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SELECTIVE SYNTHESIS OF BINUCLEAR N-SUBSTITUTED TETRAZOLES AND TETRAZOLIUM SALTS

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The selective alkylation of mononuclear tetrazoles by 2,5-dimethyl-2,5-hexanediol and of N-unsubstituted binuclear tetrazoles by tert-butyl alcohol was realized in perchloric and sulfuric acids. A series of previously unknown N-substituted binuclear tetrazoles and tetrazolium salts were synthesized. Data from X-ray crystallographic analysis of 2,5-dimethyl-2,5-di(5-phenyl-2-tetrazolyl)hexane are presented.

Keywords: binuclear tetrazolium salts, binuclear tetrazoles, alkylation, quaternization, selectivity.

The increased interest in the chemistry of N-substituted tetrazoles and also in tetrazolium complexes and salts based on them is due to the successes in the application of N-substituted tetrazoles in medicine and technology, the extensive synthetic possibilities of tetrazolium salts, the presence of a series of valuable characteristics (low-temperature ferromagnetism, heat- and light-induced spin–spin transitions, etc.) in the complexes of transition metals with N-substituted tetrazoles [1-4]. Here the overwhelming majority of the publications have been devoted to the derivatives of mononuclear tetrazoles. The binuclear and polynuclear derivatives have been studied little, and this is due to a significant degree to difficulties in their synthesis. At the same time, in addition to the above-mentioned applications, they are promising as chelating agents [5, 6] and starting compounds for the construction of one-, two-, and three-dimensional metal-containing systems [6, 7].

The most universal and accessible method for the synthesis of bi- and polynuclear N-substituted tetrazoles and tetrazolium salts is based on the alkylation of N-unsubstituted derivatives and quaternization of polynuclear N-substituted tetrazoles respectively by monofunctional agents or of mononuclear tetrazoles by polyfunctional agents in alkaline and close to neutral media, including phase-transfer conditions [1-3, 8-13]. An important disadvantage of this method, considered the only method for preparation of 2-alkyl-substituted tetrazoles and 1,3,5-trisubstituted tetrazolium salts, is the formation of mixtures of isomeric products and the associated need to separate them, which cannot always be achieved in the case of binuclear tetrazoles (e.g., [3, 12]). Our recent investigations on the alkylation and quaternization of polynuclear tetrazoles by alcohols and olefins in acidic media showed that they are promising as an approach to the selective synthesis of both 2-substituted tetrazoles [4, 14-16] and 1,3- (1,3,5-) and 1,4-substituted tetrazolium salts [17, 18].

In development of these investigations and with the aim of developing an effective method for the synthesis of binuclear N-substituted tetrazoles in the present work we studied the alkylation and quaternization processes for mono- and binuclear tetrazoles with bi- and monofunctional alcohols in acidic media. As subjects for the investigation we used readily obtainable tetrazole derivatives of the aliphatic and aromatic series and also *tert*-butyl alcohol and its bifunctional derivative 2,5-dimethyl-2,5-hexanediol, which readily generates carbocations in acidic media.

1,4-Di(5-tetrazolyl)benzene (**1a**) and di[2-(5-tetrazolyl)ethyl] ether (**1b**) are alkylated selectively by *tert*-butyl alcohol in perchloric and sulfuric acids and give high yields of X-5,5'-bis(2-*tert*-butyltetrazoles) **2a,b** (Table 1).

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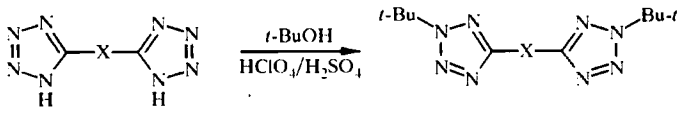
TABLE 1. The Physicochemical Characteristics of the Synthesized Compounds

