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CHEMICAL PROPERTIES AND MOLECULAR STRUCTURE OF DERIVATIVES OF sym--HEPTAZINE[1,3,4,6,7,9,9b-HEPTAAZAPHENALENE, TRI-1,3,5-TRIAZINE]†

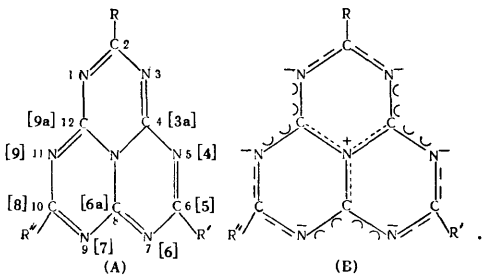
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CONTENTS

1. Introduction 400
2. Does melam exist? 400
3. Melem 401
4. Melon — the material of Pharoah's serpents 402
5. Cyameluric acid, its salts and amides 403
6. Hydromelonic acid 404
7. Other derivatives of sym-heptazine 404

I. INTRODUCTION

The system of atoms (A), comprising six carbon and seven nitrogen atoms, has been called[1] "sym-heptazine".



(A) (B)

The type of delocalisation of the π electrons of the ring and their interaction with the p electrons of the central nitrogen atom are reflected in the structural formula (B), in which a provisional system of additional symbols[2] is used to represent the case in which there is no interaction between the sym-heptazine nucleus and the substituents R. This case is discussed, with the aid of quantum mechanics, by Pauling and Sturdivant[3], who were the first to propose a structural formula of type (A) for these compounds. According to them, the order of the C–N bond is nearly 1.50 for those farthest from the centre of the molecule (like 1–2, 2–3, 6–7, etc.), 1.36 for those nearer the centre (3–4, 4–5, 7–8, etc.), and 1.28 for the central bonds. These values correspond to interatomic distances, determined from isohybrid correlation curves[4], of 1.33, 1.35, and 1.37, respectively, which agree with the values given by Pauling and Sturdivant.

† The term introduced by Russian workers[1] is retained in this translation, but the "Ring Index" gives "tri-*s*-triazine" as a preferred trivial name; the systematic numbering is indicated in square brackets on formula (A) (Ed. of Translation).

Derivatives of sym-heptazine with substituents of the type R = R′ = R″ = NH_2 and OH (melem and cyameluric acid respectively) have been known for a very long time. Melem was first obtained by Liebig[5] in 1834, and cyameluric acid by Henneberg[6] in 1850.

Since then these compounds were forgotten for a long time, and have again attracted the attention of investigators only recently. Nevertheless our knowledge of this unusual class of organic compounds is very limited. In particular, free sym-heptazine (R = R′ = R″ = H) has not yet been synthesised, and other derivatives have been studied very little. The only practical applications known are a patent on the use of cyameluric and hydromelonic acids and their salts in photography[7] and a patent on the preparation of resins from melem[8], which have not received any widespread attention.

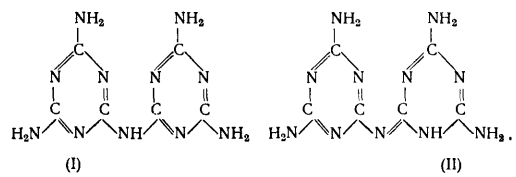
However, there is no doubt that this class of compounds holds promise. It is known, for example, that very many of them have high thermal stability, withstanding temperatures up to red heat without decomposition. At the same time these substances display a great variety of chemical properties, connected with the possibility of changing easily the nature of the substituents R, R′, and R″.

In this review the chemical and physicochemical properties of sym-heptazine derivatives are discussed with the aim of attracting investigators to greater study and application of this class of compounds.

2. DOES MELAM EXIST?

When melamine is heated at atmospheric pressure to 320°, deamination occurs to give a product which is almost insoluble in water and sparingly soluble in acids and alkalis.

Up to the present it has been considered[9,10] that the low-temperature deamination product is formed by the elimination of one molecule of ammonia from two molecules of melamine. Liebig called this product melam[11]. The structural formula (I) was proposed for melam by Klason[11], and has been adopted by recent workers[13].



