BRANCHED POLYCYCLIC TETRAZOLE SYSTEMS. 1. SYNTHESIS AND STRUCTURE OF 2-(5-TETRAZOLYL)ETHYL DERIVATIVES OF SOME CH-, OH-, AND NH-ACIDS^{*}

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The cycloaddition of dimethylammonium azide to the nitrile groups of 2-cyanoethyl derivatives of CH-, OH-, and NH-acids leads to open-chain branched structures containing terminal NH-tetrazolyl groups. An x-ray diffraction structural analysis of tris[2-(5-tetrazolyl)ethyl]nitromethane revealed steric access of the equivalent NH-tetrazolyl rings of the branched system. In going from the branched nitrile substrates to the corresponding tetrazoles, the PMR spectra show a breakdown in the resolution of the multiplet components, which had not been observed previously for monocyclic 5-substituted tetrazoles. A dependence was found for the ${}^{13}C$ NMR chemical shifts on the pK_a values, reflecting the NH-acidity of the branched polycyclic tetrazoles in water.

Open-chain branched structures having terminal azolyl groups hold promise as polydentate, nonselective ligands for binding heavy metal ions to give stable complexes [1]. Potvin [2] and Hartshorn [3] have reported the synthesis of such compounds containing imidazolyl and pyrazolyl rings at the ends of the branches. However, podands containing terminal NH-tetrazolyl fragments have not yet been obtained. On the other hand, it is precisely tetrazole-containing polydentate ligands capable of eliminating NH-protons to give quasiaromatic tetrazolates, which hold greatest interest [4, 5].

We propose a simple, general approach for the synthesis of branched polycyclic NH-tetrazole systems based on the cycloaddition of alkylammonium azides to the corresponding nitriles [6, 7].

The branched polynitrile substrates were obtained by the "cyanoethylation" reaction [8-11], which is a special case of the Michael reaction. Various CH-, OH-, and NH-acids enter this reaction. The 2-cyanoethyl derivatives obtained form a wide variety of substrates for the synthesis of 2-(5-tetrazolyl)ethyl derivatives. Nitromethane, diethyl malonate, cyclohexanone, water, and 4-amino-1,2,4-tetrazole were examined as compounds containing labile hydrogen atoms. The cyanoethylation of these substrates was carried out according to modified methods [12-16]. The physicochemical and spectra indices of branched nitriles la-le correspond to the literature values.

The transition state of the reaction of nitriles with alkylammonium azides involving 1,3-dipolar cycloaddition has rigid steric requirements. However, prolonged heating in high-boiling aprotic dipolar solvents is required and, in some cases, high pressure is necessary [6, 7].

Assuming adequate steric access of the nitrile groups and taking account of the leveling effect of the CH_2CH_2 bridge relative to the electronic effect of the substituent on the nitrile group, nitriles Ia-Ie were converted into tetrazoles IIa-IIe according to the general procedure (see Experimental). The conditions for the cycloaddition of alkylammonium azides to unbranched nitriles were taken as standard. Our kinetic data [6] served as the basis for selecting the reaction temperature and duration. Dimethylammonium azide generated *in situ* by the exchange reaction of the hydrochloride salt of dimethylamine and sodium azide in DMF was used as the 1,3-dipole. This general procedure was used to obtain previously unreported branched polycyclic tetrazoles in 50-70% yield: tris[2-(5-tetrazolyl)ethyl]nitromethane (IIa), diethyl ester of bis[2-(5-tetrazolyl)ethyl]malonic acid (IIb), 2,2,6,6-tetrakis[2-(5-tetrazolyl)ethyl]cyclohexanone (IIc), 2,2'-di(5-tetrazolyl)diethyl ether (IId), and 4-bis[2-(5-tetrazolyl)ethyl]amino-1,2,4-triazole (IIe).

*Dedicated to the memory of I. N. Goncharova.