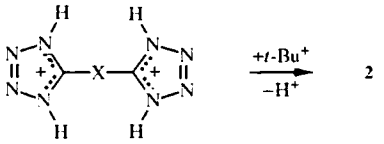
Compound	Empirical formula	Found, % / Calculated, %				mp, °C	NMR data, ppm		Yield, %
		C	H	N	Cl		^{1}H	^{13}C	
2a	$C_{16}H_{22}N_8$	59.02 / 58.88	6.90 / 6.79	34.30 / 34.33		180 decomp.	1.80 (18H, s); 8.30 (4H, s, C_6H_4)	166.92 ($C_{(5,5')}$); 132.80 (C_{arom}-$C_{(5,5')}$); 130.81 (C_{arom}); 67.85 ($CN_{(2,2')}$); 32.58 (CH_3)	91
2b	$C_{14}H_{26}N_8O$	52.25 / 52.16	8.20 / 8.13	34.67 / 34.76	–	49-51	1.67 (18H, s, $6CH_3$); 3.04 (4H, t, $2CH_2C_{(5,5')}$); 3.84 (4H, t, $2CH_2O$)	166.93 ($C_{(5,5')}$); 71.69 (CH_2O); 67.06 ($\underline{C}H_2C_{(5,5')}$); 32.64 ($CH_3$); 29.69 ($CN_{(2,2')}$)	78
3	$C_{18}H_{28}Cl_2N_8O_8$	38.78 / 38.93	5.15 / 5.08	20.27 / 20.18	13.01 / 12.77	205 decomp.	1.85 (18H, s, $6CH_3$); 4.46 (6H, s, $2CH_3N$); 8.27 (4H, s, C_6H_4)		58
5	$C_{10}H_{10}N_8$	49.70 / 49.58	4.29 / 4.16	46.39 / 46.26		208-210	4.24 (6H, s, $2CH_3$); 8.10 (4H, s, C_6H_4)	157.27 ($C_{(5,5')}$); 130.81 (C_{arom}-$C_{(5,5')}$); 132.96 (C_{arom}); 38.68 (CH_3)	67
8	$C_{22}H_{26}Cl_2N_8O_6$	42.99 / 42.80	4.49 / 4.24	18.29 / 18.15	11.65 / 11.49	170 decomp.	1.88 (18H, s, $6CH_3$); 7.55 and 8.10 (8H, two m, $2C_6H_4$); 10.96 (1H, s, 5-H and 5'-H)		90
12	$C_{22}H_{26}N_8$	65.80 / 65.65	6.80 / 6.51	27.99 / 27.84	–	173-175	1.69 (12H, s, $4CH_3$); 1.87 (4H, s, $2CH_2$); 7.44-7.55 and 7.90-8.02 (6H m 4H, two m, $2C_6H_5$)	–	76
13	$C_{18}H_{32}Cl_2N_8O_8$	36.12 / 35.90	5.97 / 6.03	20.81 / 20.93	13.36 / 13.24	150 decomp.	1.78 (12H, d, $4CH_3$); 1.82 (12H, s, 6,4 *gem*-CH_3); 2.04 (4H, s, $2CH_2$); 5.35 (2H, m, 2CH); 10.50 (1H, s, 5- and 5'-H)	–	44



1a,b **2a,b**

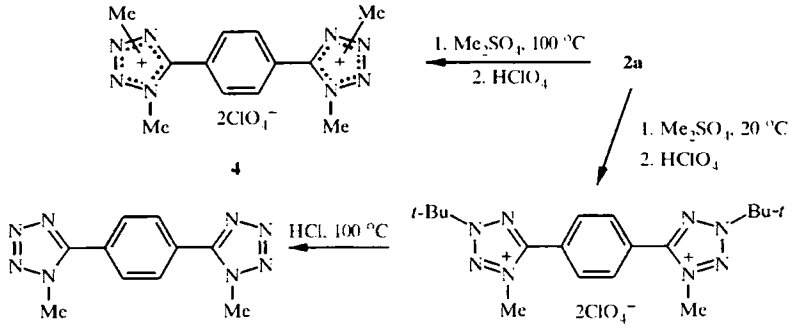
1, **2** **a** X = $-C_6H_4$-*p*-, **b** X = $-CH_2CH_2OCH_2CH_2-$

In strong acids mononuclear 5-R-tetrazoles are almost completely protonated at the $N_{(4)}$ atom, and this gives rise to the selectivity of their alkylation by alcohols [14, 19]. The observed selectivity in the alkylation of binuclear tetrazoles is also probably explained by the complete protonation of both tetrazole rings with the formation of the X-5,5'-bistetrazolium dication **3**. The latter is then attacked at the $N_{(2)}$ and $N_{(2')}$ atoms by the carbocations generated from the alcohol and is converted into the product **2**.



3

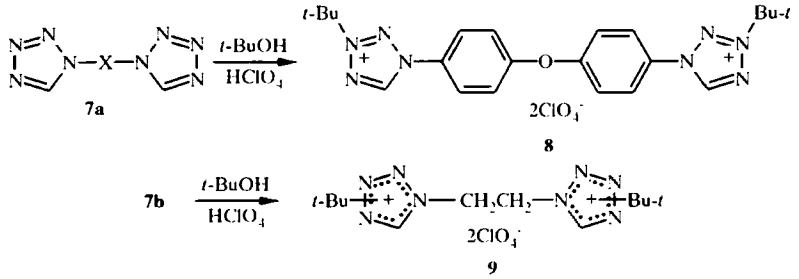
The tetrazoles **2** obtained in this way can be quaternized selectively under mild conditions (at 20-50°C), as we demonstrated for the case of the methylation of 1,4-phenylene-5,5'-bis(2-*tert*-butyltetrazole) (**2a**).