(I) (II)

The ultraviolet absorption spectrum of the low-temperature deamination product of melamine in alkaline medium[14] has an absorption band at λ_{max} = 285 mμm, whereas in the spectrum of melamine the band of longest wavelength has λ_{max} = 236 mμm. This sharp difference in the absorption spectra cannot be explained on the basis of structural formula (I), in which the two 1,3,5-triazine rings can interact only comparatively weakly through the two C–N single bonds. An attempt was therefore made to explain this result by modifying formula (I) to formula (II).

An examination of infrared spectra[15] showed formula (II) also to be unsuitable, in view of the absence from the spectrum of the deamination product of the band at 1560 cm^{-1} which is characteristic of all compounds containing a 1,3,5-triazine ring of benzenoid structure[16]. Instead of this band, absorption bands were observed at 1615, 1435, and

795 cm^{-1}, and these are characteristic of sym-heptazine derivatives (see below).

Special work was undertaken[17] to settle finally the question of the mechanism of the thermal decomposition of melamine. At the suggestion of V. G. Zavarov, a determination was made not only of the amount of ammonia liberated but also of the melamine which had reacted. Many authors[12,18] did not carry out the latter determination, and so obtained erroneous results, since the decomposition of melamine was not complete.

This work[17] showed the molar ratio of melamine which had reacted to ammonia liberated to be 1 : 1, not 1 : 0.5, as would be expected for melam. The ratio of 1 : 1 indicates that the low-temperature product of the deamination of melamine is melem, and not melam. Melam is formed neither by the decomposition of melamine nor by that of cyanamide or dicyandiamide[17].

Ratios less than 1 : 1 obtained by other workers[18] are explained by disregard of the melamine in the reaction product.

Why does deamination not go to completion?

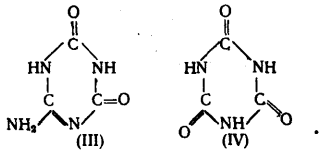
The observed phenomena can be explained on the assumption that deamination can proceed at a considerable rate only in the liquid phase. The process therefore begins at a temperature somewhat below the melting point of melamine (354°) because a small admixture of the reaction products lowers the melting point of the mixture. As the amount of melem increases, the melting point of the mixture passes through a minimum near 320° and then rises, the mixture solidifies, and deamination is retarded. At a higher temperature the mixture of melamine and melem solidifies at a larger melem content, and more complete deamination is therefore achieved under these conditions. In the presence of readily fusible compounds (*e.g.* dicyandiamide) the melting point of the mixture is lowered, and formation of melem begins at a lower temperature.

We may thus conclude that melam is not formed spontaneously in Nature, although it can probably be synthesised artificially‡.

3. MELEM

Two methods of preparing melem are known — (1) pyrolysis of ammonium thiocyanate below 260°,[5] and (2) thermal decomposition of melamine, dicyandiamide, and cyanamide[9,10,17].

Melem is[19] an amorphous white powder, sparingly soluble in water and in dilute acids and alkalis. Its solubility in acids and alkalis is 2–3 times as great as in water, and it can therefore be purified by dissolving it in a dilute acid and precipitating it by neutralisation. Boiling with 4 *N* potassium hydroxide gives cyameluric acid (R = R′ = R″ = OH), while on prolonged boiling in more concentrated alkalis the sym-heptazine ring breaks down and ammelide (III), a derivative of 1,3,5-triazine, is formed.



Under milder conditions melem can give[20] mixed amino- and hydroxy-derivatives of sym-heptazine, which can be regarded as amides of cyameluric acid — a monoamide (R = NH_2; R′ = R″ = OH) and a diamide (R = R′ = NH_2; R″ = OH).

Melem is considerably more stable in acids, and withstands brief boiling with nitric or hydrochloric acid[21]. On being heated to a high temperature in acids, it decomposes to cyanuric acid (IV) *via* intermediate products.

Melem is an amphoteric compounds with very weak acidic and alkaline properties, the latter somewhat predominating (the dissociation constants are given in Table 1). It is a by-product in the synthesis of melamine from dicyandiamide and can be present in significant quantities not only in the crude material but also in the recrystallised product[14].