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The coordinates and temperature parameters of the atoms in the structure of IIa obtained in an x-ray diffraction structural analysis are given in Table 1. A stereoscopic view of tris[2-(5-tetrazolyl)ethyl]nitromethane (IIa) and the numbering of the atoms are given in Fig. 1. The tetrazole rings and aliphatic chains connecting them to the nitro group are indicated 1, 2, and 3 with increasing indices of the carbon and nitrogen atoms. Despite the insufficient precision in the determination of this crystal structure (~ 0.022 Å and 1.4°), the major stereochemical and conformational features are rather clear. Figure 1 shows that tris[2-(5-tetrazolyl)ethyl]nitromethane (IIa) in the crystal is pincer-shaped. The major torsion angles determining its conformation are given in Table 2. The tetrazole rings are planar; the mean square deviations of the atoms from the mean square planes are 0.002 Å for ring 1, 0.014 Å for ring 2, and 0.017 Å for ring 3. The carbon atoms of the aliphatic chains connecting tetrazole rings 1 and 2 ($C_{(1)}$, $C_{(2)}$, $C_{(20)}$, $C_{(4)}$, and $C_{(5)}$) lie in a single plane within ± 0.02 Å to form an extended chain. The mean square plane through atoms $C_{(3)}$, $N_{(1)}$, $N_{(2)}$, $N_{(3)}$, and $N_{(4)}$ of tetrazole ring 1 forms an angle of 30° with the plane of this ring, while the plane of tetrazole ring 2 ($C_{(6)}$, $N_{(5)}$, $N_{(6)}$, $N_{(7)}$, and $N_{(8)}$) is twisted relative to the plane of the aliphatic chain by 37.1°. The tetrazole rings themselves are in trans orientation relative to the aliphatic chain, i.e., their $N_{(1)}$ - H and $N_{(8)}$ - H bonds are twisted by 180°. The third aliphatic chain ($C_{(20)}$, $C_{(7)}$, and $C_{(8)}$) is twisted by 87.4° relative to the plane of the aliphatic chain of tetrazole rings 1 and 2. The mean square plane of tetrazole ring 3 (C₍₉₎, N₍₉₎, N₍₁₀₎, N₍₁₁₎, and $N_{(12)}$) forms an angle of 113.0° with the plane of its aliphatic chain. The nitro group is at an angle of 107.3° relative to the plane of the aliphatic chain attached to tetrazole rings 1 and 2 and at an angle of 31.5° relative to the plane of ring 3.

Table 3 gives the values of the equivalent bond lengths averaged over the three tetrazole rings and the attached aliphatic chains. As expected in light of conjugation with the tetrazole rings, we found shortened bonds such as $C_{(2)} - C_{(3)}$ (1.48 Å) in comparison with the length of the ordinary C-C single bond (1.541 Å) [17].

The tris[2-(5-tetrazolyl)ethyl]nitromethane molecules are connected to each other in the crystal structure through a three-dimensional N-H…N network of intermolecular hydrogen bonds. Each molecule of IIa participates in six hydrogen bonds, acting as the donor in three hydrogen bonds and acceptor in three bonds $(N_{(1)}(x, y, z) - H \dots N_{(5)}(2-x, y-0.5, 0.5-z) = 2.86 \text{ Å}; N_{(8)}(x, y, z) - H \dots N_{(10)}(x-0.5, 1.5-y, -z) = 2.90 \text{ Å}; N_{(12)}(x, y, z) - H \dots N_{(4)}(x, y+1, z) = 2.78 \text{ Å}).$

In light of the conformational mobility of tris[2-(5-tetrazolyl)ethyl]nitromethane IIa relative to the C-C single bonds, the crystal packing and, in particular, the asymmetric arrangement of the intermolecular hydrogen bonds relative to the tetrazole rings probably have a significant effect on the overall molecular conformation in the crystal.

