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SYNTHESIS AND STRUCTURE OF 1-*tert*-BUTYL-3-R-TETRAZOLIUM SALTS

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An effective method was developed for the synthesis of 1,3-disubstituted tetrazolium salts by the quaternization of 2-monosubstituted tetrazoles, including functionally substituted compounds, with tert-butanol in 72% perchloric acid. An X-ray diffraction investigation of examples of this series of salts – 1-tert-butyl-3-(1-methylvinyl)- and 1,3-di-tert-butyltetrazolium perchlorates – was carried out.

Keywords: 1,3-disubstituted tetrazolium salts, 2R-tetrazoles, quaternization.

Tetrazolium salts have found the application in various regions of technology, biochemistry, medicine, and chemical analysis and are promising as phase-transfer catalysts [1, 2]. Recently interest has arisen in the use of tetrazolium salts as intermediates in organic synthesis [2], particularly for the production of mesoionic tetrazoles [3] and various heterocyclic systems (benzoxazoles [4, 5], quinazolinediones [5], aziridines, tetrazines [6], etc.). The 5-unsubstituted tetrazolium salts are of considerable interest due to the possibility of their further functionalization at the $C_{(5)}$ atom, the first examples of which were demonstrated in series of 1,3-diaryltetrazolium salts [7]. The principal and the most accessible method for the synthesis of 1,3-disubstituted tetrazolium salts includes the quaternization of 2-monosubstituted tetrazoles (2-MST) in neutral or acidic media [1, 2]. The quaternization of 2-MST in acidic media was discovered recently and has been studied little. It is known that 2-MST enter into reaction with *tert*-butanol in 48% HBF_4 at room temperature, leading to 1,3-disubstituted tetrazolium salts [8]. Higher yields of tetrazolium salts are obtained during quaternization in perchloric acid, as we demonstrated for isolated examples of the quaternization of 2-MST with diacetone alcohol [9]. Further investigation of quaternization in acidic media is of undoubted interest, since this approach makes it possible to obtain salts that cannot be obtained by other methods.

In the present work we investigated N-*tert*-butylation of a series of 2-R-tetrazoles, including functionally substituted compounds, in the presence of perchloric acid in order to develop effective methods of synthesis and increase the set of 1,3-disubstituted tetrazolium salts. In the case of the reaction of *tert*-butanol and 2-isopropyltetrazole (**1a**) in perchloric acid we studied the effect of the reagent ratio, the concentration of acid, the addition of an organic phase, and the reaction time on the yield of tetrazolium salt **2a**. The yield of the salt is reduced by decrease in acidity of the medium and by decrease in the relative amount of acid (Table 1). Additions of chloroform to 62% perchloric acid increase the quaternization rate, and this may be due to the presence of a considerable proportion of the unprotonated form of the initial tetrazole **1a**, which is clearly more active towards the *tert*-butyl cation than the protonated tetrazole **1a**. An important factor here is the good solubility of both the initial tetrazole and the final product in chloroform.

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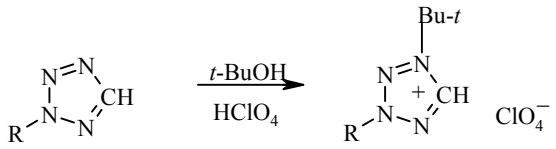
TABLE 1. The Effect of the Quaternization Conditions of Tetrazole **1a** on the Yield of Tetrazolium Salt **2a**

Experiment	Molar ratio of reagents tetrazole/acid*/alcohol	Holding time, h	Yield, %
1	1 : 1 : 1	48	57
2	1 : 2 : 2	48	93
3	1 : 2 : 1	48	96
4	1 : 2 : 1	2	23
5	1 : 2 : 1	5	43
6	1 : 2 : 1	24	75
7	1 : 2 : 1	48	96
8	1 : 2 : 1	2	5
9	1 : 2 : 1	5	12
10	1 : 2 : 1	24	50
11	1 : 2 : 1	48	66
12	1 : 2 : 1*[2]	5	31
13	1 : 2 : 1*[2]	12	39
14	1 : 2 : 1*[2]	24*[3]	48
15	1 : 2 : 1*[2]	48*[4]	63

* 72% $HClO_4$ was used in expts. 1-7, 62% $HClO_4$ in expts. 8-15.
*[2] Additional chloroform was added.
*[3] Vigorous agitation of the mixture for 12 h.
*[4] Vigorous agitation of the mixture for 24 h.

On the basis of the investigations we proposed the *t*-BuOH/72% $HClO_4$ system as an effective quaternization agent for the synthesis of 1-*tert*-butyl-3-R-tetrazolium salts **2** from 2-MST (Table 2). As a result of the use of this system functionally substituted tetrazoles as well as alkyltetrazoles were submitted successfully to *tert*-butylation; their functional groups were not affected. This quaternization system is more effective than the *t*-BuOH/48% HBF_4 system, as shown by comparison of the yields of the respective salts during the *tert*-butylation of tetrazoles **1b**,**e** in 72% $HClO_4$ and 48% HBF_4 [8].