The molecular structure of melem has been studied from infrared and ultraviolet spectra. In the infrared spectrum[15,22] three absorption bands characteristic of the sym-heptazine ring are observed, at 1605, 1475, and 802 cm^{-1} (Fig. 1). The infrared spectrum of deuteromelem[15] confirms this assignment. In the region of NH-stretching frequencies a spectrum characteristic of amides is observed: three diffuse absorption bands (3403, 3336, and 3103 cm^{-1}) indicate the presence of strong intermolecular hydrogen bonds and strong interaction between the amino-groups and the ring.

The ultraviolet spectrum of melem[23] and its ionic forms is shown in Fig. 2. The absorption spectrum of the neutral form is characterised by two intense absorption bands with maxima at 240 and 222 mμm. As expected, the intense bands of melem are displaced towards longer wavelengths in comparison with the corresponding 1,3,5-triazine derivative, which has a maximum[24] at 206 mμm.

TABLE 1.

Compound	Dissociation constants	Values from Refs. 1 and 23	Values from Ref. 27
Melem	Kb_1	10^{-12}	none
	Kb_2	$6\cdot10^{-14}$	»
	Kb_3	10^{-16}	»
	Ka_1	$2.5\cdot10^{-13}$	»
2,6-Diamino-10-hydroxy--sym-heptazine	Kb_1	$1.2\cdot10^{-12}$	none
	Kb_2	$2.5\cdot10^{-15}$	
	Ka_1	$7.9\cdot10^{-13}$	
	Ka_2	10	
2-Amino-6,10-dihydroxy--sym-heptazine	Kb_1	$6\cdot10^{-13}$	none
	Ka_1	$3.2\cdot10^{-7}$	
	Ka_2	$1.2\cdot10^{-9}$	
Cyameluric acid	Ka_1	$8.7\cdot10^{-4}$	10^{-3}
	Ka_2	$5.6\cdot10^{-7}$	$6.3\cdot10^{-7}$
	Ka_3	$4.6\cdot10^{-10}$	$1.2\cdot10^{-9}$
Hydromelonic acid	Ka_1	10	none
	Ka_2	$1.4\cdot10^{-3}$	$3.16\cdot10^{-3}$
	Ka_3	$7.7\cdot10^{-6}$	$1.26\cdot10^{-5}$

‡ *Note added in proof*. After this review had been written we became aware of a paper by Takimoto[33] showing that an extremely small quantity of melam is, nevertheless, formed in the decomposition of melamine. A method of preparing alkyl derivatives of melam from chloroalkyl derivatives of 1,3,5-triazine has been described recently[34]. A check made by us showed that this method is well reproducible and that the spectra of the compounds obtained agree with the spectra of melam given by Takimoto[33].

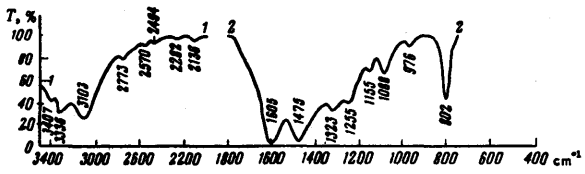


Fig.1. Infrared absorption spectrum of melem: 1) 1%, LiF prism; 2) 1%, NaCl prism (IKS-14).

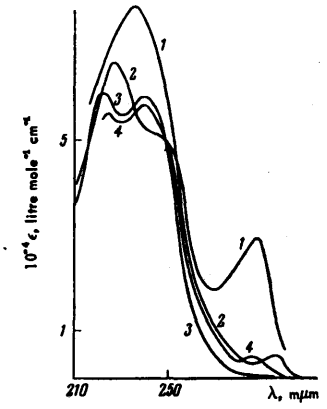
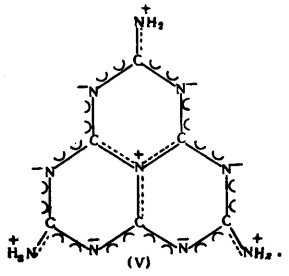


Fig.2. Ultraviolet spectra of melem at pH: 1) -1.7; 2) 1.1; 3) 7.0; 4) 14.0.

In addition to strong absorption in the 210–250 mμm region, there is comparatively weak absorption, in the spectra of the singly ionised and protonated forms, at 296 and 285 mμm respectively. The bands are very convenient for analysis, as they permit melem to be determined in a mixture with other derivatives of sym-heptazine and 1,3,5--triazine.

A detailed examination of the molecular structure of melem leads[15] to the structural formula (V).

