Novel Synthesis and X-Ray Crystal Structure of Tetra Decahydrohexaazapyrene

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الخلاصة

تم تحضير مركب رباعي ديكاهايدروهكسازابيرين من تفاعل تكاثف كلوتارالديهايد (محلوله المائي ٥٠ %) مع الهيدرازين (محلوله المائي ٨٠ %)، وكانت نسبة ناتج التفاعل (٣١ %). وشخص المركب الجديد (رباعي ديكاهايدرو-10c,10b,10,9,5,4هكسازابيرين) بواسطة التحليل الكمي الدقيق للعناصر ومطيافية الاشعة تحت الحمراء (FT-IR) والكتلة (MS) والرنين النووي المغناطيسي البروتوني و نظير الكاربون ١٣ (13CNMR, 1HNMR)، كما تم اثبات تركيبه الفراغي بواسطة حيود الأشعة السينية (X-ray).

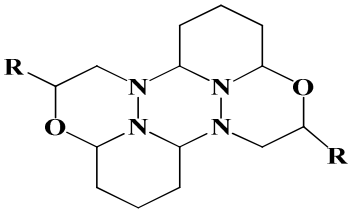
Abstract

The compound of tetradecahydrohexaazapyrene was synthesized by the reaction of condensation of glutaraldehyde (aqueous solution 50%) with hydrazine hydrate (aqueous solution 80%) with yield 31%. The new compound of tetradecahydro-4, 5, 9, 10, 10b, 10c-hexaazapyrene was Characterized by elemental analysis, FT-IR, MS, ^{1}HNMR and ^{13}CNMR spectroscopy methods. The structure of this compound was confirmed by X-ray crystallography.

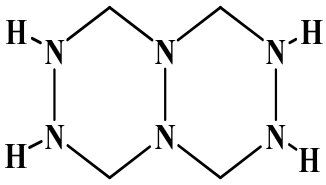
Key words: *Condensation; Hydrazine; Glutaraldehyde; X-Ray Crystallography.*

Introduction

Developments concerning polyazapolycycles compounds include X-ray crystallographic data previous studies have demonstrated that the formation of these compounds is controlled by steric and lone pair-lone pair interaction [1-9]. The reaction of hydrazinoethanol with glutaraldehyde (structure A) and hydrazine with paraformaldehyde (structure B), was first reported in 1996 and 2006 respectively, and was confirmed by X-ray crystallography [1, 2]. Glutaraldehyde is used in large area in industries as a disinfectant (antiseptic), preservative, fixative [10-12] and it plays a important role in biological systems as a cross-linking agent [13,14].



Structure A



Structure B

Experimental

Melting point was recorded with Gallenkamp melting points Apparatus. Elemental analysis was carried out in Perkin-Elmer 2400, elemental analyzer. Mass spectra were recorded on a Finnigan MRT-90 instrument (direct inlet- probe, voltage 5.0 Kv, cathode emission current 100 μA, ionizing electron energy 70 eV, ionization chamber temperature 200 °C). Perfluorokerosene was used as a standard. The resolution was $M/\Delta M$ = 10000. The injector temperature was 20 °C. ^{1}HNMR and ^{13}CNMR spectra were recorded on a Bruker WM-250 Spectrometer (250 MHz) for 2-3% solutions of the compounds under study in $CDCl_3$, internal reference TMS.

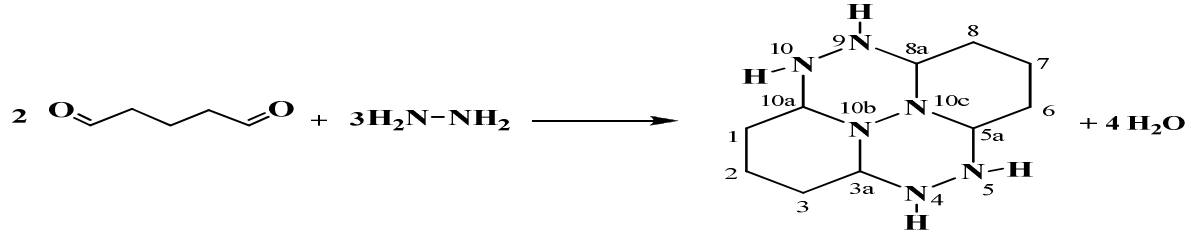
X-ray diffraction analysis, Experimental material for crystals was measured on automatic diffractometer Enraf-Nonius CAD4 (MoK_a). The course of the reactions was monitored and the purity of the product was checked by Thin Layer Chromatography (TLC) on Silufol Uv-254 plates. Spots were visualized with iodine vapor in a moist chamber. The final product was measured in the Republic of the Russian Federation.

