

Investigations of Formaldehyde Oxime, its Polymers and Coordination Compounds. I

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On the Nature of the So-Called "Triformoxime" and Isolation of
the Authentic Trimer, 1,3,5-Trihydroxyhexahydro-1,3,5-triazine

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Synopsis

Evidence obtained from chemical properties and infrared spectra shows that the so-called triform-oxime or trimeric formaldehyde oxime is actually a chain-polymer. The known acetyl and benzoyl derivatives of formaldehyde oxime are, however, derivatives of a cyclic trimer, 1,3,5-trihydroxyhexahydro-1,3,5-triazine, and are derived neither from the polymer, nor from monomeric formaldehyde oxime. Similarly, the known hydrochloride, $(\text{CH}_2\text{NOH})_3\text{HCl}$, and also other salts, contain the cyclic trimer, but on neutralization they depolymerize to formaldehyde oxime.

The cyclic trimer was isolated from partially polymerized formaldehyde oxime in the form of a molecular complex containing dioxane and in a pure state from a neutralized solution of the hydrochloride in ethanol. Both products are rapidly transformed into the insoluble polymer.

An analysis of the ^1H NMR spectra of neutralized solutions of $(\text{CH}_2\text{NOH})_3\text{HCl}$ in deuterium oxide has shown that, in aqueous solution, an equilibrium exists between monomeric and trimeric formaldehyde oxime which, at higher pH values, is shifted towards the monomeric form. The compound, which can be extracted with ether from aqueous solutions at pH *ca.* 8, is the monomer but, with HCl, CH_3I , $(\text{CH}_3\text{CO})_2\text{O}$, etc., it gives derivatives of the trimer.

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I. Introduction

While investigating the composition of the ligand in the coordination compounds¹ prepared from "triformoxime hydrochloride", $(\text{H}_2\text{CNOH})_3 \cdot \text{HCl}$ (*1*), we became interested in the nature of the polymer of formaldehyde oxime which is usually described as a trimer (*e.g.* in Beilstein's handbook and Rodd's Chemistry of Carbon Compounds). Its properties, however, are much more like those of a chain polymer. It is an amorphous solid, insoluble in most solvents, and in fact looks much like paraformaldehyde. Like the latter, it is depolymerized on heating and gives vapour of monomeric formaldehyde oxime. The spectroscopic properties of gaseous, monomeric formaldehyde oxime are well known; both its infrared (IR) spectrum^{2,3} and its microwave spectrum^{4,5} have been investigated. Condensation of the vapour yields either the white solid polymer (*2*) or the liquid monomer (*3*). The latter is rapidly transformed into the same white solid. Decomposition of *2* and *3* sometimes takes place explosively on heating, with the formation of water and hydrogen cyanide.

Monomeric formaldehyde oxime (*3*) was obtained by Dunstan and Bossi⁷ by distillation of the ether extract of an aqueous solution of formaldehyde oxime. A liquid distils at 83 °C/760 mmHg leaving a residue (*2b*) which is insoluble in ether. It is difficult to eliminate ether completely from the distillate but we have otherwise confirmed the results of Dunstan and Bossi. The ¹H NMR spectrum of the liquid in CDCl₃ shows only signals for monomeric formaldehyde oxime (see Section IV) and none which may be ascribed to a polymer.

II. Properties of the Polymeric Products

The following polymeric products were shown to give almost identical infrared spectra.

2a. The white amorphous solid obtained according to Scholl,⁶ by mixing concentrated solutions of hydroxylamine and formaldehyde.

2b. The white solid obtained according to Dunstan and Bossi,⁷ by evaporation of the ether extract of a neutralized aqueous solution of hydroxylammonium chloride and formaldehyde.

2c. The white solid which is formed from 2a or 2b on sublimation.

2d. The white solid which is formed as a residue, and in various parts of the distillation apparatus, during distillation of the monomer.

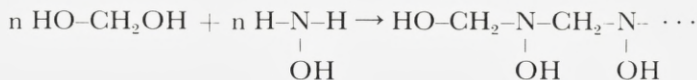
2e. The white solid which is formed from the liquid monomer (3) at room temperature (or slowly even at -80°C) or which separates rapidly from a solution of monomeric formaldehyde oxime in carbon tetrachloride.

The polymeric formaldehyde oxime is a white solid which depolymerizes at $132\text{--}134^{\circ}\text{C}$. Condensation of the vapour usually yields the polymer again. The mass spectrum of the vapour shows the presence of the molecular ion of the monomer with no indication of the formation of oligomers. The polymer is insoluble in common solvents, but on prolonged heating dissolves both in water and in some organic solvents; it does not separate again when the solutions are cooled. Ebulliometric measurements in acetone indicate the solute to be monomeric formaldehyde oxime (found $M = 50$, calc. 45).

Although all the above mentioned products (2a-e) exhibit identical infrared spectra and show no significant differences in their C, H, N analyses, the reaction with nickel(II) chloride¹ reveals a very remarkable difference between freshly prepared products formed by polymerization of the monomer (2b-e) and the products formed directly from aqueous formaldehyde and hydroxylamine (2a): the former immediately gives a very intense colour while 2a gives no reaction (or slowly develops a very faint colour); however, if 2a is first dissolved in hydrochloric acid, the same intense colour is obtained as with the other products on addition of NiCl_2 and NaOH . This difference is explained as being due to the presence of the genuine trimer (see section V) in freshly prepared polymerization products; the latter lose the ability to give a positive nickel reaction after some time because the trimer is transformed into the polymer.

Polymerization of formaldehyde oxime apparently does not take place in dilute aqueous solution. When an aqueous solution of hydroxylammonium chloride is reacted with formaldehyde and the solution is then neutralized no separation of the polymer occurs; according to our NMR spectroscopic investigation (section IV) the initially formed "triformoxime hydrochloride" (I) on neutralization is converted almost quantitatively into monomeric formaldehyde oxime. On the other hand, if the hydroxylammonium chloride is neutralized before the addition of formaldehyde, separation of the polymer begins in a few minutes. Clearly the

polymer is not formed in aqueous solution by polymerization but by polycondensation:



In this case there is the possibility that the second terminal group is also an HO-CH₂ group. This circumstance, together with differences in degree of polymerization, may account for some observed variation in the properties of the polymeric products.