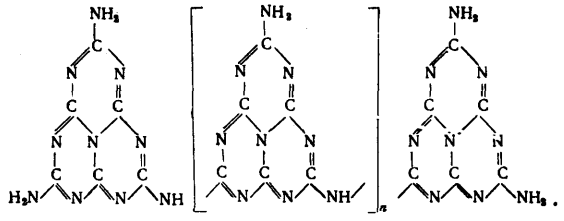


(V)

Melem is thermally stable, withstanding heating up to 450° without noticeable change. At higher temperatures it partly decomposes, forming melon and evolving ammonia, nitrogen, and cyanogen[19]. It is converted into melamine by the action of ammonia under pressure at a high temperature[19].

4. MELON — THE MATERIAL OF PHAROAH'S SERPENTS

When mercury thiocyanate is heated, fantastic structures are formed which remotely resemble a cluster of snakes ("Pharoah's serpents") and consist of the yellow substance melon, a name given to it by Liebig[5,25], who obtained melon by thermal decomposition of ammonium thiocyanate, melamine, and melem. The study of melon was continued by Klason[12] and Franklin[26]. Redemann and Lucas[13] proposed for melon a polymeric type of structural formula consisting of a number of sym-heptazine rings linked through nitrogen atoms (secondary amino-bridges).



An examination has been made[22] of the infrared spectra of specimens of melon obtained by thermal decomposition of melamine, "pseudothiocyanogen", ammonium thiocyanate, and mercury thiocyanate. These spectra (Fig. 3) were found to be identical, and therefore melon is a pure substance. A comparison of the spectra of melon and melem in the region of the lattice vibrations shows their great similarity, which supports the hypothesis[13] that melon is based on sym-heptazine rings. The greatest differences in the spectra are connected with the absorption bands of the NH bonds. A consideration of the nature of these bands[22] showed that the sym-heptazine rings are linked through secondary amino-bridges.

Absorption bands which might be assigned to 1,3,5--triazine rings were not found; May's suggestion[18] that these rings may be present in melon is therefore rejected. However, bands characteristic of 1,3,5-triazine are present in the thermal decomposition products of ammelide and ammeline.

Chemical properties also confirm the similarity of the molecular structures of melem and melon. Thus, hydrolysis of both compounds in alkalis gives cyameluric acid, and fusion with potassium thiocyanate yields hydromelonic acid (see below).

Melon is almost insoluble in water and in dilute acids and alkalis. It is thermally stable up to red heat.

It would be interesting to examine the possibility of using melon as catalyst, absorbent, ion-exchange resin, etc., but no work has yet been done on this.

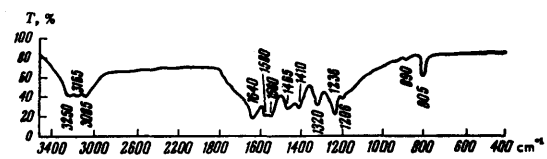
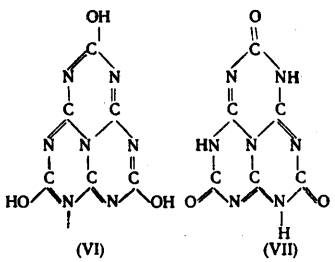


Fig.3. Infrared spectrum of melon in KBr.

5. CYAMELURIC ACID, ITS SALTS AND AMIDES

As already noted, hydrolysis of melem in alkalis gives salts of cyameluric acid (R = R′ = R″ = OH). This acid was first isolated by Henneberg[6], who ascribed to it the formula $H_3C_6O_3N_7$. The molecular structure was investigated further by Klason[12] and Franklin[26], who proposed various structural formulae, but it was only in 1937 that Pauling and Sturdivant[3] suggested the correct structural formula (VI), which is consistent with its chemical properties[27]. The choice between the hydroxy- and oxo--forms [structural formulae (VI) and (VII)] is an important question, studied in various instances by Sheinker[28], who showed that the substance usually exists as the oxo-form, but when formation of the hydroxy-form involves a large gain in energy owing to conjugation of bonds, either a tautomeric equilibrium is observed or the hydroxy-form predominates. The parallelism betwen cyameluric acid and cyanuric acid (IV) in such chemical properties as the formation of salts (*e.g.* both acids give a cuprammonium salt) and chlorides goes a little way towards answering this question, for in these cases cyanuric acid forms derivatives of the hydroxy-form.

