Reaction of 1, 1′, 2, 2′-Tetrakis (phenylamino) Ethane with Glyoxal; Synthesis of \( N^2, N^3, N^7, N^8, 1, 4, 5, 6, 9, 10 \)-Decaphenyltetradecahydro-dipyrazino [2, 3-b: 2, 3-e] Pyrazine-2, 3, 7, 8-Tetraamine and 5, 6-bis (ethoxy) -N\(^2, N^3\), 1, 4-Tetraphenylhexahydro -2, 3- Pyrazinediamine

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**ABSTRACT:** Compound \( N^2, N^3, N^7, N^8, 1, 4, 5, 6, 9, 10 \)-decaphenyltetradecahydrodipyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine (4) was prepared by condensation of 1, 1′, 2, 2′-tetrakis (phenylamino) ethane (1d) and glyoxal in EtOH or i-PrOH. Also, reaction of 1d with glyoxal in equimolar ethylene glycol in EtOH resulted \( 5, 6 \)-bis (ethoxy)-\( N^2, N^3\), 1, 4-tetraphenylhexahydro-2, 3-pyrazinediamine (5). The nature of products are sensitive to acidity, temperature and solvent. In acidic media, 4 and 5 are unstable and degraded to diimine 6.

**KEY WORDS:** Polyazapolycyclic, Hexabenzyl-hexaaza-isowortzitane, Tetraazabicyclo [3, 3, 0] octane, 1,1′, 2, 2′-tetrakis (phenylamino) ethane, \( N^2, N^3, N^7, N^8\), 1, 4, 5, 6, 9, 10-decaphenyltetradecahydro-pyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine, 5, 6-bis (ethoxy)-\( N^2, N^3\), 1, 4-tetraphenylhexa-hydro -2, 3-pyrazinediamine.

**INTRODUCTION**
Polyazapolycyclic compounds are used as initial substance for preparation of high-density, high-energy materials. These compounds are obtained by condensation of aldehydes or ketones and amines [1-10]. Also, 1,1′, 2, 2′-tetrakis substituted ethane (1) were obtained by reaction of amines and glyoxal [11]. Different substituted aryl amines and alkyl amines of tetraazabicyclo[3. 3. 0] octane (2a-e) have been synthesized by direct condensation of 1 with formaldehyde [12-18]. Furthermore, hexabenzyl - hexaaza - isowortzitane (3e) is initial substance for preparation of hexanitro-hexaazaisowortzitane (Cl\(_{20}\)), which is a most energetic compound. This molecule was obtained by reaction of 1,1′, 2, 2′-tetrakis (benzyl amino) ethane (1e) and glyoxal.

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EXPERIMENTAL

All commercially available chemical reagents were used without purification. Melting points were determined with an Electro thermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu 4300 spectrometer. NMR spectra were recorded with a Brucker 80 instrument. Mass analyses of the products were conducted with a Finnigan-Matt 8430 GC-Mass instrument. Elemental analysis was carried out with a C, H, N, O Rapid-Heraeus apparatus.

Synthesis of $N_2, N_3, N_7, N_8, 1, 4, 5, 6, 9, 10$-Decaphenyltetradecahydrodipyrazino [2, 3-b: 2, 3-e] Pyrazine-2, 3, 7, 8-Tetraamine (4)