1a–h **2a–h**

1, 2 – a R = *i*-Pr, **b** R = Me, **c** R = Et, **d** R = *t*-Bu, **e** R = $CH_2CH{=}CH_2$, **f** R = $CH(Me){=}CH_2$, **g** R = $CH(Me)CH_2Br$, **h** R = CH_2CH_2COMe

An important factor affecting the quaternization rate and the yield of tetrazolium salt is the solubility of the latter in the reaction mixture. This showed up significantly in the synthesis of the salt **2f**. A high yield of the latter (84%) is obtained after only 2 h of interaction of the reagents, whereas the yield of the product **2a** under analogous conditions amounts to only 23%. This difference is due to the low solubility of the salt **2f** in the reaction mixture – it starts to crystallize already 5-10 min after the reagents are mixed.

TABLE 2. The Characteristics of the Synthesized Compounds

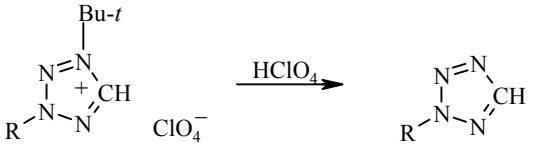
Compound	Empirical formula	mp, °C	Found, % / Calculated, %				^{1}H NMR spectrum, ppm			Yield, %
			C	H	N	Cl	$H_{cycl}C$	*t*-Bu	Other signals	
2a	$C_8H_{17}ClN_4O_4$	130-131	36.01 / 35.82	6.40 / 6.34	20.95 / 20.90	13.12 / 13.06	10.49	1.70	1.65 (d, 6H, 2Me); 5.35 (m, 1H, CH)	96
2b	$C_6H_{13}ClN_4O_4$	150 (dec.)	30.23 / 29.95	5.69 / 5.45	23.25 / 23.28	14.91 / 14.73	10.48	1.72	4.62 (s, 3H, Me)	95
2c	$C_7H_{15}ClN_4O_4$	133-135	33.21 / 33.01	6.02 / 5.94	22.12 / 22.00	13.79 / 13.92	10.51	1.73	1.64 (t, 3H, Me); 5.01 (q, 2H, CH_2)	80
2d	$C_9H_{19}ClN_4O_4$	120-122*	38.16 / 38.23	6.96 / 6.73	19.64 / 19.82	12.73 / 12.57	10.49	1.73; 1.78	—	74
2e	$C_8H_{15}ClN_4O_4$	143-145	35.91 / 36.09	5.88 / 5.64	21.20 / 21.05	13.29 / 13.16	10.51	1.73	5.50 (m, 2H, CH_2=); 5.64 (d, 2H, CH_2); 6.00 (d, 1H, CH=)	89
2f	$C_8H_{15}ClN_4O_4$	145 (dec.)	36.13 / 36.09	5.83 / 5.64	21.13 / 21.05	12.99 / 13.16	10.61	1.75	2.45 (s, 3H, Me); 5.81 (m, 1H, $CH_{2\alpha}$=); 6.30 (m, 1H, $CH_{2\beta}$=)	88
2g	$C_8H_{16}BrClN_4O_4$	78-80	27.51 / 27.67	4.85 / 4.61	16.29 / 16.14		10.64	1.73	1.80 (d, 3H, Me); 4.13 (m, 2H, CH_2); 5.75 (m, 1H, CH)	75
2h	$C_9H_{17}ClN_4O_4$	97-99	36.70 / 36.49	5.52 / 5.74	18.72 / 18.92	11.67 / 11.82	10.50	1.72	2.17 (s, 3H, Me); 3.39 (t, 2H, CH_2CO); 5.09 (d, 2H, CH_2N)	70
3a	$C_{11}H_{24}ClN_4O_5$	*[2]					10.57	1.80	1.76 (s, 6H, 2Me); 2.45 (s, 3H, MeCO); 3.39 (s, 2H, CH_2CO)	*[3]
3b	$C_{11}H_{24}ClN_4O_5$	*[2]					11.25	1.80	1.76 (s, 6H, 2Me); 2.45 (s, 3H, MeCO); 3.39 (s, 2H, CH_2CO)	*[3]

* The characteristics of the salt coincide with data in [10].

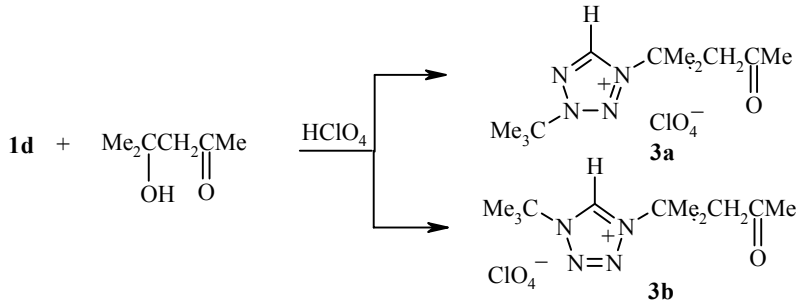
*[2] The mixture obtained in the form of a viscous oil was not separated.