4 **6** **5**

Attempts to conduct the reaction at higher temperatures (~100°C) in order to increase its rate led to a mixture of inseparable methylation products **4**. Such result is probably due to thermally induced de-*tert*-butylation of both tetrazole **2a** and the salt **5** and subsequent exhaustive nonselective methylation of the heterocycle. De-*tert*-butylation of tetrazolium salts can also be realized in an acidic medium [20], and we used this successfully for the selective synthesis of the binuclear tetrazole **6**.

Quaternization in an acidic medium takes place just as selectively for bis(4-tetrazolylphenyl) ether (**7a**). Under the influence of *tert*-butyl alcohol in perchloric acid for 12 h it gives a high yield of diperchlorate of bis[4-(3-*tert*-butyl)-1-tetrazoliodiphenyl] ether (**8**).

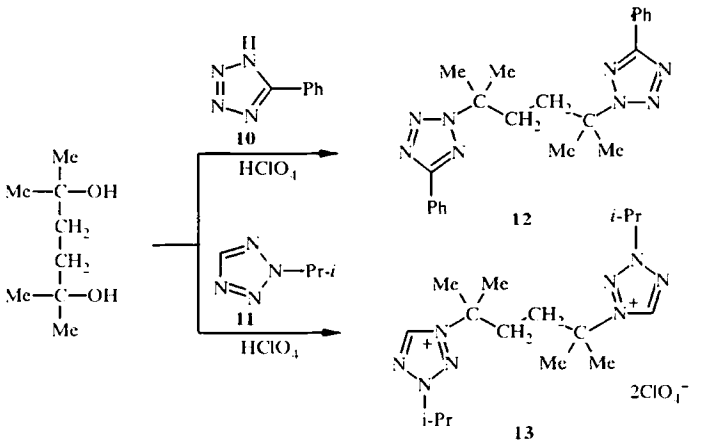


7a **8** **9**

7 **a** X = $-p$-$C_6H_4OC_6H_4$-*p*-, **b** X = $-CH_2CH_2-$

The mechanism of the selective formation of the salt **8**, like the mechanism of alkylation described above, clearly includes the preliminary stage of protonation of the initial tetrazole at the $N_{(4)}$ atom. However, the *tert*-butylation of 1,2-di(1-tetrazolyl)ethane (**7b**) under analogous conditions gave a low yield of a mixture of salts containing both unquaternized tetrazole ring and rings quaternized at the $N_{(3)}$ and $N_{(4)}$ atoms. The molar ratio of the salts, determined from the intensities of the singlet signals of the protons at the $C_{(5,5')}$ atoms in the ^{1}H NMR spectrum (at 9.34, 10.34, and 11.45 ppm), amount to 1:4.5:2.5. If the reaction mixture is kept for a long time (8 days), a high yield (96%) of the salts **9** is obtained. Here the ratio of the products from alkylation at positions 3 and 4 amounts to 1:3 (the signals of the 5- and 5'-H protons are found in the spectrum at 10.31 and 11.41 ppm). The nonselectivity of the alkylation in the case of tetrazole **7b** is probably due to the occurrence of the isomerization processes in the acidic medium, previously observed for mononuclear alkyltetrazoles [18, 21].

2,5-Dimethyl-2,5-di(5-phenyl-2-tetrazolyl)hexane (**12**) and 2,5-di(3-isopropyl-1-tetrazolio)-2,5-dimethylhexane diperchlorate (**13**) respectively were obtained selectively by the alkylation of 5-phenyl- (**10**) and 2-isopropyltetrazole (**11**) with 2,5-dimethyl-2,5-hexanediol in perchloric acid. Attempts to use 2,4-pentanediol as an alkylating agent under the indicated conditions were unsuccessful (the recovery of the initial tetrazole **10** amounted to 96%). This is evidently due to the instability of the intermediate carbocation generated from this alcohol.