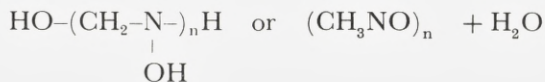
The polymeric products dissolve rapidly in hydrochloric acid, but it takes hours or even days to dissolve them in boiling water (product *2a* dissolves more slowly than products *2b-e*). Dissolution is much accelerated by the addition of NaCl and occurs with depolymerization; monomeric formaldehyde oxime distills over with the steam and polymerizes again in the condenser. Some hydrolysis also takes place. After prolonged boiling, the aqueous solution contains formaldehyde and hydroxylamine but (according to the nickel reaction) no monomeric or trimeric formaldehyde oxime. When a neutralized solution of hydroxylammonium chloride and formaldehyde is evaporated *in vacuo* a solid is formed in the condenser. This solid exhibits the same infrared spectrum as the other polymer samples.

The infrared spectra of the polymers are rather simple and apparently do not differ much from the spectrum of gaseous formaldehyde oxime, investigated by Califano and Lüttke.³ However, most of the bands should be re-assigned (see the detailed discussion of the infrared spectra of the polymers in the following publication)⁸. Only the following results from the investigation will be mentioned here: We succeeded in recording the infrared spectrum of monomeric formaldehyde oxime as a liquid film although the liquid solidified in less than 5 min. The spectrum exhibited the $\nu(\text{C}=\text{N})$ band clearly at 1630 cm⁻¹, the CH₂ twisting band at 780 cm⁻¹ and the $\nu(\text{N}-\text{O})$ band (vs) at 900 cm⁻¹ (assignments according to Ref. 3). The solidification of the film resulted in the disappearance of the two first mentioned bands and a shift of the 900 cm⁻¹ band to 840 cm⁻¹.

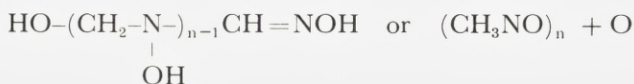
The infrared spectra of the polymeric products support the conclusion that the latter are chain polymers analogous to paraformaldehyde; the spectra are not compatible with the assumption that the polymer is "triformoxime", *i.e.* 1,3,5-trihydroxyhexahydro-1,3,5-triazine. The possibility⁹ that the polymer might be a dimer or trimer analogous to glycolaldehyde, glyceraldehyde or dihydroxyacetone is also ruled out by the infrared spectra. Furthermore, from the chemical properties of the polymers, structures of the latter type seem improbable. The infrared

spectra exhibit no bands attributable to ether linkages, so that the possibility of the chain containing $\text{CH}_2\text{-O-CH}_2$ groups seems to be ruled out.

A polymer analogous to paraformaldehyde would have the formula:

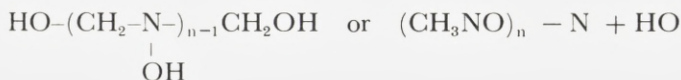


One of the terminal groups could, however, be an oxime group:



A structure of the latter type could conceivably result from an oxygen catalysed polymerization of monomeric formaldehyde oxime.

When the polymer is formed in solution from hydroxylamine and formaldehyde it may contain two $-\text{CH}_2\text{OH}$ terminal groups:



It is not possible to distinguish between the three formulae by elemental analysis when $n > ca. 10$.

The carbon and nitrogen analyses are often slightly lower, and the oxygen analyses slightly higher, than those corresponding to the formula $(\text{CH}_3\text{NO})_n$, indicating that the degree of polymerization may be no greater than corresponding to $n = 20\text{-}30$. Since the polymer is insoluble and reacts chemically only under concomitant depolymerization it has not been possible to determine its molecular weight.

III. Derivatives of Trimeric Formaldehyde Oxime

The assumption that the polymer should be trimeric has been based mainly on the isolation of a hydrochloride with the composition $(\text{CH}_3\text{NO})_3 \cdot \text{HCl}$ (1) and on the observed molecular weight of the acetyl derivative (4), which may be prepared by the addition of acetic anhydride to the above mentioned ether extract

of formaldehyde oxime.⁷ These compounds cannot, however, be prepared directly from the solid polymer. Although the latter dissolves in dilute hydrochloric acid it is not re-precipitated when the solution is neutralized, indicating that the reaction with hydrochloric acid is accompanied by depolymerization. When the polymer is dissolved in methanol containing HCl, the hydrochloride (*I*) (identity proved by its infrared spectrum) can be precipitated by the addition of ether. Acid anhydrides and acid chlorides react only slowly with the solid polymer forming triacyl derivatives of the trimer. No partially acylated derivatives of the solid polymer could be prepared.

A hydrochloride with the formula $(\text{CH}_2\text{NOH} \cdot \text{HCl})_n$ has been isolated as the initial product from the reaction of hydrogen chloride with an ether solution of formaldehyde oxime.¹⁰ However, it can only be obtained with this high HCl content when it is dried in a stream of gaseous HCl. Otherwise it rapidly loses HCl and is transformed into *I*. These crude samples of *I* usually contain more than 1, and less than 3, mol HCl (quite often we have obtained a product analysing as a dihydrochloride), but when the crude hydrochloride is dissolved in methanol and precipitated with ether the hydrochloride with the composition $(\text{CH}_3\text{NO})_3 \cdot \text{HCl}^*$ is always obtained as a well-defined and quite stable product.

The infrared spectra of the hydrochlorides with higher HCl content do not differ very much from that of *I*. However, this is not significant because the products lose HCl so easily. Sluiter¹⁰ determined the base constants of the bases present in $\text{H}_2\text{NOH} \cdot \text{HCl}$ and *I* by measurements of the catalytic effect of the hydrochlorides on ester hydrolysis and sugar inversion and obtained the values 2.4×10^{-12} and 3.0×10^{-13} , respectively. Although these values may not be very exact by modern standards, the qualitative result seems quite unambiguous: when present in an equivalent amount, $\text{CH}_2\text{NOH} \cdot \text{HCl}$ exerts a smaller catalytic effect than *I*, although it contains three times as much HCl per nitrogen atom and accordingly must be the hydrochloride of a stronger base. This latter species must either be trimeric, and therefore an isomer of the base contained in *I*, or it must be monomeric formaldehyde oxime. Sluiter favoured the first possibility and advanced the hypothesis that the loss of HCl was the result of a rearrangement of 1,3,5-trihydroxyhexahydro-1,3,5-triazine into the 2,4,6-trihydroxy isomer. This conclusion is now quite untenable and so we must conclude that the primary product is the hydrochloride of monomeric formaldehyde oxime. This is consistent with our NMR measurements on ether solutions, which reveal only signals attributable to formaldehyde oxime monomer.

* This is also the composition of commercial products sold under the name "formaldoxime hydrochloride".

The fact that a pure product with a lower HCl content than *I* is never obtained shows that we are not dealing with hydrochlorides of the chain polymer. However, over a period of time the composition of the product (*I*) sometimes changes, either because of the formation of the solid polymer (decreasing HCl content) or because of hydrolysis with the formation of hydroxylammonium chloride (increasing HCl content). A hydrobromide,⁷ hydroiodide,⁷ hydrogen nitrate,¹¹ and methiodide¹² with corresponding compositions are also known.

