

A study of condensation of propane-1,3Diamine with formaldehyde

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ABSTRACT

The condensation of formaldehyde with propane-1,3-diamine gave four products depending on the conditions of the reaction of them dimer, trimer, tetramer and pentamer of *N,N'*-bis(methylene)propane-1,3-diamine products ($CH_2=NCH_2CH_2CH_2N=CH_2$). Their structures were determined by MS, elemental analysis and 1H NMR spectroscopy methods. The structure of the pentamer was additionally determined by *X-ray* diffraction analysis.

Introduction:

The study of mass spectroscopy of products of the condensation process of formaldehyde with propane-1,3-diamine showed, that their products depend on the conditions of the reaction, which gave different products such as dimer, trimer, tetramer and pentamer *N,N'*- bis (methylene) propane -1,3-diamine, ($CH_2=NCH_2CH_2CH_2N=CH_2$). Tetramer (1) (Scheme 1) one of these products known in literature. Krassig [1] found this product with yield approaching 80% in *N,N'*-dimethylformamide is used as formalin solution.

Experimental:-

Melting points were recorded with Gallenkamp melting points Apparatus. Elemental analysis was carried out in Perkin-Elmer 2400, elemental analyzer, table (1). Mass spectra were recorded on a Finnigan MRT-90 instrument (direct inlet- probe, voltage 5.0 kV, cathode emission current 100 μ A, ionizing electron energy 70 eV, ionization chamber temperature 200 $^{\circ}C$). Perfluorokerosene was used as a standard. The resolution was $M/\Delta M = 10000$. The injector temperature was 20 $^{\circ}C$, Mass spectra table (2). 1H NMR spectra were recorded on a Bruker WM-250 spectrometer (250 MHz) for 2-3% solutions of the compounds under study in $CDCl_3$, 1H NMR table(3). X-ray diffraction analysis. Experimental material for crystals was measured on automatically diffractometer Enraf-Nonius CAD-4 (MoKa), table (4). The course of

the reactions was monitored and the purity of the products was checked by TLC on Silufol UV-254 plates. Spots were visualized with iodine vapor in a moist chamber. All final products were measured in Republic of Russian Federation.

1,3,7,9,13,15,19,21-Octaazapentacyclo-[19.3.1.13,7.19,13]unicosane (1). To 4 ml (47 mmole) propane-1,3-diamine with vigorous stirring at room temperature for 10 min, 2.85 gm (95 mmole) of formaldehyde in small portions was added with continuous stirring, until formaldehyde was completely dissolved. The reaction mixture was evaporated and the residue was recrystallized from isopropyl alcohol. 1,3,7,9,13,15-Hexaazatetracyclo [13.3.1.13,7.19,13]unicosane (2). To 8 ml (95 mmole) propane-1,3-diamine in 30 ml water with vigorous stirring at room temperature for 10 min, 5.7 gm (190 mmole) of formaldehyde in small portions was added with continuous stirring, until formaldehyde was completely dissolved. The reaction mixture was left for 24 h. and the precipitate was filtered and dried. 1,3,7,9-tetraazatricyclo[7.3.1.13,7]tetra-decane (3).

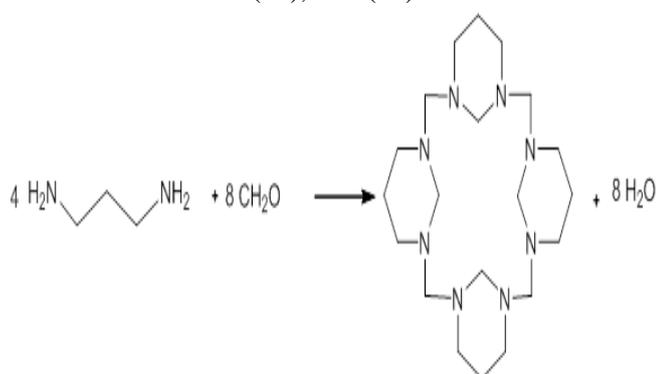
To suspended solution of formaldehyde 2.85 gm (95 mmole) in 25 ml hexane with vigorous stirring and the temperature of not above 40 $^{\circ}C$, 4 ml (47 mmole) propane-1,3-diamine was added with continuous stirring, until formaldehyde was completely dissolved. The reaction mixture was left for two days and the precipitate was filtered and dried. 1,3,7, 9,13,15 ,19,21, 25,2 7- Decaazahexa-cyclo [25.3.1. 13,7.19,13.115, 19. 121, 25] pentatria-