*[3] The total yield of the mixture of salts was 61%.

Prolonged holding of the reaction mixtures and also the individual compounds **2a**,**b** in $HClO_4$ (up to 4 days) did not indicate the formation of the isomeric 1,4-disubstituted tetrazolium salts. This indicates the absence of isomerization of 1-*tert*-butyl-3-R-tetrazolium salts to their 1,4 isomers by migration of substituent from the $N_{(3)}$ position to $N_{(4)}$, like the behavior we observed earlier for 1-R-3-*tert*-butyltetrazolium salts [10]. An essential condition for the isomerization of the compounds is clearly heterolysis of the N–$R_{migrated}$ bond and the generation of a carbocation from it. Such groups as Me and *i*-Pr, unlike *t*-Bu, do not meet the given criteria and do not migrate from $N_{(3)}$ to $N_{(4)}$. The corresponding salts do not therefore isomerize under the investigated conditions. They are partly de-*tert*-butylated, since heterolysis of the $N_{(1)}$–*t*-Bu bond occurs and the *tert*-butyl cation is generated. Possible substrates for further attack by the *tert*-butyl cation can only be the 2-R-tetrazole that forms and water, which leads to formation of the initial salt and *tert*-butanol respectively. The *tert*-butyl cation can also be converted into isobutylene and the products of its polymerization.



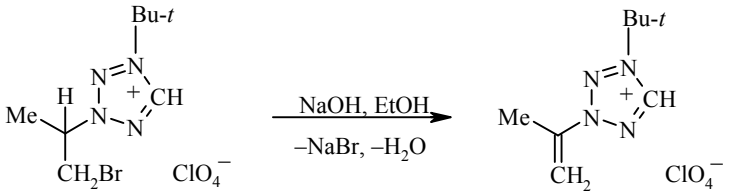
In the case of the salt **2d** (R = *t*-Bu) during heterolysis of the N–*t*-Bu bonds 1-*tert*-butyltetrazole is formed together with 2-*tert*-butyltetrazole, and it can be attacked by the *tert*-butyl cation both at the $N_{(3)}$ atom and at $N_{(4)}$ atom. The salt **2d** therefore isomerizes in perchloric acid to 1,4-di-*tert*-butyltetrazolium perchlorate [10]. The perchlorate was not found under the conditions of the synthesis of the salt **2d**. However, a mixture of the isomeric 1-(1,1-dimethyl-3-oxobutyl)-3- and 1-(1,1-dimethyl-3-oxobutyl)-4-*tert*-butyltetrazolium salts **3a** and **3b** with a predominance of the 1,3 salt **3a** was obtained during the quaternization of 2-*tert*-butyltetrazole **1d**. Their ratio, determined from the intensities of the singlets of the protons at the $C_{(5)}$ atom of the tetrazole ring, was 1:0.2.



The quaternization of 2-adamantyltetrazole by 1-adamantanol in sulfuric acid takes place in a similar manner, and the 1,4-tetrazolium salt is mostly formed [11]. However, the process is much faster (2 h). Experiments indicate a substantial effect of the nature of tetrazole, alcohol, and acid, and the concentration of the latter on the isomerization transformations of tetrazolium salts. This must be taken into consideration during the quaternization of 2-R-tetrazoles in the case of a group R capable of being eliminated in acidic media in the form of a sufficiently stable carbocation.

The synthesized salts **2** were assigned to the 1,3-disubstituted tetrazolium salts on the basis of their ^1H NMR spectra, compared with the analogous spectra for related tetrazolium salts [8-10]. The chemical shifts of the protons at the $C_{(5)}$ atom of the salts are extremely characteristic for identification of disubstituted tetrazolium salts. For 1,3-dialkyl-substituted tetrazolium perchlorates these values lie in the region of 10.2-10.6 ppm, whereas for the isomeric 1,4 salts they are at 11.0-11.8 ppm (DMSO-d_6).

1-*tert*-Butyl-3-(1-methylvinyl)tetrazolium perchlorate **2f** is of particular interest among the synthesized salts. This compound belongs to an uninvestigated class of α-methylvinyl monomers with a quaternized tetrazole ring. As well as at *tert*-butylation of 2-(1-methylvinyl)tetrazole **1f** the salt **2f** can also be obtained by dehydrobromination of its synthetic precursor **2g**.



However, the reaction is unsuitable for preparative purposes on account of the low product yield, which is probably due to cleavage of the salts **2f**,**g** by the action of the base, leading (as known for 1,3-dialkyltetrazolium salts [7]) to 1,3-disubstituted 3-cyanotriazenes.