The infrared spectrum of the hydrochloride (*I*) is rather complex and quite different from that of the polymers. A comparison with the infrared spectrum of the free trimer leaves no doubt that it is a hydrochloride of the latter.

Both the acetyl derivative (*4*) and the hydrochloride (*I*) give an instantaneous colour reaction with nickel chloride on addition of base. Since it had been shown that the ligand present in the resulting complexes is the anion of monomeric formaldehyde oxime¹ we gave serious consideration to the possibility that the hydrochloride and the acetyl derivative might be derived from monomeric formaldehyde oxime. This appeared to be supported by the fact that the infrared bands corresponding to CH₂ deformation in the acetyl and benzoyl derivatives occur at the unusually frequency of 1415 cm⁻¹, *i.e.* almost as low as for monomeric formaldehyde oxime (1410 cm⁻¹) and much lower than for the polymers (1460 cm⁻¹). However, a similar lowering of the CH₂ deformation frequency has been observed for certain heterocyclic systems¹⁴ and furthermore the infrared spectra of the acetyl and benzoyl derivatives in chloroform solution provide no indication of the presence of a double bond, even at high concentrations. That these compounds are in fact trimeric was confirmed by MS and by determination of their molecular weight in solution by various methods (cryoscopic, ebulliometric, thermoelectric).

The electric dipole moment of the acetyl derivative was found to be 3.25 debye in dioxane. This rules out the possibility that this compound might be (associated) formaldehyde *N*-acetyloxime.

Finally, the ¹H NMR spectra of the acetyl and benzoyl derivatives indicate the expected ratios of 3:2 and 5:2, respectively, for the two types hydrogen atoms in each compound. This rules out the possibility of these compounds being derivatives of a trimer analogous to glyceraldehyde or dihydroxyacetone. Accordingly it seems almost certain that these compounds are derivatives of 1,3,5-trihydroxy-hexahydro-1,3,5-triazine. To substantiate this conclusion an X-ray diffraction study of the acetyl derivative has been carried out.¹³ This shows that the acetyl derivative contains a six-membered hexahydrotriazine ring in the chair conformation with three axial *N*-acetoxy groups.

It was found that the acetyl derivative is rapidly hydrolysed by NaOH; thus to

explain the formation of metal complexes with monomeric formaldehyde oxime from 1 or 4, one has only to assume that the hexahydrotriazine ring is rapidly depolymerized in solution.

Several years ago we demonstrated (unpublished) the presence of monomeric formaldehyde oxime in aqueous solutions of 1 by IR spectroscopy (sharp band at 1620 cm^{-1} for a solution of 1 in D_2O). NMR studies have now provided evidence that in fact a reversible equilibrium is easily established between 1,3,5-trihydroxyhexahydro-1,3,5-triazine and formaldehyde oxime. Surprisingly, however, these investigations also showed that although the complexes are derived from the monomer, they are not formed directly from this but *via* the trimer.

IV. ^1H NMR Spectra

The ^1H NMR spectrum of a solution of $(\text{H}_2\text{CNOD})_3 \cdot \text{DCl}$ in D_2O ($\text{pH} = 1.1$) shows two doublets at δ 7.11 and 6.11, and two singlets at δ 4.82 and 4.65 (the δ values are pH-dependent, cf. Table 1). The first singlet is due to water. Assuming the presence of a cyclic hexahydro-1,3,5-triazine system, the other singlet at δ 4.65 can be ascribed to the methylene protons. The corresponding signal for 1,3,5-trimethoxyhexahydro-1,3,5-triazine¹⁵ occurs at δ 4.15 and that for the acetyl derivative (4) at δ 4.53. For none of these hexahydrotriazines is splitting of the signal of the methylene protons observed; this phenomenon is most likely a consequence of rapid interconversion between axial and equatorial protons at room temperature. Likewise the signal due to the methylene protons of other hexahydrotriazines,¹⁶⁻¹⁸ with the exception of 1,3,5-trinitrosohexahydro-1,3,5-triazine,¹⁶ appears only as a singlet.

The doubles at δ 7.11 and 6.61 are assigned to monomeric formaldehyde oxime. These doublets occur at δ 7.07 and 6.49 for a solution of pure, liquid formaldehyde oxime in CDCl_3 , the singlet due to the trimer being totally absent. Solutions of formaldehyde oxime in CCl_4 or ether also contain only the monomeric form (Table 1). Similar δ -values for the doublets have been found in previous studies of the ^1H NMR spectra of solutions of monomeric formaldehyde oxime prepared by extraction of aqueous solutions with various solvents and without isolation of the pure compound.¹⁹⁻²¹ The existence of the trimer was not noted in these investigations.

When distilled monomeric formaldehyde oxime is dissolved in D_2O and immediately examined by ^1H NMR, signals from both the monomeric and trimeric forms are observed in the spectrum. The integrals of these signals correspond

Table 1. Chemical shifts (δ) for methylene protons for $\text{H}_2\text{C}=\text{NOH}$ and $(\text{CH}_2\text{NOH})_3$.

solvent	trimer	monomer		
		trans	cis	J (Hz)
CCl_4 *		6.98	6.38	8.0
CDCl_3		7.07	6.49	8.5
$(\text{C}_2\text{H}_5)_2\text{O}$		7.00	6.38	9.0
$(\text{CD}_3)_2\text{CO}$	4.00	6.94	6.34	9.0
$(\text{CD}_3)_2\text{SO}$	3.84 **	6.92	6.38	9.0
D_2O pH 1.1	4.65	7.11	6.61	7.5
2.5	4.64	7.10	6.60	8.0
4.2	4.22	7.10	6.60	8.0
7.3	4.17	7.10	6.60	8.0
10.4	4.08	6.97	6.42	8.0
11.9	3.97	6.97	6.42	10.0

* The solution of $\text{H}_2\text{C}=\text{NOH}$ in CCl_4 is rapidly transformed into a gel of the polymer.

** δ for OH proton 8.25.

Table 2. Percentages of monomeric formaldehyde oxime^a, present in solutions of $(\text{CH}_2\text{NOD})_3\text{DCI}$ in D_2O as a function of pH, temperature and initial concentration of $(\text{CH}_2\text{NOD})_3\text{DCI}$ (C_0).