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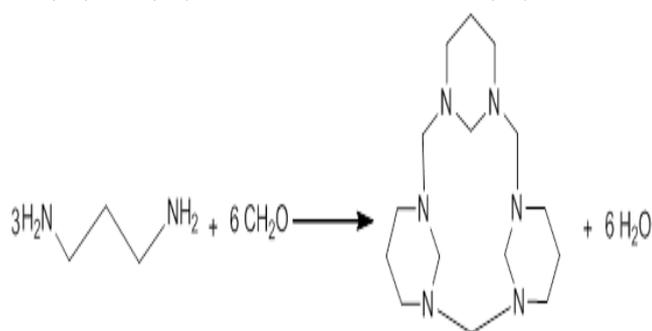
contane (4). The product (3), was recrystallized three times from hexane to obtain a monocystal pentamer.

Discussion:

We obtained product (1) with a yield approaching 96% by the addition of formaldehyde to propane-1,3-diamine without solvent This product is in conformity with what Krassig suggested (Scheme 1). In mass spectrum tetramer (1) we observed the peak of molecular ion $M^+ + 1$ with m/z 393 (34) of medium intensity and peaks of compatible ions, N,N' -bis(methylene)propane-1,3-diamine with m/z 99 (85), 98 (77), 97 (72), its dimer with m/z 197 (79) and trimer with m/z 295 (48), 293 (26).

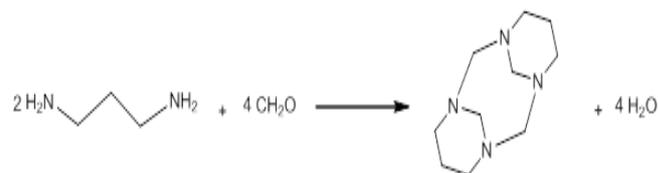


(Scheme 2). In its mass spectrum, we observed the peak of molecular ion $M^+ + 1$ with m/z 295 (21) of medium intensity and peaks of compatible ions, N,N' -bis(methylene)propane-1,3-diamine with m/z 99 (51), 98 (34), 97 (34), its dimer with m/z 197 (28).

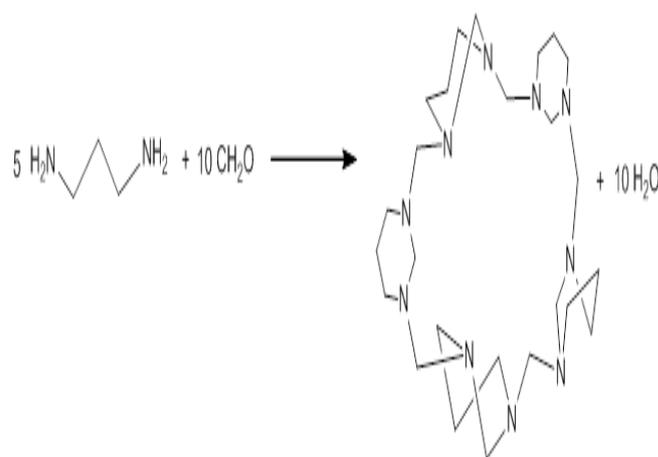


To get dimer (3) (Scheme 3), the reaction occurred in hexane at a temperature not exceeding 40°C. The mass spectrum of dimer (3) showed the peak of molecular ion $M^+ + 1$ with m/z 197 (16) of medium intensity and peak ion with m/z 99 (66), of compatible N,N' -bis(methylene)-propane-1,3-diamine. 1H NMR spectra is followed by the appearance of peaks (4H, 2CCH₂C) at δ : 1.55 (broad s), (8H,