The branched polycyclic tetrazole compounds obtained have common characteristic infrared bands at 3100-3000 cm⁻¹ related to the stretching vibrations of the NH group and characteristic bands belonging to stretching and deformation bands of the tetrazole ring [18] (see Experimental).

The signal for the nitrile carbon in the ¹³C NMR spectrum at 119-120 ppm disappears upon replacing the nitrile group by the 5-tetrazolyl group and a signal for the tetrazole ring carbon appears at 154-156 ppm. The tetrazole ring is a stronger electron-withdrawing group than the nitrile group [19], which leads to a downfield shift of all the other carbon atom signals.

The PMR spectra of tetrazoles IIa-IIe have a specific feature relative to the spectra of the starting nitriles (Fig. 2). A decrease in the spin-spin coupling constants occurs upon replacing the nitrile group by a 5-tetrazolyl group and all the classically split multiplets are transformed into poorly resolved broadened signals. This behavior results from the effect of the tetrazole rings on the molecular geometry as a whole. Elucidation of this effect requires further study.

Tetrazoles IIa-IIe are polyhydric NH-acids. A potentiometric titration study showed that the pK_a values of these compounds lie at 4.3-4.9. A correlation has been found for monocyclic 5-tetrazolyl substituents between the ¹³C NMR chemical shifts and the pK_a values reflecting the NH-acidity of the tetrazoles [20]. A similar trend has been found for branched polycyclic tetrazoles in water (Fig. 4). An exception is found for 2.2,6,6-tetrakis[2-(5-tetrazolyl)ethyl]cyclohexanone (IIc).

Atom	x	у	2	U
00	5575(23)	1578(14)	1464(5)	80(5)
O(2)	4556(25)	3101(14)	882(5)	80(5)
N(13)	5769(27)	2649(16)	1194(6)	48(5)
C(20)	7917(25)	3350(17)	1233(7)	23(5)
Cm	9462(28)	2276(16)	1416(7)	37(5)
C(2)	10009(28)	1106(16)	997(7)	36(6)
C(3)	10745(27)	-155(18)	1278(7)	34(5)
N(I)	11614(20)	-257(14)	1762(5)	34(5)
N(2)	12016(23)	-1657(16)	1891(6)	54(5)
N(3)	11362(25)	-2371(16)	1466(7)	53(5)
N(4)	10586(22)	-1458(15)	1082(5)	44(5)
C(4)	7720(29)	4459(17)	1686(7)	41 (6)
Co	6158(27)	5629(17)	1610(7)	41 (6)
C(6)	6598(22)	6841(19)	1975(7)	32(6)
N(5)	7133(21)	6828(16)	2470(7)	44(5)
N(6)	7367(23)	8231(18)	2636(6)	60(5)
N(7)	6886(22)	9046(16)	2236(7)	58(5)
N(8)	6479(20)	8223(16)	1813(6)	39(5)
C(7)	8282(26)	3994(18)	662(8)	47(6)
C(8)	10345(29)	4757(17)	644(7)	44(6)
C(9)	10427 (29)	5608(17)	142(7)	34(5)
N(9)	10602(25)	5147(14)	-366(6)	48(5)
N(10)	10509(23)	6330(15)	-681 (6)	57(5)
N(11)	10441(27)	7471(14)	-396(6)	57(5)
N(12)	10389(23)	7006(13)	126(5)	38(4)

TABLE 1. Atomic Coordinates ($\times10^4)$ and Temperature Factors (Å $^2\times10^3)$ in the Structure of Tristetrazole IIa