Temperature 39 °C. $\text{C}_0 = 0.347 \text{ mol l}^{-1}$

pH:	1.3	1.7	1.9	2.2	3.0	4.2
% monomer:	80	84	87	93	94	97

$\text{C}_0 = 0.759 \text{ mol l}^{-1}$. pH = 1.05

Temperature, °C:	25	30	35	40
% monomer:	44	56	62	65

Temperature 25 °C

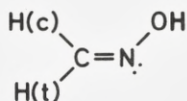
C_0 :	0.334	0.436	0.573	0.759	2.5
pH:	1.26	1.18	1.12	1.05	
% monomer:	68	63	56	44	~0

a) Calculated from the ^1H NMR spectra:

% monomer = $100(\text{M})/[(\text{M}) + 1/3(\text{T})]$, where (M) and (T) are the integrated intensities of the signals due to the monomer and the trimer.

initially to 60-70 % of the monomer and 40-30 % of the trimer ($c = ca. 1 \text{ mol/l}$). This must be considered a kinetically controlled ratio. At pH *ca.* 7 an equilibrium is slowly established but after several hours the mixture contains *ca.* 95 % of the monomer, in agreement with the results obtained starting with the hydrochloride of the trimer or the pure trimer (see later).

The AB system arises because of the difference in shielding of the methylene protons in *cis* (c) and *trans* (t) positions:



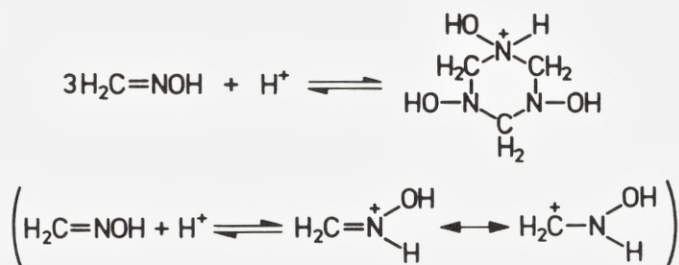
The equilibrium concentrations of the monomer and the trimer in aqueous solution can be calculated from the initial concentrations of the hydrochloride and the integrated intensities of the signals due to the methylene protons. As shown in Table 2 the ratio of monomer to trimer is dependent on the total concentration, the pH of the medium, and the temperature. The depolymerization of the trimer is favoured by diminishing concentration, increasing temperature, and increasing pH. At pH values higher than 3 only a few percent of the trimer is present in equilibrium with the monomer.

The existence of an "inactive" form of *I* has been postulated²²⁻²⁶ to explain the observation that a dilute solution of *I* does not give the usual colour reaction with metal ions (Ni^{2+} , Mn^{2+} , Fe^{2+}). As can be seen from Table 2, the degree of depolymerization of *I* increases with decreasing concentration and in very dilute solutions only monomeric formaldehyde oxime is present. Thus it must be concluded that the "inactive form" is monomeric formaldehyde oxime and that the coloured complexes are formed only at concentrations where a significant proportion of the trimer is present.

Our measurements indicate that at low pH values an equilibrium between monomeric and trimeric formaldehyde oxime is established immediately. ^1H NMR provides no indication of the formation of a hydrate of the oxime, $\text{HOCH}_2\text{-NHOH}$, and the trimerization of *3* therefore undoubtedly proceeds *via* the protonated oxime (Scheme 1).

In accordance with Scheme 1 the quantity $[\text{trimer}] \times [\text{monomer}]^{-3}$ is found to be approximately constant for a variety of initial concentrations and constant pH. At constant initial concentration, and for pH values varying between 1 and 2, the quantity $[\text{trimer}] \times [\text{monomer}]^{-3} \times [\text{H}^+]^{-1}$ is approximately constant. At pH values higher than 4 the depolymerization reaction is slow (cf. Table 3). A limiting

Scheme 1



value of the ratio trimer/monomer is reached only after several hours and is largely independent of pH. It is quite possible that the depolymerization process is in fact irreversible under these conditions. Although a small amount of the trimer is also formed from the monomer in alkaline solution this might occur via a reaction analogous to the polymerization of liquid or gaseous formaldehyde oxime, a process which is apparently an oxygen-catalyzed radical reaction.

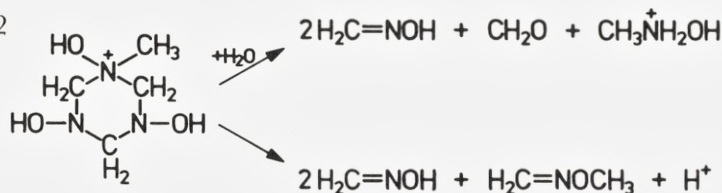
The chemical shifts and the coupling constants for the ^1H NMR resonances of formaldehyde oxime in alkaline solution are close to the values observed for solutions in non-aqueous solvents. This indicates that 3 is not transformed into its anion to any appreciable extent even at pH 12 (pK_a values near 13 have been given for various oximes²⁷). Below pH 2 the peaks broaden. This is indicative of the protonation of a base whose strength is of the order of magnitude 10^{-13} , as found by Sluiter.¹⁰ The protonation of formaldehyde oxime in strongly acid solution is also evident from polarographic measurements on 1.²² Likewise the δ -value for the trimer at pH 1 applies to the cation. That the hexahydrotriazinium ion gives rise to only one singlet is explicable on the basis of rapid exchange of the proton between the three nitrogen atoms.

The ^1H NMR spectrum of the methiodide (6) in D_2O provides no indication of the presence of a six-membered ring. In addition to the methylene signals of formaldehyde oxime, the spectrum shows signals due to formaldehyde and the N-methylhydroxylammonium ion, together with a signal at δ 3.52 which is

Table 3. Percentages of monomeric formaldehyde oxime present in solutions of the trimer, 1,3,5-trihydroxyhexahydro-1,3,5-triazine, in D_2O (35 °C; $c = 0.75 \text{ mol l}^{-1}$).

pH	Time after dissolution			
	15 min	1 h	4 h	24 h
4.2	90	91	94	94
7-9	12	35	62	83
11	33	61		96

Scheme 2



assigned to the methyl group of *O*-methylformaldehyde oxime¹⁵ (the possibility that it might originate from the methylene protons of a compound $\text{CH}_3\text{N}(\text{OH})\text{CH}_2\text{OH}$ is probably ruled out; see Experimental). The formation of *N*-methylhydroxylamine by hydrolysis proves that compound 6 is *N*-methylated. The simultaneous formation of an *O*-methyl compound must then be due to a nitrogen \rightarrow oxygen transfer of the methyl group during the decomposition (Scheme 2).

From the integrated intensities of the *N*- and *O*-methyl signals it can be seen that the two compounds are formed in approximately equal amounts. There is overlap between the methylene signals of formaldehyde oxime and its *O*-methyl derivative but the presence of the latter is confirmed by the integrated intensity of the methylene signals being higher than calculated for 2 mol of formaldehyde oxime.