4NCH₂C) at δ : 2.70 (broad s), and (8H, 4NCH₂N) at δ : 3.10 (broad s) symmetrical compound and tetramer have the same 1H NMR spectra (table 3). The products (1, 2 and 3) were determined by MS (table 2).



To get the pentamer (4) (Scheme 4), the dimer (3) was recrystallized in hexane three times, and a monocystal product was obtained. The structure of the pentamer was determined by X-ray diffraction analysis only (Fig. 1). Crystallographic parameters and a summary of data collection for structure (4) are given in (table 5); bond lengths (table 6) and valency corners (table 5).



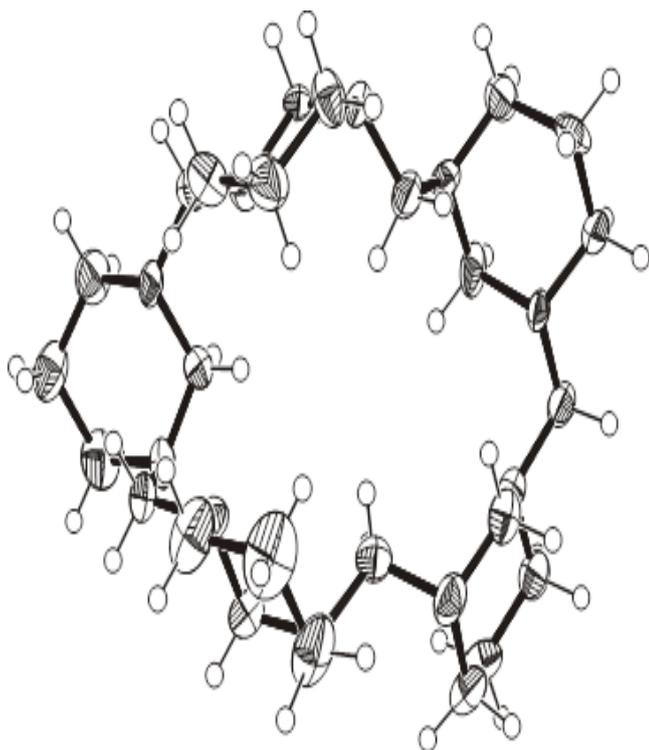


Figure 1. The molecular structure (RSA) for pentamer (4).

Conclusions:-

- 1- The study of Mass spectroscopy of products of the condensation process of formaldehyde with propane-1,3-diamine showed, that the condensation products formation depend on the reaction conditions. Therefore different products such as dimer, trimer, tetramer and pentamer N,N'-bis-(methylene)propane-1,3-diamine (CH₂=NCH₂CH₂CH₂N=CH₂), were obtained.
- 2- Tetramer was very stable; all final products were transformed into tetramer when recrystallized in isopropyl alcohol or any solvent of high boiling point.

Table 1. Melting points, yield, molecular formula [M.F] and elemental analysis of compounds (1-3).

№	m.p./ °C	Yield %	M.F	Found, (%)			Calculat ed, (%)		
1	165-166	96 (white crystals)	C ₂₀ H ₄₀ N ₈	60.79	10.49	28.04	60.85	10.39	28.25
2	115-116	100 (white crystals)	C ₁₅ H ₃₀ N ₆						

2	130-131	82 (white crystals)	C ₁₀ H ₂₀ N ₄	61.38	10.51	28.32	61.18	10.27	28.54

Table 2. Mass spectra of compounds (1-3).