In order to establish the structural features of 1,3-disubstituted tetrazolium salts, about the structure of which there are no published data, an X-ray diffraction analysis was carried out on single crystals of compounds **2d** and **2f**. Fragments of their structure, illustrating the mutual arrangement and conformation of the ions, are shown in Fig. 1, 2. The bond lengths and bond angles in the tetrazolium cations are given in Tables 3, 4.

The tetrazole ring in the cations of salts **2d** and **2f** is planar (average departure of the ring atoms from the mean-square plane 0.002 Å), and this is typical of tetrazole and its derivatives. As in the 1,3,5-trisubstituted tetrazolium cations [12, 13], in the cation of salt **2f** the $N_{(2)}$–$N_{(3)}$ and $N_{(4)}$–$C_{(5)}$ bonds are the shortest. The lengths of the other C–N and N–N bonds are intermediate between the lengths of the corresponding single and double bonds of aromatic compounds, where the carbon and nitrogen atoms have sp^2-hybridization [14]. In contrast to the structure of 1-(1-adamantyl)-5-(1-methylvinyl)tetrazole [15], in the structure of compound **2f** the torsion

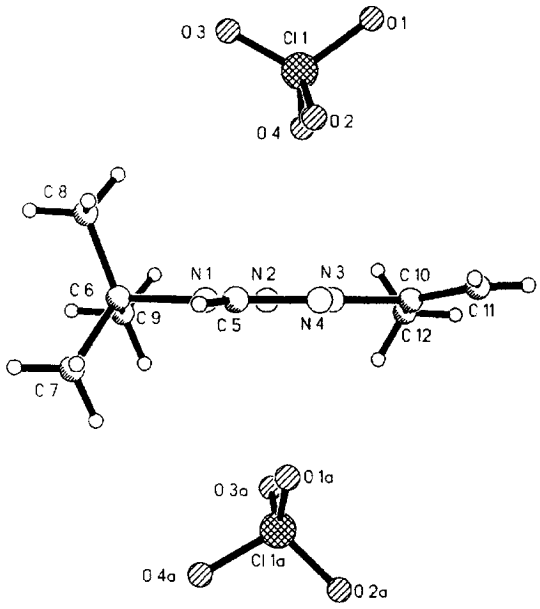


Fig. 1. Fragment of the structure of salt **2f**
(disordering of the perchlorate ion and *tert*-butyl group is not shown).

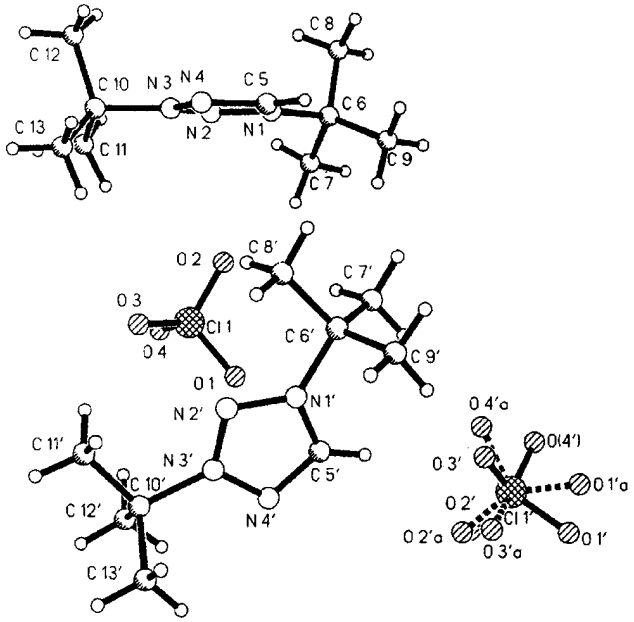


Fig. 2. Fragment of the structure of salt **2d**
(one of the perchlorate ions is disordered with respect to two positions).

angles at the $C_{(9)}$–$N_{(3)}$ bond deviate from 0° and 180° by no more than 10.6°. On the basis of these data it can be concluded that the π-systems of the C=C bond and the tetrazole ring are conjugated, while the positive charge is localized to a larger degree at the $N_{(3)}$ atom than at $N_{(1)}$, which is the quaternization center. The localization of the charge at the $N_{(3)}$ atom is confirmed indirectly by the fact that the oxygen atoms of the perchlorate ions in the structure are closest to this nitrogen atom ($d[O_{(1)}\cdots N_{(3)}]$ = 2.964(7) Å, $d[O_{(2)}\cdots N_{(3)}]$ = 2.965(7) Å, Fig. 1). The conjugation of these fragments probably also gives rise to the difference in the values of the chemical shifts of