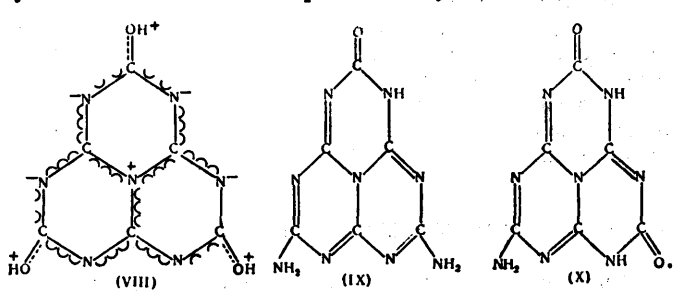


(VI) (VII)

cyameluric acid in the hydroxy-form — cyameluric acid in the oxo-form

Examination of physicochemical data is of greater importance. Thus, the magnetic susceptibility[29] supports structure (VI). The infrared spectra[15] (Fig. 4) show no bands which could be assigned to a carbonyl bond. The intense bands observed belong to the sym-heptazine ring.

This view is also confirmed by the ultraviolet spectra. Thus from Table 2, which gives data on the spectra of molecules and ions of amino- and hydroxy-derivatives of sym-heptazine[1], it is clear that there is a departure from the general regularity (in accordance with which an oxo--structure is expected) in the case of neutral cyameluric acid. A comparison of the spectra of melem and cyameluric acid[23] also supports the hydroxy-form. Thus, when the bond interaction is taken into account, the structure of cyamelluric acid can be represented by formula (VIII).



(VIII) (IX) (X)

Cyameluric acid is comparatively sparingly soluble in water[27]; its preparation from salts formed by the hydrolysis of melem is based on this property. Its dissociation constants are shown in Table 1. Salts of cyameluric

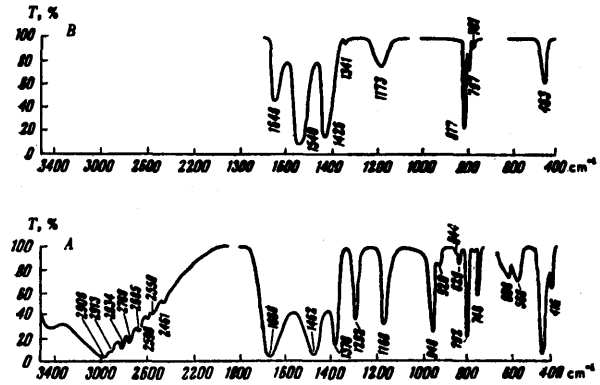


Fig.4. Infrared spectra of: *A*) cyameluric acid; *B*) potassium cyamelurate.

TABLE 2.

Arrangement of double bonds	Absorption bands	2,6,10-Triamino-sym-heptazine (melem)		2,6-Diamino-10-hydroxy-sym-heptazine		2-Amino-6,10-dihydroxy-sym-heptazine		2,6,10-Trihydroxy-sym-heptazine (cyameluric acid)	
	I	222	60 000	225	41 000	222	35 000	222	47 500
	II	240	59 000	250	33 200	263	18 300	250	17 500
	III	—	—	shoulder		shoulder		shoulder	
	I	227	65 000	220	43 000	219,5	39 500	217	53 000
	II	245	500 000	250	weak	—	—	—	—
	III	shoulder		shoulder					
		296	4000	290	2200	285	6500	280	4500
	I	236	78 000	226	43 100	218	33 000	210	51 000
	II			—	—	—	—	—	—
	III	288	29 000	286	2800	380	7200	268	10 000
	I			229	39 500	215	33 000	208	48 000
	II			—	—	235	198 000	235	15 000
	III			228	530	shoulder		shoulder	

acid which have been described[13] are the tripotassium, trisodium, cuprammonium $CuNH_4(C_6N_7O_3).NH_3$, and mercury $Hg_3(C_6N_7O_3)$ salts. The first two are soluble in water, especially in hot water, and the other two are insoluble.