№	m/z (I _{rel} (%))
1	393 [M+1] ⁺ (34), 295 (48), 209 (38), 197 (79), 126 (31), 112 (64), 105 (46), 99 (85), 83 (69), 70 (91), 56 (100).
2	295 [M+1] ⁺ (21), 197 (28), 112 (20), 99 (51), 85 (26), 83 (19), 70 (88), 59 (42), 57 (52), 56 (100), 55 (39).
3	197 [M+1] ⁺ (16), 126 (11), 112 (17), 99 (66), 85 (36), 83 (17), 70 (89), 69 (65), 58 (14), 57 (38), 56 (100).

Table 3. ¹H NMR spectra (δ, ppm) of dimer in CDCl₃

№	2CCH ₂ C	4NCH ₂ C	4NCH ₂ N
3	1.55 (broad s, 4H)	2.70 (broad s, 8H)	3.10 (broad s, 8H)

X-ray diffraction analysis. Crystallographic parameters and a summary of data collection for structure (4) are given in (table 4). The structure was solved by the direct method and refined by the least-squares method in the full-matrix anisotropic approximation for all non-hydrogen atoms. The H atoms were located geometrically and refined in the rider model with fixed isotropic thermal parameters (U_{iso}=0.082). The calculations were performed with the SHELXS86 (see Ref. 2) and SHELXS93 programs (see Ref. 3). We are grateful to Dmitry V. Albov (Department of Chemistry, Moscow State University, Russian Federation) for her assistance in carrying out X-ray diffraction analysis.

References:-

- [1]- Krassig H. (1956)// Makromol. Chem., Vol. 17, № 2, P. 77-89.
- [2]- G. M. Sheldrick, SHELX-86, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), 1993.
- [3]- G. M. Sheldrick, SHELX-86, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), 1993.

Table 4. Crystallographic parameters of structure (4) and a summary of data collection:

γ , deg.	β , deg.	α , deg.	c , Å	b , Å	a , Å	Unit cell parameters	Space group	Crystal system	Molecular weight	Molecular formula	Parameter Value
90	100.563(12)	90	22.984(3)	10.3261(14)	11.9933(19)		$P 2_1/c$	Monoclinic	490.75	$C_{25}H_{50}N_{10}$	

number of reflections / Number of independent	2865 / 316	Number of reflections with $I \geq 2\sigma(I)$	1322	Volume experiment	2865	Crystal size/mm	0.10 x 0.10 x 0.10	Range indices h, k, l	-11 ≤ h ≤ 11 0 ≤ k ≤ 10 0 ≤ l ≤ 22	Corners range θ , deg.	3-50	$\mu(K\alpha)$, mm ⁻¹	0.573	Radiation (λ , /Å)	Cu K α	Diffractometer	Enraf-Nonius CAD_4	Temperature/K	298	ρ calc., g/cm ³	1.165	Z	4	$V, \text{Å}^3$	2798.1(7)
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Density $\Delta\rho_{\max}/\Delta\rho_{\min}$ $e/\text{\AA}^3$	R -Factor $[I\sigma_2]$ $2\sigma(I)$ R_1/wR_2	GooF
0.134 / -0.143	0.0564 / 0.0881	0.847

Table 5. Valency corners ω (degree) in structure

(4)

Corner	ω
N5-C4-N3	113.0 (4)
C23-N3-C2	108.3 (4)
C4-N3-C2	110.9 (4)
C4-N3-C23	111.2 (4)
N1-C2-N3	112.7 (4)
C20-N1-C21	113.8 (4)
C2-N1-C21	111.3 (4)
C2-N1-C20	113.4 (4)
Corner	ω