The spectral characteristics and elemental analyses of the synthesized compounds agree with the proposed structures. Thus, the signals for the protons of the phenyl groups of tetrazole **12** are observed in the ^{1}H NMR spectrum in the form of two isolated multiplets, which is typical of 5-phenyl-2-R-tetrazoles [14, 16]. Compounds **8** and **13** were assigned to the 1,3-salts on the basis of the chemical shifts of their protons at the carbon atom of the ring, which differ substantially for the 1,3- and 1,4-salts and are close to the analogous characteristics of related tetrazolium salts [18, 22]. Tetrazoles **2a,b** and also **6** have signals for the carbon atom of the tetrazole ring typical of 2,5- and 1,5-disubstituted tetrazoles in the ^{13}C NMR spectrum.

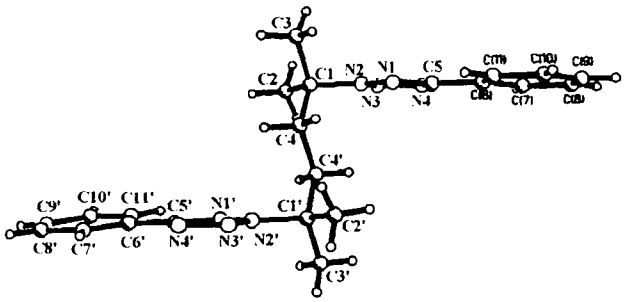


Fig. 1. The conformation of the compound **12** molecule.