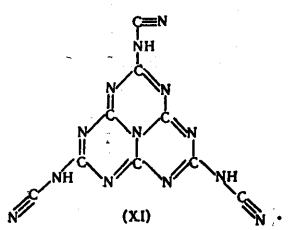
The triamide of cyameluric acid (melem) has already been described. The di- and mono-amides [(IX) and (X)] have been synthesised quite recently[20]. These substances are amorphous white powders, which decompose without melting at 350°. They are almost insoluble in water and organic solvents, but more soluble in mineral acids and alkalis, with which salts are formed. The molecular structure of the mono- and di-amides has been studied spectroscopically[1]. In contrast to cyameluric acid they

exist in the oxo-form. This is because formation of their oxo-forms is not accompanied by considerable disruption of the system of conjugated bonds.

The acid–base properties of the mono- and di-amides are given in Table 1. Ultraviolet spectral data for cyameluric acid and its amides are summarised in Table 2, in which data for the neutral molecules are located along the diagonal, those for negative ions above the diagonal (first, second, and third dissociation in sequence), and data for positive ions below the diagonal (in order of first, second, and third addition of protons).

6. HYDROMELONIC ACID

In 1835 Gmelin[30] obtained the tripotassium salt of hydromelonic acid by heating potassium ferrocyanide with sulphur. He also prepared other salts of hydromelonic acid, but was unable to establish its formula because of the inaccuracy of his analysis. Tripotassium hydromelonate was later obtained by Liebig[31] by dissolving melon in fused potassium thiocyanate. From numerous analyses of the potassium and silver salts Liebig established the empirical formula of hydromelonic acid as $C_9H_3N_{13}$. In 1886 Klason[12] suggested the structural formula $(C_3N_3)_3 \cdot (NH)_3N$, and in 1935 Franklin regarded hydromelonic acid as a derivative of hexamethylenetetramine. It was only in 1937 that Pauling and Sturdivant proposed the structural formula (XI), from the analogy between 1,3,5-triazine tricyanamide $C_3N_3(HNCN)_3$ and hydromelonic acid $C_6N_7 \cdot (HNCN)_3$.



(XI)

Hydrolytic decomposition of hydromelonic acid in acidic and alkaline media with formation of cyameluric acid, ammonia, and carbon dioxide confirms structure (XI). The ultraviolet[23] and infrared[15] spectra are also consistent with this structure, if bond interaction is taken into account. Thus, all three bands characteristic of the sym-heptazine ring are observed in the infrared spectrum (Fig. 5).

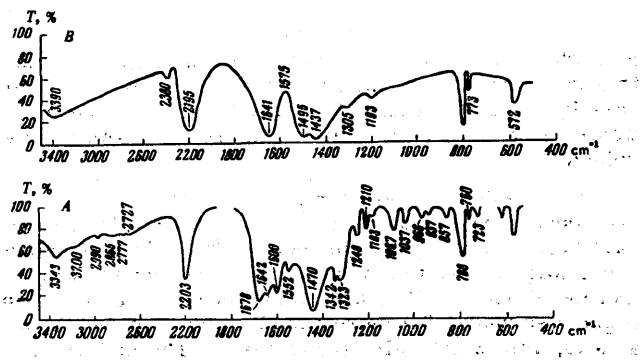


Fig.5. Infrared spectra of: *A*) hydromelonic acid; *B*) potassium hydromelonate.

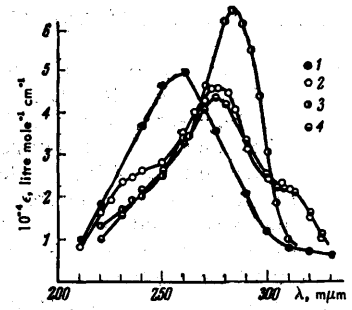


Fig.6. Ultraviolet spectra of hydromelonic acid at pH:
1) -2; 2) 0.7; 3) 7.0; 4) 9.0.