C29-N11-C10	108.9 (4)	N9-C10-N11	113.1 (5)	C10-N9-C27	108.8 (5)	C8-N9-C10	114.1 (4)	N9-C8-N7	110.7 (4)	C6-N7-C8	111.5 (4)	C6-N7-C26	111.6 (5)	N7-C6-N5	112.7 (5)	C4-N5-C6	110.5 (4)	C24-N5-C6	110.2 (4)	C24-N5-C4	111.9 (4)
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C33-N17- C18	N17-C16- N15	C16-N15- C14	C32-N15- C14	C32-N15- C16	N13-C14- N15	C12-N13- C30	C14-N13- C30	C14-N13- C12	N13-C12- N11	C10-N11- C12	C29-N11- C12
111.6(5)	109.8(4)	109.2(4)	109.8(4)	111.0(4)	111.5(4)	110.7(4)	109.8(4)	113.2(5)	110.2(4)	110.6(4)	109.9(4)

C24-C25- C26	N5-C24- C25	N3-C23- C22	C23-C22- C21	N1-C21- C22	N1-C20- N19	C18-N19- C20	C35-N19- C20	C35-N19- C18	N19-C18- N17	C18-N17- C16	C33-N17- C16
110.4(5)	111.7(4)	110.6(4)	110.4(4)	112.0(4)	110.6(4)	111.1(4)	113.6(4)	110.6(4)	111.8(4)	111.1(4)	112.6(4)

N7-C26- C25	113.0 (5)
N9-C27- C28	113.2 (5)
C27-C28- C29	110.4 (6)
N11-C29- C28	107.8 (5)
N13-C30- C31	112.9 (4)
C32-C31- C30	109.6 (5)
N15-C32- C31	110.3 (5)
N17-C33- C34	110.9 (5)
C35-C34- C33	109.1 (5)

N19-C35- C34	115.3 (4)
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Table 6. Bond lengths in structure (4)

bond	d
N1-C2	1.424 (5)
N1-C20	1.437 (6)
N1-C21	1.467 (5)
C2-N3	1.493 (5)
N3-C4	1.456 (5)
N3-C23	1.458 (6)
C4-N5	1.452 (6)
N5-C24	1.437 (5)
N5-C6	1.470 (6)
C6-N7	1.444 (6)
N7-C26	1.457 (6)
N7-C8	1.477 (5)
C8-N9	1.425 (6)
N9-C10	1.446 (5)
N9-C27	1.462 (6)
C10-N11	1.466 (6)
N11-C29	1.448 (6)
N11-C12	1.468 (5)
C12-N13	1.459 (6)
N13-C14	1.438 (6)
N13-C30	1.470 (6)
C14-N15	1.474 (5)
N15-C32	1.443 (5)
N15-C16	1.469 (6)
C16-N17	1.468 (6)
N17-C33	1.446 (6)
N17-C18	1.461 (5)
C18-N19	1.459 (5)
N19-C35	1.441 (6)
N19-C20	1.459 (5)
C21-C22	1.517 (5)
C22-C23	1.480 (6)
C24-C25	1.500 (6)
C25-C26	1.522 (7)
C27-C28	1.506 (7)
C28-C29	1.542 (7)
C30-C31	1.543 (6)
C31-C32	1.492 (7)
C33-C34	1.532 (6)
C34-C35	1.500 (6)

دراسة تكاثف بروبان - ٣، ١ - ثنائي أمين مع الفورمالديهايد

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الخلاصة

من خلال دراسة تكاثف مركب الفورمالديهايد مع مركب بروبان - ٣، ١ - ثنائي أمين أعطت أربعة نواتج كل على حده وحسب ظروف التفاعل وهي ثنائي، ثلاثي، رباعي وخماسي للمونومير N,N' -بس (مثيلين) بروبان - ٣، ١ - ثنائي أمين $CH_2=NCH_2CH_2CH_2N=CH_2$. وهذه المركبات شخصت بواسطة طيف الكتلة، تحليل العناصر (CHN) وطيف الرنين النووي المغناطيسي (1H NMR). إن التركيب الخماسي قد شخص بواسطة تحليل انحراف الأشعة السينية (X-ray).