TABLE 2. Major Torsion Angles in Tristetrazole IIa

Angle	ω (deg)	Angle	ω (deg)
$C_{(20)} - C_{(1)} - C_{(2)} - C_{(3)}$	-155,0	$N_{(5)} - N_{(6)} - N_{(7)} - N_{(8)}$	-3,9
$C_{(1)} - C_{(20)} - C_{(4)} - C_{(5)}$	-177,0	$N_{(6)} - N_{(7)} - N_{(8)} - C_{(6)}$	4,0
$C_{(1)} - C_{(20)} - C_{(7)} - C_{(8)}$	-59,9	$N_{(7)} - N_{(8)} - C_{(6)} - N_{(5)}$	-2,5
$C_{(1)} - C_{(2)} - C_{(3)} - N_{(1)}$	-25,4	$N_{(8)} - C_{(6)} - N_{(5)} - N_{(6)}$	0,1
$C_{(1)}-C_{(2)}-C_{(3)}-N_{(4)}$	152,5	$O_{(1)} - N_{(13)} - C_{(20)} - C_{(7)}$	146,3
$C_{(3)} - N_{(1)} - N_{(2)} - N_{(3)}$	0,2	$O_{(2)} - N_{(13)} - C_{(20)} - C_{(1)}$	-152,0
N(1)-N(2)-N(3)-N(4)	0,3	$C_{(20)} - C_{(7)} - C_{(8)} - C_{(9)}$	-167.7
$N_{(2)} - N_{(3)} - N_{(4)} - C_{(3)}$	-0,7	$C_{(7)} - C_{(20)} - C_{(1)} - C_{(2)}$	-47.6
$N_{(3)} - N_{(4)} - C_{(3)} - N_{(1)}$	0,8	$C_{(7)} - C_{(20)} - C_{(4)} - C_{(5)}$	53,9
$N_{(4)}-C_{(3)}-N_{(1)}-N_{(2)}$	-0,6	$C_{(7)} - C_{(8)} - C_{(9)} - N_{(9)}$	-71,3
$O_{(1)} - N_{(13)} - C_{(20)} - C_{(1)}$	21,6	$C_{(7)} - C_{(8)} - C_{(9)} - N_{(12)}$	110,5
$O_{(1)} - N_{(13)} - C_{(20)} - C_{(4)}$	-93,6	$C_{(9)} - N_{(9)} - N_{(10)} - N_{(11)}$	4,7
$C_{(20)} - C_{(4)} - C_{(5)} - C_{(6)}$	-161,5	N(9) - N(10) - N(11) - N(12)	-2,9
$C_{(4)} - C_{(20)} - C_{(1)} - C_{(2)}$	-175,8	$N_{(10)} - N_{(11)} - N_{(12)} - C_{(9)}$	0,0
$C_{(4)} - C_{(20)} - C_{(7)} - C_{(8)}$	64,9	$N_{(11)} - N_{(12)} - C_{(9)} - N_{(9)}$	2,9
$C_{(4)} - C_{(5)} - C_{(6)} - N_{(5)}$	-42,6	$N_{(12)}-C_{(9)}-N_{(9)}-N_{(10)}$	-4,5
$C_{(4)} - C_{(5)} - C_{(6)} - N_{(8)}$	137,1	$O_{(2)} - N_{(13)} - C_{(20)} - C_{(4)}$	92,8
$C_{(6)} - N_{(5)} - N_{(6)} - N_{(7)}$	2,4	$O_{(2)}-N_{(13)}-C_{(20)}-C_{(7)}$	-27,3

Thus, analysis of the three-dimensional structure and physicochemical properties of the polycyclic NH-tetrazoles synthesized suggests promise for these compounds as polydentate ligands for binding metal ions to give stable complexes.

EXPERIMENTAL

The ¹H and ¹³C NMR spectra were taken on a Bruker AC-200 spectrometer at 200 and 50.3 MHz, respectively, in DMSO-d₆ solution. The IR spectra were taken on a Specord M-80 spectrometer for KBr pellets. The acidity of the compounds



Fig. 1. Stereoscopic views of tris[2-(5-tetrazolyl)ethyl]nitromethane IIa. The oxygen, nitrogen, and carbon atoms are given by spheres whose radii are proportional to the thermal vibration parameters.