To a solution of 2.46 gr (6 mmol) of 1,1’, 2, 2’-tetrakis (phenyl amino) ethane in 20 ml i-PrOH at 0 °C, 0.435 gr glyoxal (40% aqueous solution, 3 mmol) was added drop wise. The solution was stirred at 0-5 °C for 5 h. The precipitate was filtered and washed with cold EtOH to give, 2.88 gr (45.3% yield) of 4, mp 157.5-158 °C. IR (KBr) cm$^{-1}$; 3384(NH). M/z=1018(M$^+$). Elemental analysis, C$_{68}$H$_{62}$N$_{10}$, calculated: C, 80.15; H, 6.09; N, 13.75, found: C, 80.24; H, 6.30; N, 13.17. $^1$H-NMR (CDCl$_3$) $\delta$: 6.63-7.49(m, 50H, CH Ar), 3.38-3.49 (m, 4H, CH$_2$). By addition of D$_2$O to the NMR sample, the NH signal disappeared and doublet CH protons quickly collapsed into a singlet at $\delta$ 5.01. $^{13}$C-NMR (CDCl$_3$) $\delta$: 145.40, 144.95, 144.27, 130.29, 122.71, 119.83, 119.36, 117.99, 114.33, 113.97, 76.64 (CH), 73.06 (CH). The 4 was obtained in EtOH under similar condition. Recrystallization of 4 in the hot i-ProH leads to 6. But, recrystallization from EtOH gives 1.97 gr of a precipitate of 5,6-bis (ethoxy) $N_2, N_3$, 1, 4-tetraphenylhexahydro-2, 3-pyrazinediamine (5) mp 188-189 ºC. IR (KBr) cm$^{-1}$; 3397 (NH), M/z = 508 (M$^+$). Elemental analysis, C$_{32}$H$_{36}$N$_{4}$O$_{2}$, calculated: C, 75.59; H, 7.08; N, 11.02, found: C, 75.60; H, 7.05; N, 11.09. $^1$H-NMR (CDCl$_3$) $\delta$: 6.69-7.37(m, 20H, CHAr), 5.19 (s, 2H, CH), 5.19-5.30 (d, 2H, J=10.6 Hz, CH), 5.50-5.63 (d, 2H, J=10.6 Hz, NH), 2.98-3.66 (ABq, 4H, J=7.0 Hz, CH$_2$) 1.01-1.18 (t, 6H, J=7.0 Hz, CH$_3$). By addition of D$_2$O to the NMR sample, the NH signal disappeared and doublet CH protons quickly collapsed into a singlet at $\delta$ 5.24. $^{13}$C-NMR (CDCl$_3$) $\delta$: 146.31, 144.87, 130.21, 130.68, 119.61, 114.42, 114.01, 85.71 (CH), 71.59 (CH), 61.87 (CH$_2$), and 14.53 (CH$_3$).

Synthesis of 5, 6-bis (ethoxy)-$N_2, N_3$, 1, 4-Tetraphenylhexahydro-2, 3-Pyrazinediamine (5)

To a solution of 2.46 gr (6 mmol) of 1,1’, 2, 2’-tetrakis (phenyl amino) ethane in 20 ml EtOH at 0-5 °C, 0.87 gr glyoxal (40% aqueous solution, 6 mmol) was added drop wise. The solution was stirred at room temperature for 72 h. The precipitate was filtered and washed with cold EtOH to give, 2.13 gr (67% yield) of 5, mp 180-187 °C. Recrystallization from EtOH gave a white precipitate of 5, mp 188.5-189 ºC, with general properties (IR, NMR) identical with the product 5 discussed above.
RESULTS AND DISCUSSION

Condensation of 1,1', 2, 2'-tetrakis (phenyl amino) ethane (1d) with glyoxal in EtOH (or i-PrOH) produced N2, N3, N7, N8, 1, 4, 5, 6, 9, 10-decaphenylertridecahydrodi-pyrazino [2, 3-b: 2, 3-e] pyrazine-2, 3, 7, 8-tetraamine (4). Also, reaction of 1d with glyoxal in equimolare of reactant in EtOH resulted in 5, 6-bis (ethoxy) N2, N3, 1, 4-tetraphenylhexahydro-2, 3-pyrazinediamine (5).

In addition, compound 5 can be obtained by recrystallization of compound 4 in EtOH. The conditions of these reaction were studied. It was found that, the nature of products is sensitive to acidity, temperature and solvent. Increasing the temperature reduces the yield of 4 and 5, but results in production to compound 6 (above 30 °C, the final product is only the compound 6).

The compound 5 is stable at room temperature; while 4 is degraded to 6 during 3 days. As was mentioned, so at pH = 5 product 4, decomposes to 6 in few minutes. In contrasted the compound 5 is more stable and decomposes in 48 h. This data show that, the compound 5 is thermo daynimal stable product. The mechanisms of formation and decomposition of polyazapolycyclic amine compounds has been studied [11, 14, 16-18]. It should be noted, that we could not produce the compound 3d from proper reactance.

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