Tetradecahydro-4, 5 ,9, 10, 10b, 10c-hexaazapyrene 3. To 7.5 ml (0.3 mole, 80% W/V in water) hydrazine with vigorous stirring at room temperature for 30 min. was added dropwise 8 ml (0.2 mole, 50% W/V in water) glutaraldehyde and continuous stirring 12 hs. The reaction mixture was evaporated under reduced pressure and residue was recrystallized from 2-propanol and gave 3.2 g, colorless crystal. The properties of compound 3 are shown in (table 1-4). X-ray analysis of compound 3. Single crystal was prepared by allowing 2-propanol solution of the compound to stand for two weeks. This crystallographic data is shown in (**Table 5-7**).

Results and Discussion

The new structure including tetraheterocycles with six nitrogen in two rings and two piperidine rings by condensation of two molecules of glutaraldehyde with three molecules of hydrazine hydrate. Piperidines and their derivatives are pharmacologically active and form an essential part of the molecular structure for important drugs [15]. The piperidino group is a feature of the antihistaminic agent [16] and narcotic analgesics [17]. We predict that the title compound has a biological activity.

Cage compound was prepared by the reaction of hydrazine hydrate with glutaraldehyde (1,5-pentanedial) in aqueous solution, was stirred for 12 hr. at room temperature and gave a novel structure tetradecahydro-4,5,9,10,10b,10c-hexaazapyrene with yield 31% in one step as shown in (**Scheme 1**). The structure of this product was assigned as tetradecahydro-4, 5, 9, 10, 10b, 10c-hexaazapyrene 3 on the basis of the following observations. Product 3, derived from 1 and 2, showed a molecular ion peak at *m/z* 224 (35), which was consistent with the sum of 2: 3 molecules each of 1and 2 after eliminating four molecules of water. The FT-IR spectrum revealed the absence of amino and carbonyl groups. The ^{1}HNMR spectrum showed C-1, C-2, and C-3 methylene groups as two singlets at δ 1.4, 1.85 ppm to C-3a and C-10a methine protons as a singlet at δ 1.95 ppm and (4H) N-H group as a singlet at δ 4.4 ppm. The ^{13}CNMR spectrum indicated three methylene carbons at δ 25.83, 24.91 and 14.9, and two methine carbons at δ 70.24 and 58.22, which supports a symmetrical structure; moreover, its product was shown to have a symmetry axis by X-ray. The title compound crystallizes with two molecules of water (**Figure 1**). The crystal data of the 3 adduct ($C_{10}H_{24}N_6O_2$) areas follows; monoclinic, space group *P 2$_1$/c*, a= 9.5380(17) Å, b= 16.2113(17) A°, c= 9.186(3) A°, α= 90, β= 114.74(3), γ= 90, V=1290.0(6) A° ^{3}, Z=4, crystal_density (ρ calc.) =1.341 g /cm^{-3}.