TABLE 3. The Bond Lengths (*d*) in the Cations of Salts **2d** and **2f**

Bond	Salt **2f,** *d*, Å	Salt **2d**	
		cation 1, *d*, Å	cation 2, *d*, Å
$N_{(1)}$–$N_{(2)}$	1.316(3)	1.322(2)	1.316(3)
$N_{(1)}$–$C_{(5)}$	1.337(3)	1.334(3)	1.334(3)
$N_{(2)}$–$N_{(3)}$	1.299(3)	1.292(3)	1.290(3)
$N_{(3)}$–$N_{(4)}$	1.334(3)	1.330(3)	1.325(3)
$N_{(4)}$–$C_{(5)}$	1.300(4)	1.303(3)	1.314(3)
$N_{(1)}$–$C_{(6)}$	1.508(3)	1.510(3)	1.517(3)
$C_{(6)}$–$C_{(7)}$	1.531(6)	1.521(4)	1.517(4)
$C_{(6)}$–$C_{(8)}$	1.501(6)	1.508(4)	1.513(4)
$C_{(6)}$–$C_{(9)}$	1.485(6)	1.493(4)	1.511(4)
$C_{(6)}$–$C_{(7')}$	1.53(2)	—	—
$C_{(6)}$–$C_{(8')}$	1.54(3)	—	—
$C_{(6)}$–$C_{(9')}$	1.58(4)	—	—
$N_{(3)}$–$C_{(10)}$	1.440(3)	1.506(3)	1.516(3)
$C_{(10)}$–$C_{(11)}$	1.329(4)	1.498(4)	1.508(5)
$C_{(10)}$–$C_{(12)}$	1.440(5)	1.487(4)	1.514(4)
$C_{(10)}$–$C_{(13)}$	—	1.515(4)	1.517(4)

TABLE 4. The Bond Angles (ω) in the Cations of Salts **2d** and **2f**

Angle	Salt **2f,** ω, deg.	Salt **2d**	
		cation 1, ω, deg.	cation 2, ω, deg.
$N_{(2)}$–$N_{(1)}$–$C_{(5)}$	108.9(2)	108.63(18)	109.2(2)
$N_{(3)}$–$N_{(2)}$–$N_{(1)}$	103.66(18)	103.73(17)	103.84(19)
$N_{(2)}$–$N_{(3)}$–$N_{(4)}$	114.54(19)	114.77(18)	114.73(19)
$C_{(5)}$–$N_{(4)}$–$N_{(3)}$	102.6(2)	102.56(19)	102.9(2)
$N_{(4)}$–$C_{(5)}$–$N_{(1)}$	110.3(2)	110.3(2)	109.3(2)
$N_{(2)}$–$N_{(1)}$–$C_{(6)}$	121.19(19)	119.30(18)	122.3(2)
$C_{(5)}$–$N_{(1)}$–$C_{(6)}$	129.9(2)	132.07(19)	128.5(2)
$N_{(2)}$–$N_{(3)}$–$C_{(10)}$	121.3(2)	121.68(18)	123.4(2)
$N_{(4)}$–$N_{(3)}$–$C_{(10)}$	124.2(2)	123.54(18)	121.9(2)
$N_{(1)}$–$C_{(6)}$–$C_{(7)}$	104.4(3)	107.4(2)	106.6(2)
$N_{(1)}$–$C_{(6)}$–$C_{(8)}$	105.5(3)	107.3(2)	108.0(2)
$N_{(1)}$–$C_{(6)}$–$C_{(9)}$	108.6(3)	107.6(2)	106.8(2)
$C_{(9)}$–$C_{(6)}$–$C_{(8)}$	112.7(4)	113.7(3)	111.6(3)
$C_{(9)}$–$C_{(6)}$–$C_{(7)}$	111.1(4)	111.8(3)	111.7(3)
$C_{(8)}$–$C_{(6)}$–$C_{(7)}$	113.9(5)	108.7(3)	111.8(3)
$N_{(1)}$–$C_{(6)}$–$C_{(7')}$	110.4(8)	—	—
$N_{(1)}$–$C_{(6)}$–$C_{(8')}$	106.1(10)	—	—
$N_{(1)}$–$C_{(6)}$–$C_{(9')}$	103.0(9)	—	—
$C_{(7')}$–$C_{(6)}$–$C_{(8')}$	115(2)	—	—
$C_{(7')}$–$C_{(6)}$–$C_{(9')}$	109(2)	—	—
$C_{(8')}$–$C_{(6)}$–$C_{(9')}$	113(3)	—	—
$N_{(3)}$–$C_{(10)}$–$C_{(11)}$	117.1(3)	107.3(2)	108.0(2)
$N_{(3)}$–$C_{(10)}$–$C_{(12)}$	114.1(2)	106.5(2)	106.0(2)
$N_{(3)}$–$C_{(10)}$–$C_{(13)}$	—	106.6(2)	106.2(2)
$C_{(11)}$–$C_{(10)}$–$C_{(12)}$	128.8(3)	113.0(3)	111.5(3)
$C_{(11)}$–$C_{(10)}$–$C_{(13)}$	—	110.6(3)	112.5(3)
$C_{(12)}$–$C_{(10)}$–$C_{(13)}$	—	112.4(3)	112.1(3)