TABLE 2. The Bond Lengths and Bond Angles in Compound **12**

Bond	*d*, Å	Angle	ω, deg.
$C_{(1)}$–$N_{(2)}$	1.508(7)	$N_{(2)}$–$C_{(1)}$–$C_{(2)}$	108.0(5)
$C_{(1)}$–$C_{(2)}$	1.522(9)	$N_{(2)}$–$C_{(1)}$–$C_{(3)}$	107.9(5)
$C_{(1)}$–$C_{(3)}$	1.529(8)	$C_{(2)}$–$C_{(1)}$–$C_{(3)}$	110.4(5)
$C_{(1)}$–$C_{(4)}$	1.532(7)	$N_{(2)}$–$C_{(1)}$–$C_{(4)}$	107.8(4)
$C_{(5)}$–$N_{(1)}$	1.326(7)	$C_{(2)}$–$C_{(1)}$–$C_{(4)}$	112.9(5)
$C_{(5)}$–$N_{(4)}$	1.349(9)	$C_{(3)}$–$C_{(1)}$–$C_{(4)}$	109.5(5)
$C_{(5)}$–$C_{(6)}$	1.458(9)	$C_{(4')}$–$C_{(4)}$–$C_{(1)}$	115.1(4)
$C_{(6)}$–$C_{(7)}$	1.366(9)	$N_{(1)}$–$C_{(5)}$–$N_{(4)}$	111.6(7)
$C_{(6)}$–$C_{(11)}$	1.40(1)	$N_{(1)}$–$C_{(5)}$–$C_{(6)}$	124.2(6)
$C_{(7)}$–$C_{(8)}$	1.40(1)	$N_{(4)}$–$C_{(5)}$–$C_{(6)}$	124.2(6)
$C_{(8)}$–$C_{(9)}$	1.31(1)	$C_{(7)}$–$C_{(6)}$–$C_{(11)}$	116.6(8)
$C_{(9)}$–$C_{(10)}$	1.33(1)	$C_{(7)}$–$C_{(6)}$–$C_{(5)}$	122.8(7)
$C_{(10)}$–$C_{(11)}$	1.37(1)	$C_{(11)}$–$C_{(6)}$–$C_{(5)}$	120.6(6)
$N_{(1)}$–$N_{(2)}$	1.326(6)	$C_{(6)}$–$C_{(7)}$–$C_{(8)}$	121.2(9)
$N_{(2)}$–$N_{(3)}$	1.311(6)	$C_{(9)}$–$C_{(8)}$–$C_{(7)}$	119.2(9)
$N_{(3)}$–$N_{(4)}$	1.347(9)	$C_{(8)}$–$C_{(9)}$–$C_{(10)}$	123(1)
$C_{(4)}$–$C_{(4')}$	1.516(6)	$C_{(9)}$–$C_{(10)}$–$C_{(11)}$	119(1)
$C_{(1')}$–$N_{(2')}$	1.494(7)	$C_{(10)}$–$C_{(11)}$–$C_{(6)}$	121.0(8)
$C_{(1')}$–$C_{(2')}$	1.539(8)	$N_{(2)}$–$N_{(1)}$–$C_{(5)}$	102.2(5)
$C_{(1')}$–$C_{(3')}$	1.530(8)	$N_{(3)}$–$N_{(2)}$–$N_{(1)}$	114.8(5)
$C_{(1')}$–$C_{(4')}$	1.528(7)	$N_{(3)}$–$N_{(2)}$–$C_{(1)}$	124.5(6)
$C_{(5')}$–$N_{(1')}$	1.338(7)	$N_{(1)}$–$N_{(2)}$–$C_{(1)}$	120.7(5)
$C_{(5')}$–$C_{(6')}$	1.48(1)	$N_{(3)}$–$N_{(4)}$–$C_{(5)}$	106.5(5)
$C_{(6')}$–$C_{(7')}$	1.357(9)	$N_{(2')}$–$C_{(1')}$–$C_{(2')}$	107.7(5)
$C_{(6')}$–$C_{(11')}$	1.331(9)	$N_{(2')}$–$C_{(1')}$–$C_{(3')}$	107.9(5)
$C_{(7')}$–$C_{(8')}$	1.41(1)	$C_{(2')}$–$C_{(1')}$–$C_{(3')}$	111.1(5)
$C_{(8')}$–$C_{(9')}$	1.37(1)	$N_{(2')}$–$C_{(1')}$–$C_{(4')}$	107.3(4)
$C_{(9')}$–$C_{(10')}$	1.36(1)	$C_{(2')}$–$C_{(1')}$–$C_{(4')}$	113.0(5)
$C_{(10')}$–$C_{(11')}$	1.39(1)	$C_{(3')}$–$C_{(1')}$–$C_{(4')}$	109.6(5)
$N_{(1')}$–$N_{(2')}$	1.330(6)	$C_{(4)}$–$C_{(4')}$–$C_{(1')}$	115.3(4)
$N_{(2')}$–$N_{(3')}$	1.319(6)	$N_{(1')}$–$C_{(5')}$–$N_{(4')}$	111.9(6)
$N_{(3')}$–$N_{(4')}$	1.301(9)	$N_{(1')}$–$C_{(5')}$–$C_{(6')}$	123.1(6)
		$N_{(4')}$–$C_{(5')}$–$C_{(6')}$	125.0(6)
		$C_{(7')}$–$C_{(6')}$–$C_{(11')}$	119.5(9)
		$C_{(7')}$–$C_{(6')}$–$C_{(5')}$	120.1(7)
		$C_{(11')}$–$C_{(6')}$–$C_{(5')}$	120.4(6)
		$C_{(6')}$–$C_{(7')}$–$C_{(8')}$	120.0(9)
		$C_{(9')}$–$C_{(8')}$–$C_{(7')}$	120.8(8)
		$C_{(8')}$–$C_{(9')}$–$C_{(10')}$	117.1(8)
		$C_{(9')}$–$C_{(10')}$–$C_{(11')}$	121.9(8)
		$C_{(10')}$–$C_{(11')}$–$C_{(6')}$	120.7(8)
		$N_{(2')}$–$N_{(1')}$–$C_{(5')}$	102.1(5)
		$N_{(3')}$–$N_{(2')}$–$N_{(1')}$	112.0(6)
		$N_{(3')}$–$N_{(2')}$–$C_{(1')}$	126.2(5)
		$N_{(1')}$–$N_{(2')}$–$C_{(1')}$	121.8(4)
		$N_{(2')}$–$N_{(3')}$–$N_{(4')}$	107.5(6)
		$N_{(3')}$–$N_{(4')}$–$C_{(5')}$	106.5(6)

The results of X-ray crystallographic analysis confirm the structure of compound **12** proposed on the basis of the ^{1}H NMR spectrum. Its molecule consists of two identical fragments, and we used this for numbering the atoms. The conformation of the molecule is shown in Fig. 1, and the bond lengths and bond angles are given in Table 2. Analysis of the obtained data show that all the rings in the molecule are planar; the average deviations of the atoms forming the rings are 0.003 Å (the $N_{(1)}$–$C_{(5)}$ ring), 0.007 Å (the $N_{(1')}$–$C_{(5')}$ ring), 0.004 Å (the $C_{(6)}$–$C_{(11)}$ ring),

TABLE 3. The Coordinates (in fractions of the unit cell, $\times 10^4$) and the Equivalent Isotropic Temperature Parameters of the Atoms in the Structure of Compound **12**