1 **2** **٣**

Scheme 1

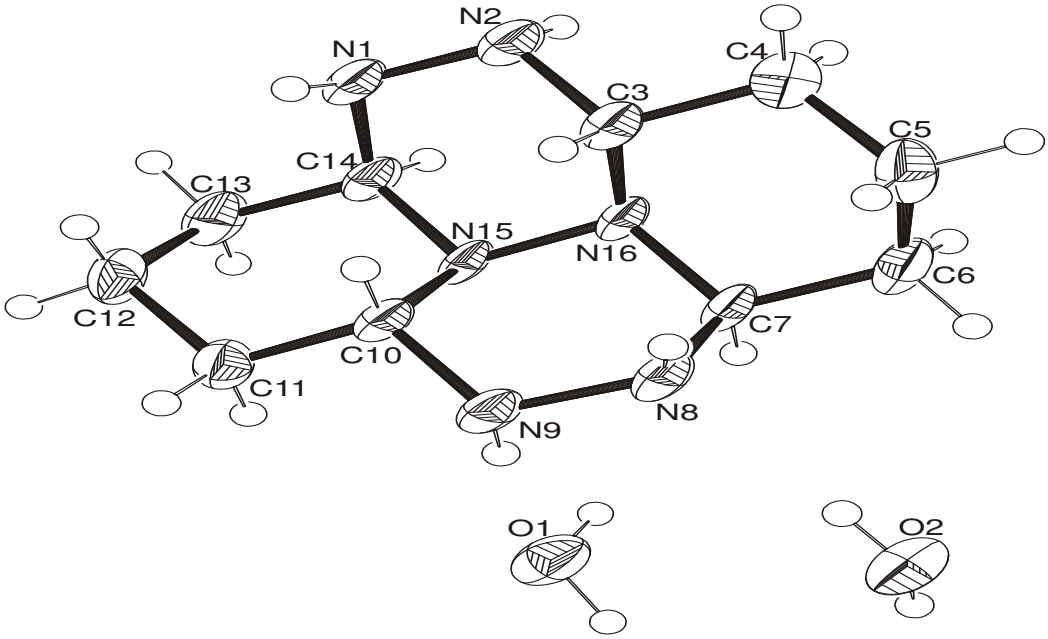


Fig. 1: A computer generated drawing of the molecule 3

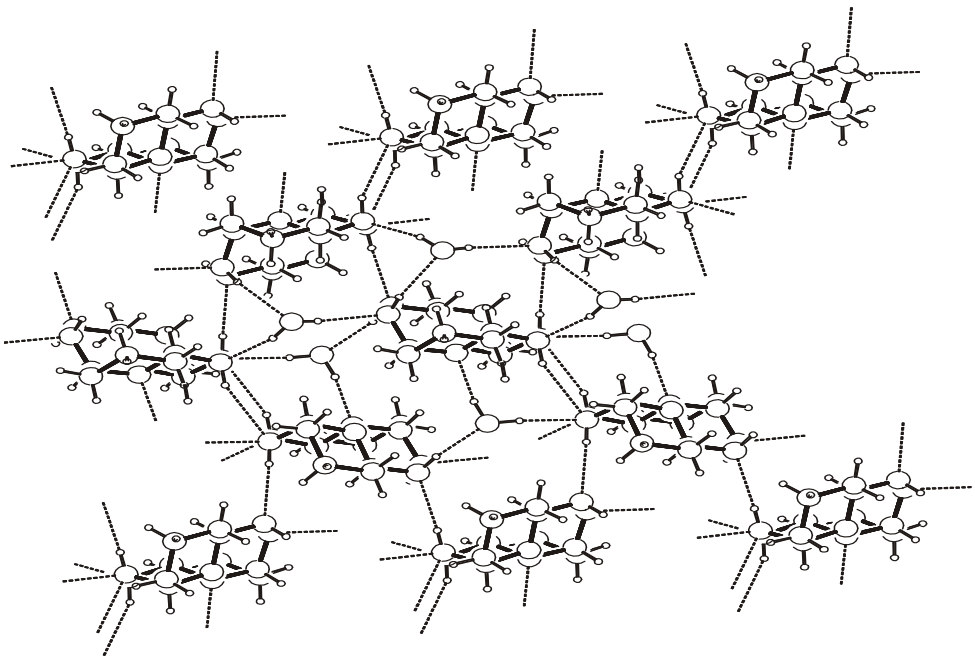


Fig. 2: Dashed lines in the packing of the molecules 3.

Conclusions

We obtained a new polyheterocycles structure tetradecahydro-4, 5, 9, 10, 10b, 10c-hexaazapyrene derived from hydrazine and glutaraldehyde. The ^{1}HNMR, ^{13}CNMR, elemental analysis and mass spectrum were done successfully to determine the structure. The structure of this compound was confirmed by X-ray crystallography and it was shown to have a symmetry axis.

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

Comp.	m.p./ ºC	Yield %	M.F	Found, (%)			Calculated, (%)		
٣	204–205	31 (colorless crystals)	$C_{10}H_{24}N_6O_2$	46.4	9.25	32.8	46.14	9.28	32.28

Table 2: Mass spectra of compounds 3.

Comp.	m/z (I_{rel} (%))
3	224 (35), 193 (98), 135 (76), 123 (75), 112 (16), 97 (100), 56 (86).

Table 3: ^{1}HNMR spectrum (Chem. Shift , ppm) in $CDCl_3$ solvent of compounds 3.

Comp.	CH_2	CH	NH
3	1.4, 1.85 (2s, 12H)	1.95 (s, 4H)	4.4 (s, 4H)

Table 4: ^{13}CNMR spectrum (Chem. Shift , ppm) in $CDCl_3$ solvent of compounds 3.

Comp.	(C-1,3,6,8)	(C-2,7)	(C-3a,5a,8a,10a)
3	25.83 , 24.91	14.9	70.24 , 58.22

X-ray diffraction analysis. Crystallographic parameters and a summary of data collection for structure 3 are given in (**Table 5-7**). 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 (Uiso=0.082). The calculations were performed with the SHELXS-97 [18] and SHELXS-97 programs [19].

Table 5: Crystallographic parameters of structure 3 and a summary of data collection.