Fig. 2. Methylene group signals in the PMR spectra of tris(2-cyanoethyl)nitromethane Ia and tris[2-(5-tetrazolyl)-ethyl]nitromethane IIa.

studied was determined by potentiometric titration. The crystallographic calculations were carried out using the SHELXTL-81 programs.

Tris(2-cyanoethyl)nitromethane (Ia). A sample of 30.42 g (574 mmoles) acrylonitrile was added dropwise to a cooled mixture of 10 g (0.5 mmole) benzyltriethylammonium chloride and 0.02 g (0.5 mmole) NaOH in 50 ml 1,4-dioxane and 2 ml water at a rate such that the temperature of the reaction solution did not exceed 40-45 °C. The reaction solution was maintained at room temperature for 2 h and neutralized by adding dilute hydrochloric acid. The crystalline precipitate was then filtered off, washed with water, and dried to give 23.8 g (66%) trinitrile Ia as colorless needles with mp 114 °C (from ethanol). PMR spectrum: 2.29 (6H, t, J = 8.1 Hz, $CH_2C \equiv N$), 2.61 ppm (6H, t, J = 8.1 Hz, $CH_2C \equiv N$). ¹³C NMR spectrum: 119.5 ($C \equiv N$), 91.1 ($C - NO_2$), 29.4 ($CH_2CH_2C \equiv N$), 11.6 ppm ($CH_2C \equiv N$). IR spectrum: 2240 ($C \equiv N$), 1550, 1344 cm⁻¹ (NO_2). Found: C, 54.90; H, 5.84; N, 25.55%. Calculated for $C_{10}H_{12}N_4O_2$: C, 54.53; H, 5.49; N, 25.44%.

Attention: The rapid addition of acrylonitrile may lead to strong overheating and spillover of the reaction mixture due to the high exothermicity of the cyanoethylation reaction.

TABLE 3. Bond Lengths in Tristetrazole IIa Averaged Over the Three Equivalent Fragments

Bond	1 (Å)	Bond	1 (Å)	Bond	I (Å)
$C_{(20)}-C_{(1)}$ $C_{(1)}-C_{(2)}$ $C_{(2)}-C_{(3)}$	1,53(2) 1,55(2) 1,48(2)	$C_{(3)} - N_{(1)}$ $N_{(1)} - N_{(2)}$ $N_{(2)} - N_{(3)}$	1,34(2) 1,36(2) 1,30(2)	N(3)N(4) N(4)C(3)	1,38(2) 1,31(2)

TABLE 4. Correlation of ¹³C NMR Signals of the Tetrazole Carbon and the pK_a Values

Com- pound	¹³ C signal in tetra- zole ring	pKa	Com- pound	¹³ C signal in tetra- zole ring	pKa
IIa	155,1	4,37	ll d	154,0	4,75
Пb	155,4	4,35	11e	153,9	4,78
Пс	156,1	4,99			

Diethyl Ester of Bis(2-cyanoethyl)malonic Acid (Ib). A sample of 13.25 g (250 mmoles) acrylonitrile was added dropwise to a cooled mixture of 16 g (100 mmoles) diethyl malonate, 0.1 g (0.5 mmole) benzyltriethylammonium chloride, and 0.02 g (0.5 mmoles) NaOH in 50 ml 1,4-dioxane and 2 ml water at a rate such that the temperature of the reaction mixture did not exceed 40-45°C. The reaction mixture was maintained at room temperature for 2 h, neutralized by adding dilute hydrochloric acid, and poured into 200 ml water cooled to 5°C. The water-insoluble oily liquid gradually crystallized to give colorless cubes, which were filtered off, washed with water, and dried to give 23.64 g (89%) dinitrile Ib. Needle crystals with mp 61-62°C were obtained from ethanol. PMR spectrum: 1.19 (6H, t, J = 7.3 Hz, CH₂C = N), 2.49 (4H, t, J = 7.3 Hz, CH₂CH₂C = N), 4.17 ppm (4H, q, J = 7.3 Hz, CH₂ in OEt). ¹³C NMR spectrum: 169.1 (C=O), 119.7 (C = N), 61.8 (CH₂ in OEt), 55.2 (C_{quat}), 27.6 (CH₂CH₂C = N), 13.7 (CH₂C = N), 12.1 ppm (CH₃ in OEt). IR spectrum: 2240 (C = N), 1740, 1720, 1690 (CO₂), 1465, 1445 (CH₂), 1370, 1275, 1200, 1180, 1100, 1025, 865 cm⁻¹. Found: C, 58.34; H, 7.12; N, 10.47%. Calculated for C₁₃H₁₈N₂O₄: C, 58.64; H, 6.81; N, 10.51%.