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å · 10^3)
$C_{(1)}$	1685(6)	2978(5)	662(3)	68(2)
$C_{(2)}$	1002(7)	3559(7)	80(4)	96(2)
$C_{(3)}$	481(6)	2297(5)	1020(4)	80(2)
$C_{(4)}$	3010(5)	2195(5)	494(3)	67(2)
$C_{(5)}$	3362(7)	4634(5)	1869(3)	68(2)
$C_{(6)}$	4224(7)	4807(5)	2454(4)	66(2)
$C_{(7)}$	4617(10)	5864(7)	2673(4)	101(3)
$C_{(8)}$	5426(11)	5997(9)	3241(5)	115(3)
$C_{(9)}$	5803(10)	5088(9)	3571(6)	120(3)
$C_{(10)}$	5447(11)	4032(9)	3389(5)	125(4)
$C_{(11)}$	4669(9)	3877(7)	2833(4)	103(5)
$N_{(1)}$	3022(5)	3620(4)	1629(2)	66(1)
$N_{(2)}$	2264(5)	3892(4)	1105(2)	65(1)
$N_{(3)}$	2119(7)	4990(4)	1004(4)	84(2)
$N_{(4)}$	2820(7)	5486(4)	1502(3)	86(2)
$C_{(1')}$	5695(6)	2012(5)	42(3)	66(1)
$C_{(2')}$	6365(7)	1445(6)	640(3)	90(2)
$C_{(3')}$	6896(6)	2690(5)	-321(3)	81(2)
$C_{(4')}$	4351(6)	2784(5)	190(3)	67(2)
$C_{(5')}$	4137(6)	270(5)	-1158(3)	65(2)
$C_{(6')}$	3309(7)	64(5)	-1761(4)	68(2)
$C_{(7')}$	3202(9)	-1008(6)	-2001(4)	104(3)
$C_{(8')}$	2426(13)	-1201(7)	-2579(4)	125(3)
$C_{(9')}$	1814(9)	-313(7)	-2915(4)	98(3)
$C_{(10')}$	1917(8)	740(7)	-2649(4)	98(2)
$C_{(11')}$	2680(8)	927(6)	-2076(4)	86(2)
$N_{(1')}$	4399(5)	1314(4)	-926(2)	63(1)
$N_{(2')}$	5141(5)	1086(4)	-389(2)	63(1)
$N_{(3')}$	5334(7)	-18(5)	-304(4)	82(2)
$N_{(4')}$	4682(7)	-538(4)	-779(3)	90(2)

and 0.011 Å (the $C_{(6')}$–$C_{(11')}$ ring). The four rings are almost coplanar. The angle between the tetrazole rings in the molecule is 1.9(4)°, and the angles between the phenyl and tetrazole rings are 3.9(4)° and 6.1(4)° (the last value corresponds to the fragment of the molecule with the atoms marked by primes).

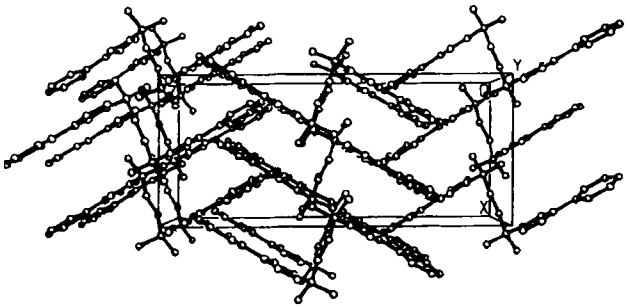


Fig. 2. The stacking of the molecules in the crystal structure of compound **12**.

The small difference in the bond lengths in the tetrazole rings (0.04 Å) and also the range of values for the bond angles (102-115°, Table 2) are typical of 2,5-disubstituted tetrazoles [23-25]. Here the smallest angle is observed at the $N_{(1)}$ and $N_{(4)}$ atoms, and the largest is observed at the substituted nitrogen atoms. It should be mentioned that the morphology of the single crystals, i.e., their laminarity, gave rise to the large standard deviations in the obtained bond lengths and bond angles. The stacking of the molecules in the structure (Fig. 2) is determined largely by van der Waals interactions (there are no short intermolecular contacts in the structure).

EXPERIMENTAL

The NMR spectra of solutions in DMSO-d_6 and acetone-d_6 (in the case of compounds **2a,b**) were recorded on a Tesla BS-567A spectrometer at 100.028 (^{1}H) and 25.142 MHz (^{13}C). The initial 5-phenyltetrazole (**10**) and 1,4-di(5-tetrazolyl)benzene (**1a**) [26], 2-isopropyltetrazole (**11**) [14], 1,2-di(1-tetrazolyl)ethane (**7b**) [27], bis[4-(1-tetrazolyl)phenyl] ether (**8**) [28], bis[2-(5-tetrazolyl)ethyl] ether (**1b**) [29], and 2,5-dimethyl-2,5-hexanediol [30] were obtained by known methods, references to which are given after the compound numbers.