The C≡N frequency is here 2245 cm^{-1}, which is close to its value in acetonitrile (2249 cm^{-1}) and somewhat greater than in cyanamide. This is easily explained by the cyameluric acid nucleus being more electrophilic than the cyanide group and attracting the lone pair of electrons of the nitrogen atom. The frequency of the C≡N group in potassium hydromelonate (2180 cm^{-1}) is intermediate between the C≡N frequencies in cyanamide and the sodium salt of cyanamide

$$H_2\overset{+}{N}{=}{=}C{=}\overset{-}{N},$$

and

$$Na^+[HN{=}{=}C{=}N^-]^-,$$

(2220 and 2096 cm^{-1}). This is explained by the negative charge on the nitrogen atom being partly transferred to the cyameluric nucleus, so that the state of the cyanamide nitrogen in the hydromelonate is closer to the state of this atom in cyanamide. There are two bands in the 1400–1700 cm^{-1} region of the spectrum of potassium hydromelonate, at 1655 and 1430 cm^{-1}. The latter band is characteristic of the cyameluric nucleus, just as a band at 1560 cm^{-1} is characteristic of a 1,3,5-triazine ring. The other band, at 1655 cm^{-1}, is apparently determined to a considerable extent by the nature of the outer part of the molecule.

The absorption band in the 802 cm^{-1} region (794 cm^{-1} in the spectrum of potassium hydromelonate) is also characteristic of derivatives of cyameluric acid. In the ultraviolet spectrum of the molecular-ion forms of hydromelonic acid (Fig. 6) the absorption maximum is shifted, as compared with melem, to longer wavelengths (250–290 mμm); this indicates a very strong interaction of the cyameluric ring with the nitrile group through two C=N bonds. There must then be a larger positive charge on the secondary amino-nitrogen atom, which facilitates N–H dissociation. Hydromelonic acid must therefore be regarded as a strong acid (Table 1).

7. OTHER DERIVATIVES OF sym-HEPTAZINE

Other derivatives of sym-heptazine are reported in only one paper[13].

1. Trichloro-sym-heptazine (cyameluryl trichloride) is prepared[13] by the reaction of potassium cyamelurate with phosphorus pentachloride in a sealed tube at 100–139°.

After removal of phosphoryl chloride and potassium chloride, a light yellow powder remained which was insoluble in organic solvents (chloroform, anisole, nitrobenzene, acetonitrile, and *o*-dichlorobenzene were tested). The substance does not melt but it sublimes (probably with partial oxidation). Cyameluric acid can be used in place of potassium cyamelurate for the preparation of trichloro--sym-heptazine.

2. *NN'N"*-Tribenzyl-sym-heptazine *NN'N"*-tribenzyl cyamelurate)is formed[13] by the interaction of equimolecular quantities of sodium cyamelurate and chlorobenzene in a sealed tube at 100° for 24 h, followed by heating at 156° for 12 h. Extraction with benzene and further recrystallisation from ethanol gives colourless needle-shaped crystals which melt at 283–284°.

Saponification with aqueous potassium hydroxide gives *N*-benzylbenzamide, indicating that an *N*-derivative of sym-heptazine had been formed.

3. Trimethyl-sym-heptazine is obtained[13] by treating cyameluric acid twice with excess of diazomethane. The chemical and physicochemical properties of this substance have not been studied.

No reports of the preparation of other derivatives of sym-heptazine are available to us.

It is clear from this review that derivatives of sym--heptazine are among the least studied classes of organic compounds. Apart from two patents, no use has yet been made of these compounds. In contrast to derivatives of 1,3,5-triazine, which have been widely used for a comparatively long time in various branches of industry and in agriculture, the potential of sym-heptazine derivatives has not been fully exploited. Their present position is comparable to that of 1,3,5-triazine derivatives 10–15 years ago.

Can one regard the use of these compounds in industry and agriculture as promising? In our opinion, one can. The stability of the sym-heptazine nucleus give confidence that derivatives will be used for the production of thermostable plastics, as catalysts for processes taking place at 300–400°, etc.

The strong interaction of the sym-heptazine ring with amino- and hydroxy-groups makes them highly polar, and this, together with the low solubility of these compounds, suggests possible use as adsorbents and ion-exchange resins. The high nitrogen content (up to 70% in some cases) indicates the possibility of using sym-heptazine derivatives in agriculture. The similarity in chemical structure of sym-heptazine derivatives to a number of physiologically active (including anticarcinogenic) substances suggests that they may be useful in pharmacology.

There is thus good reason to expect a brisk development of research furthering the application of this promising class of organic compounds, and it will not be surprising if derivatives of sym-heptazine are produced on a large scale in industry in the very near future.

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