The ^1H NMR spectrum of the methiodide (6) in $\text{DMSO}-d_6$ indicates that the compound decomposes immediately in this medium with the formation of formaldehyde oxime and its *O*-methyl derivative¹⁵ but without the formation of *N*-methylhydroxylamine. The hydrochloride (1) is also immediately and completely transformed into the oxime on dissolution in $\text{DMSO}-d_6$.

At higher concentrations of $(\text{H}_2\text{CNOD})_3 \cdot \text{DCl}$ in D_2O , and at higher temperatures, abnormal results are sometimes obtained: For example, in some experiments the concentration of the monomer was found to decrease with increasing temperature. This indicates that in addition to trimerization a chain polymerization may set in, as is also evident from the precipitation of the solid polymer in more concentrated solutions. As a result of this complication, and because the instrument used in this investigation does not give data of sufficient precision for the calculation of thermodynamic constants, we did not carry out a great number of measurements. However, we feel that we have demonstrated that formaldehyde oxime may polymerize to a cyclic trimer and that the trimer is nearly completely depolymerized on neutralisation.

NMR spectroscopy also sheds light on the following rather puzzling observations made during various preparations of formaldehyde oxime:

- a) When formaldehyde is added to an aqueous solution of hydroxylammonium

chloride and the solution is neutralized, extraction with a few portions of ether usually gives lower yields of formaldehyde oxime than when the hydroxylammonium chloride solution is made alkaline before the addition of formaldehyde. However, continuous extraction with ether furnished a good yield of the oxime.

b) When the solution of hydroxylammonium chloride and formaldehyde is made alkaline (pH 10-11) before extraction with ether, the yields of the oxime diminish markedly. When the ether extracts no longer give a positive reaction with nickel(II) the aqueous phase still gives a positive reaction.

These observations are explicable on the basis of the following results obtained by ^1H NMR spectroscopy of solutions with concentrations similar to those employed in preparative procedures (2.5 M):

Formaldehyde and hydroxylammonium chloride react in aqueous solution rapidly and quantitatively with the formation of *I*, and at sufficiently high concentrations no monomeric oxime is formed. A solution obtained by adding formaldehyde to a neutralized solution of hydroxylammonium chloride shows signals for both the oxime and the trimer, but the latter signal disappears slowly. Immediate extraction with ether may therefore give a low yield of the oxime whereas continuous extraction extended over several hours gives a good yield.

If the hydroxylammonium chloride solution is made alkaline before the addition of formaldehyde the resulting solution displays only the signals of the oxime; this procedure might therefore seem to be the more convenient for the preparation of the oxime (and was used in the original paper by Dunstan and Bossi⁷). However, at high concentrations the oxime may polymerize to the insoluble polymer which separates as a gel-like precipitate before the oxime has been extracted.

The ^1H NMR spectrum of a solution of *I* which is suddenly made alkaline reveals the presence of a considerable amount of the trimer. This is simply because the equilibrium corresponding to pH ca. 1 is "frozen", the depolymerization of the trimer occurring only slowly in alkaline solution. Because of its great hydrophilicity the trimer cannot be extracted with ether. When the pH of the solution is adjusted to 3-4 the trimer depolymerizes and the monomer can then be obtained by extraction of the neutralized solution.

The ^1H NMR spectra show no new signals when an excess of hydroxylammonium chloride or formaldehyde is employed (with or without addition of NaOH), *i.e.* there is no indication of the formation of the species $\text{CH}_2(\text{NHOH})_2$ or $\text{HON}(\text{CH}_2\text{OH})_2$.

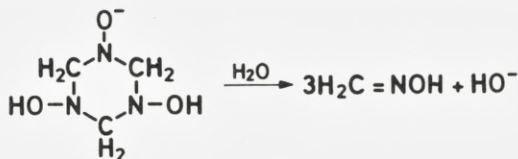
V. Isolation of free 1,3,5-Trihydroxyhexahydro-1,3,5-Triazine

The above mentioned measurements indicate that the free base is present in an alkaline solution of *I*, but attempts to extract it with ethyl acetate or pentyl alcohol (after extraction of the monomer with ether) were unsuccessful because it polymerized during evaporation of the solvents. The authentic trimer was successfully isolated as a dioxane adduct in the following manner: Formaldehyde oxime remaining after evaporation of an ether solution immediately polymerizes exothermically when the temperature is around 0 °C. If the product is extracted with dioxane before it has completely solidified some of it goes into solution, and on removal of the solvent in vacuum a white solid is obtained whose composition corresponds approximately to $(\text{CH}_2\text{NOH})_3 \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}_2$. This substance is soluble in water and gives a positive nickel reaction. An aqueous solution shows initially only the ^1H NMR signals of the trimer and of dioxane, but weak signals for the monomer soon appear. After some hours the signals of the monomer become very strong while that of the trimer diminishes. At room temperature the solid substance rapidly loses dioxane and is transformed into the insoluble polymer.

We finally succeeded in preparing a solvent-free product in the manner described in the Experimental. After recrystallization from ethyl acetate, analyses and MS proved it to have the formula $\text{C}_3\text{H}_9\text{N}_3\text{O}_3$ and ^1H NMR showed it to be the desired free base, **7**. It is a colourless substance which is readily soluble in water and alcohols but is insoluble in ether, chloroform, benzene, etc. At room temperature it is rapidly transformed into the insoluble polymer. A prerequisite for this transformation is ring-opening, which is catalyzed by acids and bases (see below) and probably also by oxygen and certain metal ions. When the compound has been purified meticulously it can be kept unchanged for months in a refrigerator at -20 °C. The presence of small amounts of the polymer in the trimer is revealed by its IR spectrum and gives rise to turbidity of aqueous solutions.

At pH *ca.* 7 the trimer is only slowly transformed into formaldehyde oxime (Table 3 and Fig. 1) but at pH values lower than 4 equilibrium is established almost instantaneously (Scheme 2 and Fig. 1). The transformation is also (irreversibly) base-promoted but is only reasonably rapid at pH values higher than 10. Depolymerization in this case probably proceeds *via* the anion (Scheme 3).

