gel was formed which liquefied within 3 hr. with separation of (XXI) m.p. 178°. This modification A (crystal conglomerates) solidified upon heating above its melting point with conversion into modification B (microcrystalline), m.p. 193°. (Modification B was obtained directly by slowly cooling a hot solution of XXI in ligroin, thereby preventing gel formation.) The ligroin mother liquor was evaporated to dryness and the solid residue was recrystallized from ethanol to give hexaheptylmelem (XVI), m.p. 65–67°. This compound was identified by its undepressed mixed melting point with a sample of XVI prepared from I and di-*n*-heptylamine.

Anal. of XXI: Calcd. for $C_{44}H_{50}N_{10}$: C, 73.50; H, 7.01; N, 19.49. Found (crystal modification A): C, 73.25; H, 6.92; N, 19.50. Found (crystal modification B): C, 73.43; H, 6.81; N, 19.37.

Bis(di-α-pyridylamino)chlorotri-*s*-triazine (**XXIII**).—A mixture of cyameluric chloride (I, 7.0 g., 0.025 mole), di-α-pyridylamine (25.7 g., 0.15 mole), and xylene (200 ml.) was refluxed for 2 hr., then cooled and filtered to give 22.0 g. of filter residue. Extraction of the residue with hot chloroform led to a separation of the reaction mixture into a soluble and an insoluble part. The former product was recrystallized from large amounts of ethyl acetate to give pure di-α-pyridylamine hydrochloride monohydrate; m.p. 187–189°.

Anal. Calcd. for $C_{10}H_{12}ClN_3O$: C, 53.22; H, 5.36; Cl, 15.71; N, 18.62. Found: C, 53.22; H, 5.19; Cl, 15.83; N, 18.74.

Previously, only the trihydrate (m.p. 115°) has been described in literature.

The chloroform-insoluble product consisted of impure XXIII. It is insoluble in common organic solvents and could not be recrystallized even from pyridine, nitromethane, or Cellosolve.

Hexa-α-pyridylmelem (**XXIV**).—A mixture of crude bis-(di-α-pyridylamino)chlorotri-*s*-triazine (XXIII, 13.6 g., 0.025 mole), di-α-pyridylamine (12.8 g., 0.075 mole), and sodium-dried decaline (200 ml.) was refluxed for 3 hr. under a blanket of nitrogen, then cooled and filtered by suction. The filter residue was thoroughly washed with water and ethanol to give chlorine-free crude XXIV (12 g., 70%) which was recrystallized from nitromethane.

The following two procedures are representative of the Friedel–Crafts reactions performed with cyameluric chloride (I).

Triphenyltri-*s*-triazine (**XXV**).—Cyameluric chloride (I, 16.6 g., 0.06 mole) was added in small portions, with stirring, to a suspension of aluminum chloride (16 g., 0.12 mole) in benzene (200 ml.) at 60° within 90 min. After another 30 min. at 60°, the mixture was cooled to 30° and filtered by suction. The filter cake was treated with hot water, filtered, dried, and recrystallized from large amounts of xylene.

Tris(x-methylphenyl)tri-*s*-triazine (**XXXII**).—The reaction of cyameluric chloride (I, 11.1 g., 0.04 mole) with toluene (200 ml.) in the presence of aluminum chloride (10.7 g., 0.08 mole) was conducted in the same manner as described for the preparation of XXV. A black viscous slurry was obtained as reaction product which turned solid upon boiling with water (200 ml.) for 5 min. Purification of the crude XXXII was achieved by dissolving in hot xylene and subsequent reprecipitation with petroleum ether.

Tris(x,x′-dimethylphenyl)tri-*s*-triazine (**XXXIII**), **tris-(x,x′,x″-trimethylphenyl)tri-*s*-triazine** (**XXXIV**) and **tris-(2,3,5,6-tetramethylphenyl)tri-*s*-triazine** (**XXVII**) were recrystallized from benzene; **tris(2,4,6-trimethylphenyl)-tri-*s*-triazine** (**XXVI**) from xylene. **Tris(x,x′-diethylphenyl)-tri-*s*-triazine** (**XXXVI**) was purified by precipitation from acetone at −50°, while **tris(x,x′,x″-triethylphenyl)tri-*s*-triazine** (**XXXVII**) was dissolved in hot benzene and reprecipitated with petroleum ether. In the case of **tris(x-ethylphenyl)tri-*s*-triazine** (**XXXV**) partial separation of the mixture of isomers was achieved by recrystallization from different alcohols. The product obtained from methanol melted at 160–75°, whereas the product recrystallized twice from ethanol melted at 130–145°, the analyses of both products being in agreement with the formula of XXXV.

Acknowledgment.—This research was supported in part by the U.S. Air Force under Contract AF 33(616)-6342 monitored by Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, Wright-Patterson AFB, Ohio. The authors are also indebted to Dr. C. J. Grundmann for his suggestion to investigate the class of compounds dealt with in this article.