2,2,6,6-Tetrakis(2-cyanoethyl)cyclohexanone (Ic). A sample of 26.5 ml acrylonitrile was added dropwise to a cooled mixture of 9.8 g (100 ml) cyclohexanone, 0.1 g (0.5 mmole) benzyltriethylammonium chloride, and 0.02 g (0.05 mmole) NaOH in 40 ml tertiary-butyl alcohol and 2 ml water at a rate such that the temperature of the reaction mixture did not exceed 40-45°C. The reaction mixture was maintained at room temperature for 2 h and neutralized by adding dilute hydrochloric acid. The crystalline precipitate was filtered off, washed with water, and dried to give 25.76 g (81%) tetranitrile Ic as colorless crystals with mp 164-165°C (from acetone). PMR spectrum: 1.65 (6H, s, γ -CH₂ and 2 β -CH₂ in cyclohexanone), 1.85 (8H, m, J = 14.6 Hz, a- and e-CH₂CH₂C \equiv N), 2.33 ppm (8H, t, J = 14.6 Hz, CH₂C \equiv N), 1³C NMR spectrum: 214.9 (C=O), 120.7 (C \equiv N), 49.6 (C_{quat}), 31.6 (*m*-CH₂ in cyclohexanone), 30.8 (CH₂CH₂C \equiv N), 15.7 (γ -CH₂ in cyclohexanone), 11.6 ppm (CH₂C \equiv N). IR spectrum: 2450 (C \equiv N), 1720, 1675 (C=O), 1540, 1460 cm⁻¹. Found: C, 69.47; H, 7.36; N, 17.99%. Calculated for C₁₈H₂₂N₄O: C, 69.65; H, 7.14; N, 18.05%.

2,2'-Dicyanodiethyl Ether (Id). A mixture of 26.5 g (500 mmoles) acrylonitrile, 25 ml 1,4-dioxane, and 5 ml 10% aq. NaOH was stirred for 5 h at 45°C. The reaction mixture was neutralized by adding dilute hydrochloric acid and dioxane was distilled off on a rotary evaporator. The residue was distilled at 161-163°C (5 mm Hg) to give 13 g (40%) dinitrile Id. PMR spectrum: 2.70 (4H, t, J = 5.8 Hz, $CH_2C \equiv N$), 3.66 ppm (4H, t, J = 5.8 Hz, $CH_2CH_2C \equiv N$). ¹³C NMR spectrum: 118.9 (C = N), 65.2 (CH₂CH₂C = N), 18.2 ppm (CH₂C = N). IR spectrum: 2888 (CH₂), 2248 (C = N), 1484, 1416 (CH₂), 1260, 1228, 1120 cm⁻¹ (-O-). Found: C, 57.80; H, 6.71; N, 22.34%. Calculated for C₆H₈N₂O: C, 58.05; H, 6.50; N, 22.57%.