Scheme 3



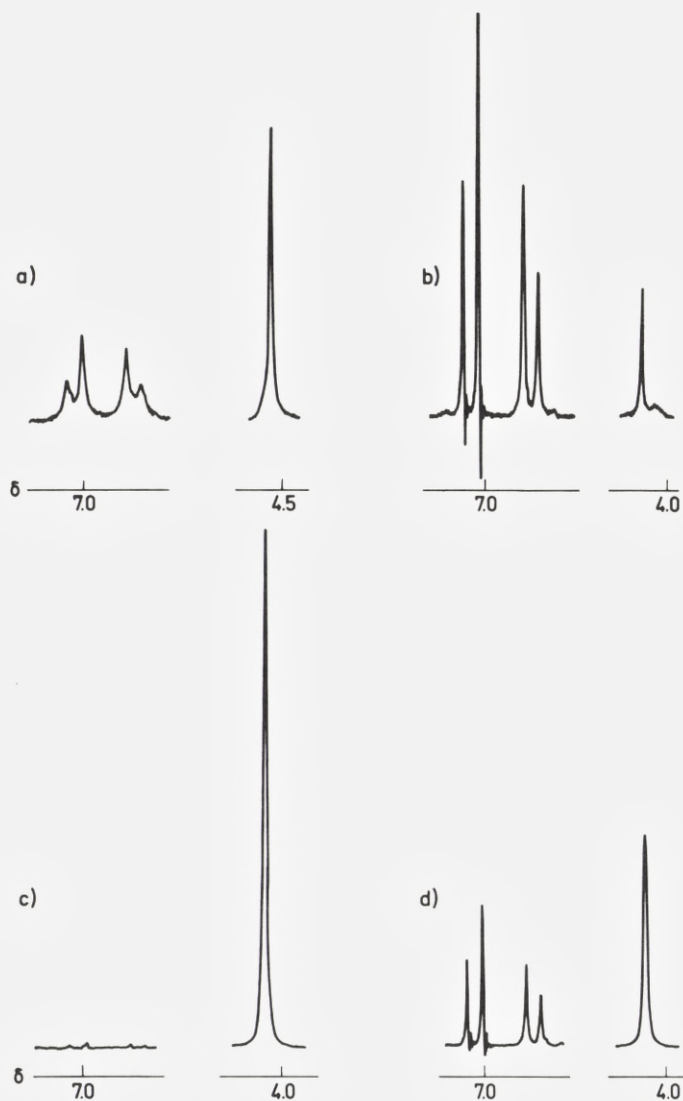


Fig. 1.

^1H NMR spectra of solutions of 1,3,5-trihydroxyhexahydro-1,3,5-triazine in D_2O with or without addition of DCl .

a) pH 2.5;

b) 4.2;

c) pH 7, recorded 10 min after dissolution;

d) pH 7 after 24 h.

Potentiometric titrations indicate 7 to be a very weak acid with a pK_a value near 11. Since it is a trivalent acid and is transformed into formaldehyde oxime, which is also an acid, it would be very difficult to determine a more precise value.

In alcohols the transformation of 7 into the monomer 3 is much slower than in water. In methanol only traces of 3 are formed after 24 h. Compound 7 is also soluble in DMSO and (in contrast to the hydrochloride or methiodide) is not detectably transformed into the monomer in this solvent.

On addition of peroxodisulfate to an alkaline solution of 7 a red colour develops. It was shown by ESR spectroscopy that this colour reaction is due to the formation of free radicals. These are probably derived from the anion of the trimer but their exact nature has not been established. The free radical derived from the monomer²⁸ is not formed under these conditions. A pink colour also develops when a concentrated solution of 1 is neutralized, probably due to oxidation of 7 by atmospheric oxygen.

Compound 7 is easily acylated by acetic anhydride or benzoyl chloride to give derivatives 4 and 5 which are identical with those prepared from the monomer. On heating, the benzoyl derivative forms benzoic acid and HCN. 1,3,5-Triazine could neither be detected in this reaction nor when 7 was heated with dehydrating agents (*cf.* the formation of 1,3,5-triazine from formamide²⁹). In the latter case 7 was transformed into the polymer.

VI. Experimental

The 60 MHz ^1H NMR spectra were measured using a Varian A-60 A instrument. Sodium 3-(trimethylsilyl)propanesulfonate (DSS) was used as internal standard for D_2O solutions, and TMS for the measurements in CDCl_3 and CCl_4 . The temperature at which the spectra were recorded was determined from the position of the signals of ethylene glycol. Infrared spectra were recorded on a Perkin Elmer Model 337 grating spectrophotometer. Mass spectra were obtained with an AEI-902 mass spectrometer at 70 eV using the direct sample-insertion system.

For the determination of the dipole moment of the acetyl derivative 4 a Dipol-meter DM 01 instrument from Wissenschaftlich-Technische Werkstätten, Weilheim, was used.

For pH measurements, a pH meter 22 from Radiometer, Copenhagen, was used. Melting points (corrected) were determined with a Kofler hot-stage microscope.

Oxygen analyses were carried out by the Unterzaucher method. We thank Mr.

R. Amsler of the NOVO Microanalytical Laboratory for performing these analyses.

Elemental analyses agree within ± 0.4 % units with the calculated values, unless the values found have been given.

1,3,5-Trihydroxyhexahydro-1,3,5-triazinium chloride, "triformoxime hydrochloride" (1).

a) Hydroxylammonium chloride (40 g) was added with stirring to aqueous formaldehyde (40 %; 44 ml); it rapidly dissolved and the temperature rose to *ca.* 35 °C. The solution was then evaporated almost to dryness *in vacuo*. Benzene (200 ml) was added and most of it removed by distillation *in vacuo*. This treatment was repeated and ethanol (150 ml) was added to the residue. The mixture was cooled overnight in a refrigerator and the crystalline precipitate was collected, washed with a little cold ethanol and dried *in vacuo* over KOH. Yield: 29,5 g (90 %) of colourless crystals with m.p. 132-133 °C (closed tube; decomp.). This procedure furnishes a pure product directly.

The solution of 1 can also be prepared by stirring a suspension of paraformaldehyde in an aqueous solution of hydroxylammonium chloride at 60 °C until dissolution is complete. This method was used for the preparation of $(D_2CNOH)_3 \cdot HCl$ from paraformaldehyde- d_2 .

b) Compound 1 has also been prepared several times by the original procedure⁷, *i.e.* by bubbling dry HCl through a cooled ether solution of formaldehyde oxime prepared as for compound 3. In this case the crude product contains excess of HCl and must be recrystallized, preferably by dissolving it in warm ethanol, adding ether until precipitation begins and then cooling at ≤ 0 °C. Recrystallization results in considerable loss of material (30-40 %), and it was shown that this is due to extensive solvolysis to formaldehyde and hydroxylamine taking place in the hot alcoholic solution. Anal. $C_3H_{10}ClN_3O_3$: C, H, N, Cl.