the protons at the $C_{(5)}$ atom in the ^{1}H NMR spectrum of salt **2f** and salts **2a**,**e**. For the salt **2f** the signal of the given proton is shifted downfield by ~0.1 ppm. However, in spite of the fairly high mobility of this proton, there is no clearly defined C–H···O interaction between them and the oxygen atoms of the perchlorate ion. The shortest distance between the hydrogen atom at $C_{(5)}$ and the oxygen atoms of the perchlorate anion amounts to 2.276(4) Å ($d(C_{(5)}\cdots O_{(2')})$ = 3.145(7) Å, $\omega(C_{(5)}–H\cdots O_{(2')})$ = 153(3)°), which is somewhat shorter than the analogous value for 1-(2-methyl-4-oxopentan-2-yl)-4-methyltetrazolium perchlorate [9] [2.37(3) Å]. However, these values are in the critical region of lengths of intermolecular contacts giving rise to the greatest discussions concerning crystallographic evidence for the presence or absence of hydrogen bonds [16]. Meanwhile, the data in [16] apply to C–H···O contacts of intermolecular type, while in the salts that we investigated there is ion–ion interaction. Therefore the regions for the existence of hydrogen bonds may be somewhat different. The position of the vinyl group in relation to the heterocycle in the crystal structure corresponds to the s-*trans*(N_2) conformation, which agrees with the high population of this conformation (72.1%) in the unquaternized tetrazole **1f** (according to the data from nonempirical calculation in the 6-31G**//STO-3G basis set) and provides further evidence for the insignificant effect of the substituent (by virtue of its remoteness) on the stereochemical structure of 2-alkenyltetrazoles [17].

TABLE 5. The Coordinates (in Unit Cell Fractions, $\times 10^4$) and Equivalent Isotropic Temperature Factors of the Atoms in the Structure of Salt **2d**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq) (Å^2 × 10^3)
$N_{(1)}$	6588(2)	2340(2)	4202(1)	46(1)
$N_{(2)}$	5732(2)	2536(2)	3511(1)	47(1)
$N_{(3)}$	6548(2)	2459(2)	2646(1)	44(1)
$N_{(4)}$	7894(2)	2214(2)	2728(2)	59(1)
$C_{(5)}$	7889(2)	2134(3)	3722(2)	58(1)
$C_{(6)}$	5999(3)	2381(3)	5322(2)	57(1)
$C_{(7)}$	4626(4)	3408(4)	5171(3)	97(1)
$C_{(8)}$	5710(5)	1140(4)	6054(3)	107(1)
$C_{(9)}$	7037(4)	2652(6)	5725(3)	121(2)
$C_{(10)}$	5997(3)	2617(2)	1639(2)	52(1)
$C_{(11)}$	4520(4)	3420(4)	1627(3)	99(1)
$C_{(12)}$	6123(6)	1337(3)	1747(4)	118(2)
$C_{(13)}$	6893(5)	3273(5)	648(3)	104(1)
$N_{(1')}$	9374(2)	6892(2)	1800(2)	50(1)
$N_{(2')}$	9286(2)	7152(2)	762(2)	51(1)
$N_{(3')}$	8603(2)	8322(2)	382(2)	51(1)
$N_{(4')}$	8239(3)	8849(2)	1109(2)	69(1)
$C_{(5')}$	8731(3)	7919(2)	2011(2)	66(1)
$C_{(6')}$	10120(3)	5602(2)	2577(2)	58(1)
$C_{(7')}$	9132(3)	5250(3)	3616(2)	78(1)
$C_{(8')}$	10453(4)	4711(3)	2007(3)	88(1)
$C_{(9')}$	11427(3)	5715(4)	2806(3)	90(1)
$C_{(10')}$	8233(3)	9051(3)	-800(2)	61(1)
$C_{(11')}$	8612(4)	8138(4)	-1348(3)	85(1)
$C_{(12')}$	6678(3)	9666(3)	-727(3)	85(1)
$C_{(13')}$	9063(5)	10004(4)	-1335(3)	109(1)
$Cl_{(1)}$	5788(1)	6373(1)	1730(1)	62(1)
$O_{(1)}$	6154(3)	7224(2)	1981(2)	89(1)
$O_{(2)}$	6105(6)	5209(3)	2572(3)	169(2)
$O_{(3)}$	6514(5)	6333(4)	746(3)	163(2)
$O_{(4)}$	4393(4)	6778(5)	1598(5)	194(2)
$Cl_{(1')}$	8463(1)	8556(1)	4778(1)	66(1)
$O_{(1')}$*	9209(7)	9035(8)	5126(9)	173(4)
$O_{(2')}$*	7359(5)	9515(4)	4282(6)	133(3)
$O_{(3')}$*	9312(9)	7780(8)	4264(6)	161(3)
$O_{(4')}$*	7798(8)	7815(8)	5748(6)	201(4)
$O_{(1'A)}$*^{2}	9019(16)	8248(13)	5696(9)	103(4)
$O_{(2'A)}$*^{2}	7850(70)	9430(40)	3960(30)	501(17)
$O_{(3'A)}$*^{2}	9455(18)	8960(20)	3860(17)	187(11)
$O_{(4'A)}$*^{2}	8244(16)	7490(9)	4821(16)	112(6)

* Population of position 0.726(9).
*^{2} Population of position 0.274(9).