4-[Bis(2-cyanoethyl)amino]-1,2,4-triazole (Ie). A sample of 13.25 g (250 mmole) acrylonitrile was added to a cooled solution of 8.4 g (100 mmoles) 4-amino-1,2,4-triazole and 0.1 g NaOH in 8 ml water at a rate such that the temperature of the reaction mixture did not exceed 40-45°C. The suspension formed was filtered off and washed with ethanol to give 14.15 g (74%) dinitrile Ie as colorless needles with mp 175.5-176.0°C (from ethanol). PMR spectrum: 2.50 (4H, t, J = 6.2 Hz, $CH_2C \equiv N$), 3.40 (4H, t, J = 6.2 Hz, $CH_2CH_2C \equiv N$). 8.75 ppm (2H, s, triazole CH). ¹³C NMR spectrum: 142.1 (C-triazole), 118.6 (C \equiv N), 53.2 ($CH_2CH_2C \equiv N$), 15.8 ppm (CH₂C $\equiv N$). IR spectrum: 3110, 2950 (CH₂), 2270 (C $\equiv N$), 1500, 1420, 1280, 1170, 1140, 1070, 1010, 880, 670 cm⁻¹. Found: C, 50.71; H, 5.24; N, 44.50%. Calculated for C₈H₁₀N₆: C, 50.52; H, 5.30; N, 44.18%.

General Method for the Preparation of Tetrazoles IIa-IIe. A solution of 25 mmoles 2-cyanoethyl derivative, 10% equimolar excess of sodium azide and the hydrochloride salt of dimethylamine relative to each nitrile group of the substrate in 50 ml DMF was maintained for 15-20 h at 100-115°C. The sodium chloride precipitate was filtered off. The filtrate was evaporated, dissolved in 100 ml distilled water, and acidified to pH < 2 by adding dilute hydrochloric acid. The precipitate formed was filtered off, washed with distilled water, and crystallized from ethanol or ethanol – DMF.

Tris[2-(5-tetrazolyl)ethyl]nitromethane (IIa). The product yield was 5.25 g (60%), mp 211°C (dec., ethanol). PMR spectrum: 2.55 (6H, br.s, CH₂T), 2.96 (s, <u>CH₂CH₂T</u>), 15.83 ppm (3H, s, NH), T = 5-tetrazolyl. ¹³C NMR spectrum: 155.1 (C-tetrazole), 92.7 (C-NO₂), 32.0 (<u>CH₂CH₂T</u>), 17.9 ppm (CH₂T). IR spectrum: 3200-3000 (NH), 1584, 1352 (NO₂), 1432, 1240, 1108, 1048, 1024 cm⁻¹ (tetrazole). Found: C, 34.79; H, 4.19; N, 52.61%. Calculated for C₁₀H₁₅N₁₃O₂: C, 34.38; H, 4.33; N, 52.13%

Diethyl Ester of Bis[2-(5-tetrazolyl)ethyl]malonic Acid (IIb). The product yield was 4.50 g (51%), mp 184°C (dec., ethanol). PMR spectrum: 1.20 (6H, br.s, CH₃ in OEt), 2.30 (4H, br.s, CH₂T), 2.80 (4H, br.s, $\underline{CH_2CH_2T}$), 4.15 (4H, br.s, CH₂ in OEt), 15.9 ppm (2H, br.s, NH). ¹³C NMR spectrum: 170.1 (C=O), 155.4 (C-tetrazole), 61.6 (CH₂ in OEt), 56.1 (C_{quat}), 29.6 ($\underline{CH_2CH_2T}$), 18.3 (CH₂T), 13.9 ppm (CH₃ in OEt). IR spectrum: 3100-3000 (NH), 1720, 1648, 1552 (CO₂), 1444, 1240, 1192, 1088, 1048 cm⁻¹ (tetrazole). Found: C, 44.88; H, 6.16; N, 31.33%. Calculated for C₁₃H₂₀N₈O₄: C, 44.31; H, 5.72; N, 31.80%.