The chloride 1 is very soluble in ethylene glycol, cellosolve, DMF and similar solvents but only slightly soluble in cold methanol or ethanol and insoluble in most other organic solvents.

Main IR bands (KBr): 3220 vs, 3040 m, 2840 s, 2620 s, 2520 m, 1538 m, 1436 m, 1405 s, 1345 m, 1300 vw, 1252 w, 1202 s, 1178 s, 1130 m, 1040 m, 970 m, 948 s, 798 s, 710 w, 620 m, br, 560 s, 548 s, 500 w, 433 s.

Poly(formaldehyde oxime) (2). The various forms of 2 were prepared either from aqueous solution (2a) according to Scholl⁶ or by spontaneous polymerization of gaseous or liquid formaldehyde oxime (2b-e). Some 20 different samples have yielded practically identical infrared spectra. Their analytical composition is somewhat variable (C 24.6-27.3; H 6.51-6.88; N 28.4-31.7; O 34.8-38.6) but shows

no apparent correlation with the method of preparation. (Representative analyses: Found (C, H, N, O): *2a* 25.7; 6.88; 31.7; 34.8. *2d* 26.3; 6.70; 30.5; 35.7. *2e* 25.8; 6.51; 30.0; 37.5. Calc. for $(\text{CH}_3\text{NO})_n$: C 26.65; H 6.66; N 31.1; O 35.5.)

The polymer may be prepared in good yield by heating a mixture of *1* and CaO in a sublimation apparatus. In this process the trimer is depolymerized and the monomer condenses on the cool surface where it rapidly becomes transformed into the polymer. This method was also used to prepare $(\text{D}_2\text{CNOH})_n$ for the infrared spectroscopic investigation.⁸

The products *2b-e* may give a positive nickel reaction due to traces of the trimer. The latter may be removed simply by washing with hot water or ethanol.

The mass spectra of the polymers were identical to that of the monomer. There was no indication of the formation of ions heavier than those formed from the monomer.

The white, amorphous (according to X-ray powder diagrams) solids are insoluble in all solvents except those in which depolymerization can take place. Krässig and Ringsdorf³⁰ found the molecular weight of *2* to be *ca.* 150 in caprolactam, but this result is due to depolymerization to the trimer *7*. When *2* was dissolved in molten caprolactam the presence of *7* could be proved by the colour reaction with nickel(II) chloride.

The polymers are easily dissolved in strong acids. Solutions in 1 M DCl/D₂O show only the NMR signal of the hexahydrotriazinium ion. The polymers are also soluble in warm NaOH. Solutions in 1 M NaOD/D₂O show only the signals of formaldehyde oxime. These solutions give a negative reaction with nickel(II) chloride, showing that the coloured complexes are not formed directly from the monomer. When the alkaline solutions are acidified and again made alkaline there is a strong, positive nickel(II) reaction.

On boiling a suspension of *2* in benzene with acetic anhydride or benzoyl chloride the derivatives of the trimer (*4* and *5*) are formed.

Formaldehyde oxime (3). A solution of *1*, prepared according to *1a*, was diluted with 100 ml of water, cooled in ice and adjusted to pH 8 with 10 M NaOH. When the solution became neutral a faint red colour developed. The solution was extracted continuously with 300 ml of ether for 24 h. After that time the pH of the solution was 9 and the aqueous phase gave a negative nickel(II) reaction while the ether phase gave a strongly positive reaction. After drying the ether phase (MgSO_4) the bulk of the solvent was removed *in vacuo*. The remaining liquid was distilled at normal pressure, the receiver being cooled in dry-ice/acetone. Gas chromatography and ¹H NMR indicated that the liquid still contained some ether. It was therefore redistilled, removing practically all the remaining ether; b.p. 82-83 °C

(759 mmHg), m.p. -5°C . At room temperature the oxime polymerizes completely in a few minutes. It can be kept at -80°C for some time but not without the formation of some of the polymer.

^1H NMR spectrum, see Table 1.

MS [m/e (% rel.int.)]: 46 (2), 45 (100, [M]), 44 (9), 43 (6), 32 (2), 30 (5), 29 (2), 28 (32, [M-OH]), 27 (25, [M-H₂O]), 26 (2).

1,3,5-Triacetoxyhexahydro-1,3,5-triazine (4). Acetic anhydride (4 ml) was added to the carefully dried ether solution (40 ml) of formaldehyde oxime prepared as above and the solution was kept for several days in a refrigerator until colourless crystals of the acetyl derivative had formed. Yields are very variable. M.p. $132-133^{\circ}\text{C}$ (TLC-pure; lit.⁷ 133°C). Anal. $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_6$: C, H, N. The compound is readily soluble in water, ethanol and chloroform, slightly soluble in CCl_4 , and insoluble in ether. It can be recrystallized from ethyl acetate. It is easily hydrolysed in alkaline solution (when 0.1 M NaOH was added to an aqueous solution at such a rate as to maintain a pH value of 10.5 hydrolysis was complete in *ca.* 2 h).

This compound could be prepared in higher yield from the trimer (7): 400 mg of 7 was dissolved in 1 ml of acetic anhydride and the solution was kept for one day at room temperature. Excess acetic anhydride was removed *in vacuo*. The residue was dissolved in chloroform and the solution was washed with water, dried with MgSO_4 and concentrated *in vacuo*. On addition of ether 450 mg of 4 were obtained.

The same compound has also been obtained from the polymer (see under 2) or by passing ketene through a solution of formaldehyde oxime in ether. In the latter case the resulting solution was distilled *in vacuo* and the fraction passing over at $34-60^{\circ}\text{C}$ (12 mmHg) was recrystallized from abs. ethanol.

Dipole moment (dioxane, 20°C): 3.25 D.

Mol.wt. (thermoelectric meth., CHCl_3): 260 ± 2 , calc. 261. ^1H NMR (CDCl_3): δ 4.53 (s, 2H), 2.08 (s, 3H).

IR (KBr): 3020 w, 2940 w, 1750 vs, 1415 m, 1363 s, 1240 vs, 1200 vs, 1142 s, 1040 m, 1002 m, 972 m, 943 m, 895 s, 880 s, 802 s, 648 m. Most of these bands can be assigned to the groups CH_2 , CH_3 , and O-COCH_3 . The strong doublet at $880 + 895\text{ cm}^{-1}$ (in CHCl_3 a singlet at 887 cm^{-1}) is assigned to $\nu(\text{N-O})$ and the 1040 cm^{-1} band to $\nu(\text{C-N})$.