X-Ray Crystallographic Investigation of Compound 12. Single crystals of compound **12** were obtained by crystallization from ethanol at 293 K. A prismatic crystal (size 0.42 × 0.36 × 0.08 mm) was selected for X-ray crystallographic analysis. The compound crystallizes in the rhombic syngony, space group $Pca2_1$. The unit cell parameters are: a = 8.866(2), b = 11.730(2), c = 20.938(4) Å; V = 2177.5(7) Å^3; Z = 4; $d_{X\text{-ray}}$ = 1.228 g/cm^3; μ = 0.78 cm^{-1}. A three-dimensional set of X-ray diffraction data was collected on a Nicolet R3m automatic four-circle diffractometer with MoK_α radiation, a graphite monochromator, a $\theta/2\theta$ scanning, and $2\theta_{max}$ = 55°. The structure was solved by the direct method. The positions of the hydrogen atoms were calculated geometrically. The structure was refined by full-matrix least-squares treatment with regard to the anisotropy of the thermal vibrations of the nonhydrogen atoms. The hydrogen atoms were refined in terms of the "rider" model. The final values of the uncertainty factors were: R_1 = 0.0649, wR_2 = 0.1603 ($I > 2\sigma(I)$); R_1 = 0.1146, wR_2 = 0.2192 (all data); goodness of fit $GOOF$ = 1.000. All the calculations were made using the SHELX-97 software (PC version) [31-33]. The coordinates and equivalent isotropic temperature parameters of the atoms are given in Table 3.

Procedure for the *tert*-Butylation of Binuclear Tetrazoles. Solution of tetrazole **1a,b, 7a,b**) (0.011 mol) and *tert*-butyl alcohol (2.2 ml, 0.023 mol) in 72% perchloric acid (20 ml) or 96% sulfuric acid (15 ml) (for tetrazole **1b**) was kept at 20°C for 2 or 12 h (in the case of tetrazoles **7a,b**). The reaction mixture was diluted with water (20 ml) or poured onto ice (for tetrazole **1b**). The precipitated product was separated, washed with water, dried under vacuum, and recrystallized from ethanol (tetrazole **2a**), ether–hexane 1:1 (tetrazole **2b**), or acetonitrile (salt **8**).

1,4-Diphenylene-5,5'-bis(3-*tert*-butyl-1-methyl-1-methyltetrazolium) Diperchlorate (5). Mixture of tetrazole **2a** (3.26 g, 0.01 mol) and dimethyl sulfate (7.5 ml, 0.08 mol) was stirred at 20-50°C for 4 days. The reaction mixture was then poured into water (60 ml), 62% perchloric acid (10 ml) was added, and the mixture was stirred for 1 h. The precipitate was separated, washed with water, and dried under vacuum. Colorless crystalline salt **5** (3.20 g, 0.058 mol) was obtained. The product was recrystallized from ethanol–acetonitrile 1:1.

1,4-Phenylene-5,5'-bis(1-methyltetrazole) (6). Suspension of the salt **5** (3.2 g, 0.058 mol) in 36% hydrochloric acid (50 ml) was kept on a boiling water bath for 10 h, and then cooled to room temperature. The precipitate was separated, washed with water, and dried under vacuum. Colorless crystalline product (1.10 g, 0.039 mol) was obtained. The product was recrystallized from water.

Procedure for the Alkylation by 2,5-Dimethyl-2,5-hexanediol. A solution of tetrazole **10** or **11** (0.060 mol) and 2,5-dimethylhexanediol (0.5 g, 0.034 mol) in 72% perchloric acid (10 ml) was stirred for 2 h and 3 days respectively and then diluted with water. The precipitated product was separated, washed with water, dried under vacuum, and recrystallized from ethanol.