In contrast to salt **2f**, in the unit cell of salt **2d** there are two structurally nonequivalent tetrazolium cations and two perchlorate anions. Comparison of data from structural analysis of the salts **2f** and **2d** indicates that the nature of the substituents has little effect on the parameters of the 1,3-disubstituted tetrazole ring. The bond lengths and the values of the corresponding angles in the cations of salt **2d** differ little and are close to the analogous characteristics of the salt **2f**. In the rings of the cations of compound **2d** the shortest is the $N_{(2)}$–$N_{(3)}$

TABLE 6. The Coordinates (in Unit Cell Fractions, $\times 10^4$) and Equivalent Isotropic Temperature Factors of the Atoms in the Structure of Salt **2f**

Atom	*x/a*	*y/b*	*z/c*	*U*(eq) ($Å^2 \times 10^3$)
$N_{(1)}$	5367(2)	3762(2)	3467(1)	50(1)
$N_{(2)}$	5273(3)	2690(2)	3559(1)	50(1)
$N_{(3)}$	3809(3)	2546(2)	3931(2)	51(1)
$N_{(4)}$	2936(3)	3468(2)	4081(2)	65(1)
$C_{(5)}$	3953(4)	4220(2)	3787(2)	62(1)
$C_{(6)}$	6926(4)	4292(2)	3080(2)	63(1)
$C_{(7)}$*	6048(9)	5074(6)	2319(6)	104(3)
$C_{(8)}$*	7992(11)	4860(7)	3901(5)	123(3)
$C_{(9)}$*	7968(9)	3424(4)	2671(6)	99(2)
$C_{(7')}$*[2]	6590(30)	5526(19)	2940(30)	87(9)
$C_{(8')}$*[2]	8620(30)	4000(60)	3770(40)	190(30)
$C_{(9')}$*[2]	6880(70)	3730(40)	2090(30)	160(20)
$C_{(10)}$	3208(4)	1464(2)	4145(2)	66(1)
$C_{(11)}$	1861(5)	1400(3)	4653(3)	100(1)
$C_{(12)}$	4207(6)	589(2)	3784(3)	106(1)
$Cl_{(1)}$	7465(1)	2615(1)	6145(1)	64(1)
$O_{(1)}$*[3]	7123(7)	1980(5)	6985(5)	81(2)
$O_{(2)}$*[3]	5795(11)	3097(9)	5800(8)	116(3)
$O_{(3)}$*[3]	8970(16)	3265(11)	6290(9)	157(4)
$O_{(4)}$*[3]	7822(13)	1800(5)	5429(5)	97(2)
$O_{(1')}$*[4]	7240(40)	2140(20)	6779(14)	203(13)
$O_{(2')}$*[4]	6260(40)	3293(13)	5657(13)	140(8)
$O_{(3')}$*[4]	8490(20)	3539(10)	6580(12)	98(5)
$O_{(4')}$*[4]	8340(40)	2090(20)	5650(20)	191(11)

* Population of position 0.82(2).
*[2] Population of position 0.18(2).
*[3] Population of position 0.67(2).
*[4] Population of position 0.33(2).

bond, and this once again demonstrates that the centers of quaternization and localization of the positive charge in the tetrazole ring do not coincide and also that there is substantial conjugation in the $N_{(1)}$–$N_{(2)}$=$N_{(3)}$ fragment. Further evidence for this can be obtained from the fact that exhaustive *tert*-butylation of tetrazole, 1-*tert*-butyltetrazole [10], and 2-*tert*-butyltetrazole gave salts having identical spectral and physicochemical characteristics and not giving melting point depressions in mixed melting tests.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Tesla BS 567A spectrometer at 100 Hz (DMS0-d_6). The initial tetrazoles were obtained by the familiar procedures: 2-isopropyl- and 2-*tert*-butyltetrazoles – according to [18]; 2-(1-methylvinyl)- and 2-(2-bromo-1-methylethyl)tetrazole – [19]; 2-(3-oxobutyl)tetrazole – [20]. 2-Methyl-, 2-ethyl-, and 2-allyltetrazoles were obtained by alkylation of tetrazole with alkyl halides according to the method [21].