MS [m/e (% rel.int.)]: 261 (1, [M]), 201 (1, [M- $\text{CH}_3\text{CO}_2\text{H}$]), 174 (9, [M- $\text{CH}_2\text{NOCOCH}_3$]), 132 (6, [174 - CH_2CO]), 88 (25, [$\text{CH}_2\text{NHOCOCH}_3^+$]), 60 (21, [$\text{CH}_3\text{CO}_2\text{H}^+$]), 45 (27), 44 (14), 43 (100, [CH_3CO^+]), 42 (29), 32 (14), 27 (12).

1,3,5-Tribenzoyloxyhexahydro-1,3,5-triazine (5). An aqueous solution of hydroxylammonium chloride (20 g) and formaldehyde (40 %, 22 g) was neutralized and shaken with benzoyl chloride (40 g), keeping the solution neutral by addition of sodium carbonate. The white precipitate (30 g) which separated was collected and extracted with boiling ethanol-water (1:1) acidified with HCl, and the insoluble material was recrystallized from chloroform-ethanol. Yield 14 g (33 %) with m.p. 176-177 °C (TLC-pure; lit.⁷ 159). Anal. $C_{24}H_{21}N_3O_6$: C, H, N. Mol.wt. 447 (MS). 1H NMR ($CDCl_3$): δ 5.00 (s, 2H); 7.0-8.0 (m, 5H). The IR spectrum is dominated by the strong bands due to the benzoyl groups. The following bands can with reasonable certainty be assigned to the triazine system: 1415 (δ CH_2), 950, 830, and 780 cm^{-1} .

The acidic ethanolic solution remaining after treatment of the crude product yielded on addition of water a solid which on recrystallization from ethanol-water gave 8 g of *O,N*-dibenzoylhydroxylamine (dibenzohydroxamic acid); m.p. 166-167 °C (lit.³¹ 165).

Compound 5 has also been prepared from the polymer (2; *q.v.*), and from the trimer (7): compound 7 (270 mg) was dissolved in pyridine (5 ml) and benzoyl chloride (840 mg) was added dropwise to the solution while cooling in ice. The final solution was diluted with water and extracted with chloroform. Work-up of the solution yielded 300 mg of 5.

Compound 5 decomposes on melting with the formation of HCN together with a white sublimate, identified as benzoic acid, and a dark brown residue (polymer of HCN). 1,3,5-Triazine could not be detected.

N-Methyl-1,3,5-trihydroxyhexahydro-1,3,5-triazinium iodide (6).

An excess of methyl iodide (10 g) was added to an extract (cf. 3) containing *ca.* 2 g of formaldehyde oxime in 50 ml of ether.¹² Slightly yellow crystals (4.9 g) separated from the solution when this was kept for some days in a refrigerator at 0-5 °C. They could not be recrystallized but were washed with ether. The compound melted with decomposition near 100 °C. Anal. $C_4H_{12}IN_3O_3$: C, H, N. It is readily soluble in water, methanol or dimethyl sulfoxide but is simultaneously decomposed with the formation of formaldehyde oxime. In aqueous solution the other products formed are formaldehyde, *N*-methylhydroxylammonium ion and formaldehyde *O*-methyloxime.

1H NMR (D_2O): δ 6.57 (d), 7.06 (d), 4.79 (s, CH_2O), 3.00 (s, $CH_3NH_2OH^+$), 3.52 (s, $-OCH_3$).

The compound $CH_3N(OH)-CH_2-N(OH)CH_3$, prepared according to Ulrich and Sayigh³², shows two peaks in $CDCl_3$ at δ 3.43 (2H) and 2.60 (6H); in D_2O it shows 4 peaks at δ 3.72, 3.52, 2.68 and 2.64, probably because of partial hydro-

lysis to $\text{CH}_3\text{N}(\text{OH})\text{CH}_2\text{OH}$. On acidification of the D_2O solution there are only two signals at δ 3.00 and 3.51. However, the latter is a broad peak which is quite different from the 3.52 peak seen for the solution of the methiodide.

The IR spectrum of the methiodide is similar to that of the hydrochloride (1).

1,3,5-Trihydroxyhexahydro-1,3,5-triazine (7). The hydrochloride 1 (17 g) was suspended in water (15 ml). The suspension was cooled in ice, and a solution of KOH (5.6 g) in water (10 ml) was added gradually until pH was *ca.* 7. Ethanol (250 ml) was added and the precipitated KCl was collected and discarded. The solution was concentrated *in vacuo* and the remaining water was removed by repeated evaporation with addition of ethanol and benzene. Finally, the solution was evaporated to dryness and the residue was extracted with 400 ml of boiling ethyl acetate. Only part of the material dissolved but on cooling the solution and decanting it from the crystalline residue renewed treatment of the latter with a further portion of the solvent caused most of it to dissolve. Ether (400 ml) was added to the combined ethyl acetate solution and the crystals were collected after cooling overnight. Yield 5.7-6.9 g (42-51 %). For analytical purposes 1 g of product was recrystallized from 60 ml of ethyl acetate (yield 0.5 g). Traces of ethyl acetate were removed by drying under high vacuum until the IR spectrum showed no absorption in the 1700 cm^{-1} range.

Anal. $\text{C}_3\text{H}_9\text{N}_3\text{O}_3$: C, H, N. Slow evaporation of the ethyl acetate solution yields compound 7 as large, colourless crystals.

Compound 7 sublimes perceptibly even at 50°C , the vapour being the monomer. It melts essentially unchanged (IR spectrum) at $114\text{--}115^\circ\text{C}$ but the melt is fairly rapidly transformed (*via* the monomer) into the polymer. On heating 7 with dehydrating agents such as CaO or CaC_2 it is similarly transformed into the polymer (no 1,3,5-triazine could be detected). ^1H NMR spectra, see Tables 1 and 3 and Figure 1. Main IR bands (KBr): 3420 vs, 3200 sh, 3110 vs, 2950 w, 2880 vs, 1490 sh, 1470 s, 1430 m, 1380 s, 1365 sh, 1305 w, 1292 m, 1245 w, 1168 s, 1005 m, 970 sh, 955 s, 918 s, 815 m, 795 s, 730 s, 710 sh, 585 m, 572 s, 560 sh, 505 m, 440 sh, 430 m.

Compound 7 forms a dioxane adduct (m.p. *ca.* 90°C) which according to elemental analyses has the composition $\text{C}_3\text{H}_9\text{N}_3\text{O}_3 \cdot \frac{1}{2}\text{C}_4\text{H}_8\text{O}_2$. Its ^1H NMR spectrum in D_2O shows the proton signals of 7 and of dioxane (δ 3.72) in the expected ratio (3:2). Its infrared spectrum exhibits only the absorption bands of 7 and dioxane. At room temperature it loses dioxane and is transformed into the polymer.

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