Parameter	Value
Molecular formula	$C_{10}H_{24}N_6O_2$
Molecular weight	260.35
Crystal system	Monoclinic
Space group	*P* $2_1/c$
Unit cell parameters	
a, Å	9.5380(17)
b, Å	16.2113(17)
c, Å	9.186(3)
α, deg.	90
β, deg.	114.74(3)
γ, deg.	90.00
V, Å^3	1290.0(6)
Z	4
ρ calc., g /cm^{-3}	1.341
Temperature/K	٢٩٨
Diffractometer	Enraf—Nonius CAD4
Radiation (λ /Å)	Cuk\a
μ(K_α), mm^{-1}	0.794
Crystal size/mm	0.24 X 0.22 X 0.20
θ/deg	0.005
R_{wp}	0.0880
R_{exp}	0.0757
R_p	0.0847
χ^2	0.935

Table 6: Bond lengths *d* (A°) in structure 3

bond	d	bond	d
N1 – N2	1.442(2)	C3 – H3	0.9800
N1 – C14	1.476(3)	C4 – C5	1.533(3)
N1 – H1	0.88(2)	C4 – H4A	0.9700
N2 – C3	1.460(2)	C4 – H4B	0.9700
N2 – H2	0.906(18)	C5 – C6	1.520(3)
C3 – N16	1.487(3)	C5 – H5A	0.9700
C3 – C4	1.504(3)	C5 – H5B	0.9700
C6 – C7	1.518(3)	C11 – H11B	0.9700
C6 – H6A	0.9700	C12 – C13	1.526(3)
C6 – H6B	0.9700	C12 – H12A	0.9700
C7 – N8	1.469(2)	C12 – H12B	0.9700
C7 – N16	1.472(2)	C13 – C14	1.509(3)
C7 – H7	0.9800	C13 – H13A	0.9700
N8 – N9	1.449(2)	C13 – H13B	0.9700
N8 – H8	0.87(2)	C14 – N15	1.460(2)
N9 – C10	1.466(2)	C14 – H14	0.9800
N9 – H9	0.92(2)	N15 – N16	1.454(2)
C10 – N15	1.482(2)	O1 – H1A	0.96(4)
C10 – C11	1.506(3)	O1 – H1B	0.94(3)
C10 – H10	0.9800	O2 – H2A	0.92(4)
C11 – C12	1.528(3)	O2 – H2	0.80(3)
C11 – H11A	0.9700		

Table 7: Valency corners ω (degree) in structure 3

Corner	ω	Corner	ω
N2-N1-C14	111.97(15)	H4A-C4-H4B	108.1
N2-N1-H1	106.3(14)	C6-C5-C4	109.97(19)
C14-N1-H1	112.9(14)	C6-C5-H5A	109.7
N1-N2-C3	113.06(16)	C4-C5-H5A	109.7
N1-N2-H2	103.3(12)	C6-C5-H5B	109.7
C3-N2-H2	107.7(11)	C4-C5-H5B	109.7
N2-C3-N16	109.15(16)	H5A-C5-H5B	108.2
N2-C3-C4	109.59(18)	C7-C6-C5	112.86(17)
N16-C3-C4	110.43(16)	C7-C6-H6A	109.0
N2-C3-H3	109.2	C5-C6-H6A	109.0
N16-C3-H3	109.2	C7-C6-H6B	109.0
C4-C3-H3	109.2	C5-C6-H6B	109.0
C3-C4-C5	110.75(19)	H6A-C6-H6B	107.8
C3-C4-H4A	109.5	N8-C7-N16	114.25(14)
C5-C4-H4A	109.5	N8-C7-C6	110.63(16)
C3-C4-H4B	109.5	N16-C7-C6	109.80(17)
C5-C4-H4B	109.5	N8-C7-H7	107.3
N16-C7-H7	107.3	C13-C12-H12A	109.8
C6-C7-H7	107.3	C11-C12-H12A	109.8
N9-N8-C7	112.92(15)	C13-C12-H12B	109.8
N9-N8-H8	108.5(16)	C11-C12-H12B	109.8
C7-N8-H8	114.6(16)	H12A-C12-H12B	108.2
N8-N9-C10	112.82(16)	C14-C13-C12	112.65(17)
N8-N9-H9	104.2(14)	C14-C13-H13A	109.1
C10-N9-H9	105.4(14)	C12-C13-H13A	109.1
N9-C10-N15	110.56(14)	C14-C13-H13B	109.1
N9-C10-C11	109.39(17)	C12-C13-H13B	109.1
N15-C10-C11	109.07(15)	H13A-C13-H13B	107.8
N9-C10-H10	109.3	N15-C14-N1	114.61(16)
N15-C10-H10	109.3	N15-C14-C13	110.70(17)
C11-C10-H10	109.3	N1-C14-C13	111.53(16)
C10-C11-C12	111.41(18)	N15-C14-H14	106.5
C10-C11-H11A	109.3	N1-C14-H14	106.5

C12-C11-H11A	109.3	C13-C14-H14	106.5
C10-C11-H11B	109.3	N16-N15-C14	107.76(15)
C12-C11-H11B	109.3	N16-N15-C10	112.38(13)
H11A-C11-H11B	108.0	C14-N15-C10	114.55(14)
C13-C12-C11	109.38(17)	N15-N16-C7	107.48(15)
N15-N16-C7	107.48(15)	H1A-O1-H1B	105(2)
C7-N16-C3	114.91(15)	H2A-O2-H2B	116(3)

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