Procedure for the Synthesis of Salts 2. To solution of tetrazole **1** (0.045 mol) in 7.4 ml of 72% perchloric acid we added 4 ml (0.045 mol) of *tert*-butanol. The mixture was kept at room temperature for 48 h. The final product **2** was precipitated by the addition of 40 ml of water, the solution was cooled to 0°C, and the product was recrystallized from ethanol. If 62% perchloric acid was used its volume was 9.4 ml. The quaternization of tetrazole with diacetone alcohol was conducted similarly. The yields of the salts are reported in Tables 1 and 2.

Treatment of Salts 2a,b in Perchloric Acid. Solution of the salt (0.018 mol) in 72% perchloric acid (20 ml) was kept at room temperature for 4 days. The product was precipitated by the addition of water (60 ml), and the solution was then cooled to 0°C. The yields of the salts **2a**,**b** were 52 and 44% respectively. In the case of the salt **2a** tetrazole **1a** was isolated with a yield of 40% by further extraction of the aqueous solution with chloroform and distillation of the latter. Its characteristics agreed with published data [18].

Dehydrobromination of Salt 2g. To solution of the salt **2g** (8.4 g, 0.024 mol) in ethanol (150 ml) we added dropwise solution of sodium hydroxide (1 g, 0.025 mol) in ethanol (150 ml). The mixture was stirred at room temperature for 1 h. Ethanol was removed under vacuum. The residue was recrystallized from isopropyl alcohol. Yield of the salt **2f** 3.0 g (0.011 mol, 47%).

X-ray Diffraction Investigation of Compound 2d. Single crystals of the salt **2d** were obtained by crystallization from ethanol at 298 K. A prismatic crystal (0.78 × 0.76 × 0.56 mm in size) was selected for X-ray crystallographic analysis. A three-dimensional set of X-ray diffraction data was obtained on a Nicolet R3m automatic four-circle diffractometer with MoKα radiation, a graphite monochromator, a θ/2θ scan, and $2\theta_{max} = 55°$. The total number of measured reflections was 7274, and the number of unique reflections was 6674 ($R_{int} = 0.0098$). The compound crystallizes in the triclinic system in space group $P1$. The parameters of the unit cell were as follows: $a = 10.280(3)$, $b = 12.374(3)$, $c = 13.534(4)$ Å; $\alpha = 64.02(2)$, $\beta = 76.49(2)$, $\gamma = 69.74(2)°$; $V = 1445.0(7)$ Å^3; $Z = 4$; $d_{X\text{-ray}} = 1.300$ g/cm^3; $\mu = 2.77$ cm^{-1}. The structure of the compound was interpreted by the direct method (SIR97 [22]). The positions of the hydrogen atoms were calculated by geometry. Refinement (SHELX-97 [23]) was made by full-matrix least-squares treatment with allowance for the anisotropy of the thermal vibrations of the nonhydrogen atoms. The hydrogen atoms were refined using the "rider" model. The final values of the uncertainty factors were: $R_1 = 0.0593$, $wR_2 = 0.1772$ ($I > 2\sigma(I)$); $R_1 = 0.0777$, $wR_2 = 0.1936$ (all data); goodness of fit, $GOOF = 1.080$. Absorption was not taken into account. The coordinates and the equivalent isotropic temperature factors of the atoms are given in Table 5.

X-ray Crystallographic Investigation of Compound 2f. Single crystals of the salt **2f** were obtained by crystallization from ethanol at 298 K. A prismatic crystal (0.60 × 0.52 × 0.48 mm in size) was selected for X-ray crystallographic analysis. In view of its instability in air the crystal was sealed in a glass capillary. A three-dimensional set of X-ray diffraction data was obtained on a Nicolet R3m automatic four-circle diffractometer with MoKα radiation, a graphite monochromator, a θ/2θ scan, and $2\theta_{max} = 55°$. The total number of measured reflections was 3184, and the number of unique reflections was 2863 ($R_{int} = 0.0183$). The compound crystallizes in the monoclinic system, space group $P2_1/n$. The unit cell parameters were as follows: $a = 7.514(3)$, $b = 12.192(4)$, $c = 14.367(6)$ Å; $\beta = 97.86°$; $V = 1303.8(9)$ Å^3; $Z = 4$; $d_{X\text{-ray}} = 1.359$ g/cm^3; $\mu = 3.03$ cm^{-1}. The structure was interpreted by the direct method (SIR97 [22]). Refinement (SHELX-97 [23]) was made by full-matrix least-squares treatment with allowance for the anisotropy of the thermal vibrations of the nonhydrogen atoms. The hydrogen atoms were treated as for the compound **2d**. The final values of the uncertainty factor were: $R_1 = 0.0651$, $wR_2 = 0.1777$ ($I > 2\sigma(I)$); $R_1 = 0.0866$, $wR_2 = 0.1989$ (all data); goodness of fit, $GOOF = 1.025$. Absorption was not taken into account. The coordinates and the equivalent isotropic temperature factors of the atoms are given in Table 6.

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