2,2,6,6-Tetrakis[2-(5-tetrazoly])ethyl]cyclohexanone (IIc). The product yield was 8.70 g (72%), mp 195°C (dec., ethanol – DMF). PMR spectrum: 1.80 (6H, br.s, γ -CH₂ and 2 β -CH₂ in cyclohexanone ring), 1.95 (8H, br.s, <u>CH₂CH₂T</u>), 2.75 (8H, br.s, CH₂T), 15.8 ppm (4H, br.s, NH). ¹³C NMR spectrum: 216.6 (C=O), 156.1 (C-tetrazole), 50.3 (C_{quat}), 33.9 (<u>CH₂CH₂T</u>), 32.6 (β -CH₂), 18.2 (CH₂T), 16.3 ppm (γ -CH₂). IR spectrum: 3200-3000 (NH), 1778, 1690, 1660 (C=O), 1574, 1490, 1448, 1376, 1250, 1072 cm⁻¹ (tetrazole). Found: C, 44.36; H, 5.77; N, 45.95%. Calculated for C₁₈H₂₆N₁₆O: C, 44.81; H, 5.43; N, 46.45%.

2,2'-Di(5-tetrazolyl)diethyl Ether (IId). The product yield was 2.75 g (52%), mp 198.5°C (dec., ethanol. PMR spectrum: 3.10 (4H, br.s, CH_2T), 3.75 (4H, br.s, CH_2CH_2T), 15.90 ppm (2H, br.s, NH). ¹³C NMR spectrum: 154.0 (C-tetrazole), 67.2 (CH_2CH_2T), 23.9 ppm (CH_2T). IR spectrum: 3200-3000 (NH), 1706, 1614, 1574, 1562, 1486, 1444, 1428, 1384, 1362, 1246, 1202, 1126, 1084, 1066, 1042 cm⁻¹ (tetrazole). Found: C, 34.70; H, 4.85; N, 53.60%. Calculated for $C_6H_{10}N_8O$: C, 34.28; H, 4.79; N, 53.31%.

4-Bis[2-(5-tetrazolyl)ethyl]amino-1,2,4-triazole (IIe). The product yield was 5.07 g (73%), mp 236°C (dec., ethanol – DMF). PMR spectrum: 2.85 (4H, br.s, CH_2T), 3.60 (4H, br.s, CH_2CH_2T), 8.75 (2H, s, triazole CH), 15.00 ppm (2H, br.s, NH). ¹³C NMR spectrum: 153.9 (C-tetrazole), 142.3 (C-triazole), 55.6 (CH_2CH_2T), 21.5 ppm (CH_2T). IR spectrum: 3100-3000 (NH), 1616, 1560, 1508, 1464, 1444, 1280, 1248, 1216, 1160, 1120, 1096, 1048, 1000, 920, 888, 664 cm⁻¹ (tetrazole and 1,2,4-triazole). Found: C, 35.10; H, 3.74; N, 61.02%. Calculated for $C_8H_{12}N_{12}$: C, 34.78; H, 4.38; N, 60.84%.

X-Ray Diffraction Structural Analysis of tris[2-(5-Tetrazolyl)ethyl]nitromethane (IIa). The crystals for the x-ray diffraction structural analysis were obtained as fine threads from a concentrated aqueous solution of tris[2-(5-tetrazolyl)-ethyl]nitromethane IIa by slow evaporation of the solvent at room temperature. Space group P2₁2₁2₁. Unit cell parameters: $a = 6.623(1), b = 9.459(1), c = 24.695(3); \alpha = \beta = \gamma = 90^{\circ}, V = 1547.1(0.6) Å^3, Z = 4$. The collection of the experimental data and determination of the unit cell parameters were carried out on a Nicolet P3 automatic diffractometer using $\theta/2\theta$ scanning and MoK_{α} radiation. The structure was solved by the direct method and refined by the full-matrix method of least squares isotropically for O, N, and C. The positions of the hydrogen atoms were determined from the Fourier difference maps. The final divergence factor R = 4.9% for 340 reflection with $I \ge 3\sigma(I)$. The relatively high R factor and small number of reflections were due to the imperfection and small size of the crystals (0.1 × 0.05 × 0.35 mm).

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