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REFERENCES

1. R. N. Butler, *Comprehensive Heterocyclic Chemistry. II* (Eds. A. R. Katritzky, C. W. Rees, E. F. V. Scriven), Vol. 4, Pergamon Press, Oxford (1996), p. 621.
2. G. I. Koldobskii and V. A. Ostrovskii, *Usp. Khim.*, **63**, 847 (1994).
3. V. A. Ostrovskii and G. I. Koldobskii, *Ross. Khim. Zh.*, No. 2, 84 (1997).
4. P. N. Gaponik, *Chemical Problems of the Creation of New Materials and Technologies* [in Russian] (Ed. V. V. Sviridov), Minsk (1998), p. 185.
5. A. J. Downard, P. J. Steel, and J. Steenwijk, *Aust. J. Chem.*, **48**, 1643 (1995).
6. C. Janiak, T. G. Scharmann, K. W. Brzezinka, and P. Reich, *Chem. Ber.*, **128**, 323 (1995).
7. R. W. Saalfrank, K. Schobert, S. Trummer, and A. Wolski, *Z. Naturforsch.*, **50b**, 642 (1995).
8. V. G. Kitaeva, D. T. Beresnev, R. I. Ishmetova, and G. L. Rusinov, *Zh. Org. Khim.*, **31**, 620 (1995).
9. V. I. Boev, E. M. Krasnikov, A. I. Moskalenko, E. I. Pil'ko, L. V. Snegur, V. N. Babin, and Yu. S. Nekrasov, *Zh. Obshch. Khim.*, **67**, 1386 (1997).
10. A. V. Sachivko, V. P. Tverdokhlebov, and I. V. Tselinskii, *Ross. Khim. Zh.*, No. 2, 119 (1997).
11. S. A. Gromova, M. I. Barmin, I. B. Karaulova, A. N. Grebenkin, and V. V. Mel'nikov, *Zh. Org. Khim.*, **34**, 1094 (1998).
12. R. N. Butler and A. F. M. Fleming, *J. Heterocycl. Chem.*, **34**, 691 (1997).
13. J. Torres, J. L. Lavandera, P. Cabildo, R. M. Claramuni, and J. Elguero, *J. Heterocycl. Chem.*, **25**, 771 (1988).
14. A. O. Koren' and P. N. Gaponik, *Khim. Geterotsikl. Soedin.*, No. 12, 1643 (1990).
15. A. O. Koren' and P. N. Gaponik, *Khim. Geterotsikl. Soedin.*, No. 9, 1280 (1991).
16. S. V. Voitekhovich, P. N. Gaponik, and A. O. Koren, *Mendeleev Commun.*, No. 1, 41 (1997).
17. P. N. Gaponik, S. V. Voitekhovich, A. S. Lyakhov, and I. I. Maruda, *Khim. Geterotsikl. Soedin.*, No. 9, 1222 (1999).
18. P. N. Gaponik, S. V. Voitekhovich, I. I. Maruda, A. A. Kulak, and O. A. Ivashkevich, *Pol. J. Chem.*, **72**, 2247 (1998).
19. A. O. Koren, P. N. Gaponik, and V. A. Ostrovskii, *Int. J. Chem. Kinet.*, **25**, 1043 (1993).
20. A. O. Koren, P. N. Gaponik, O. A. Ivashkevich, and T. V. Kovalyova, *Mendeleev Commun.*, No. 1, 10 (1995).
21. P. N. Gaponik and S. V. Voitekhovich, *Zh. Org. Khim.*, **34**, 788 (1998).
22. P. N. Gaponik, Yu. V. Grigor'ev, T. N. Andreeva, and I. I. Maruda, *Khim. Geterotsikl. Soedin.*, No. 7, 915 (1995).
23. K. Yamaguchi, A. Ohsawa, T. Kaihoh, and T. Itoh, *Acta Crystallogr.*, **C46**, 1161 (1990).
24. Zi-yi Zhang and N. Zou, *Chem. Research Chinese Univ.*, **10**, 373 (1994).
25. F. H. Allen and O. Kennard, *Chem. Design Automation News*, **8**, 31 (1993).
26. W. G. Finnegan, R. A. Henry, and R. Lofqist, *J. Am. Chem. Soc.*, **80**, 3908 (1958).
27. P. N. Gaponik, V. P. Karavai, and Yu. V. Grigor'ev, *Khim. Geterotsikl. Soedin.*, No. 11, 1521 (1985).
28. Yu. V. Grigor'ev, I. I. Maruda, and P. N. Gaponik, *Vestsi AN Belarusi*, No. 4, 80 (1997).
29. M. I. Ermakova, I. A. Shikhova, and N. I. Latosh, *Zh. Obshch. Khim.*, **51**, 174 (1981).
30. D. D. Coffman and E. L. Jenner, *J. Am. Chem. Soc.*, **80**, 2872 (1958).
31. G. M. Sheldrick, *Program for Crystal Structure Refinement*, Gottingen (1997).
32. G. M. Sheldrick, *Acta Crystallogr.*, **A46**, 467 (1990).
33. G. M. Sheldrick, Z. Dauter, K. S. Wilson, and L. Sieker, *Acta Crystallogr.*, **D49**, 18 (1993).