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Dedicated to Full Member of the Russian Academy of Sciences V.A. Tartakovskii on the 70th Anniversary of His Birth

Tetrazoles: XLIV.* Synthesis and Chemical Properties of 5-Substituted 2-Triphenylmethyltetrazoles**

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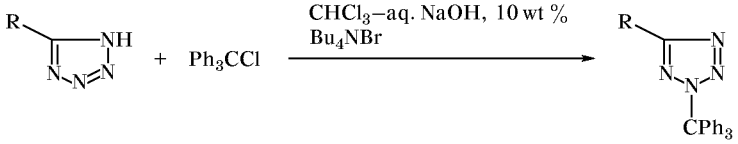
Abstract—Tritylation of tetrazole and its 5-substituted derivatives with triphenylmethyl chloride under conditions of phase-transfer catalysis regioselectively yields the corresponding 5-substituted 2-trityltetrazoles which can be used to protect N–H bonds in nitrogen-containing heterocycles and O–H bonds in primary alcohols. Thermolysis of 2-trityltetrazoles in benzonitrile leads to 3,6-disubstituted 1,2,4,5-tetrazines. Thermal transformation of the same compounds in dodecane follows a radically different mechanism, resulting in formation of difficultly accessible 8,8-diphenylheptafulvenes. The structure of the latter was proved by X-ray analysis.

Temporary protection of the N–H bond in tetrazoles is necessary when these compounds are used in the synthesis of drugs [2–8] and complex ligands for biomimetic studies [9], as well as in the functionalization of tetrazole [10–12] and 5-substituted tetrazoles [13–15]. It was noted that triphenylmethyl group, whose protective properties are determined mainly by steric factor, is superior to the other groups which are commonly used to protect the tetrazole N–H bond [2, 3, 6, 16]. The reason is that introduction of trityl group into a substrate molecule is always regioselective and almost is not accompanied by side processes which could reduce the yield of the tritylation product.

It was shown previously [9, 13, 17] that treatment of 5-methyl- and 5-aryltetrazoles with triphenylmethyl chloride or 4,4′-dimethoxytriphenylmethyl chloride under conditions of phase-transfer catalysis gives the corresponding N^2-trityl derivatives in high yield. From the preparative viewpoint, advantages of the phase-transfer procedure are obvious. Unlike noncatalytic methods, this procedure does not require the use of anhydrous solvents and inert atmosphere.

Scheme 1.



Ia–Im **IIa–IIm**

I, R = H (**a**), Me (**b**), $PhCH_2$ (**c**), PhCH(Et) (**d**), $PhOCH_2$ (**e**), 4-$CH_3OC_6H_4$ (**f**), Ph (**g**), 4-ClC_6H_4 (**h**), 4-$NO_2C_6H_4$ (**i**), CH_3S (**j**), PhS (**k**), 3-pyridyl (**l**), 4-pyridyl (**m**).

* For communication XLIII, see [1].

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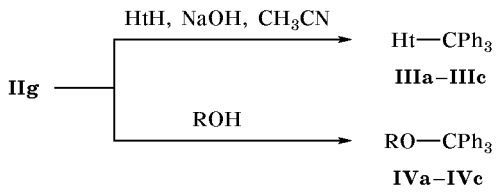
In continuation of our studies in the field of N–H bond protection in tetrazole derivatives, we examined tritylation of tetrazole and a series of 5-substituted tetrazoles under conditions of phase-transfer catalysis. The reactions were carried out at 20°C in a two-phase system consisting of aqueous sodium hydroxide and chloroform, and tetrabutylammonium bromide was used as phase-transfer catalyst. These conditions ensured a high rate of the process, and the corresponding N^2-trityl derivatives were formed in 40–93% yield (Scheme 1). Presumably, the relatively low yield (24%) of tetrazole **IId** is explained by steric effect of the 5-substituent.

Chemical properties of *N*-trityltetrazoles have been studied very poorly. It is known that treatment of 5-methyl-2-trityl- and 5-(2-biphenylyl)-2-trityltetrazoles with acetic, trifluoroacetic, hydrochloric, and sulfuric acids results in removal of the trityl protection [2, 3, 6, 13]. 2-Trityltetrazoles prepared by tritylation with triphenylmethyl chloride on a polymeric support [15] and 2-(4,4′-dimethoxytriphenylmethyl)-5-phenyltetrazole [9] are deprotected in a similar way. 2-Trityltetrazoles **IIa**–**IIm** follow the above general relations. They undergo smooth deprotection to the corresponding 5-substituted tetrazoles by the action of 15% hydrochloric acid at 20°C. On the other hand, 2-trityltetrazoles are relatively stable in weakly alkaline and neutral media, so that they can be used as reagents for protection of N–H bonds in nitrogen-containing heterocycles and O–H bonds in alcohols.

Heterocyclic substrates having an N–H bond can be tritylated with 2-trityltetrazoles in acetonitrile at 80°C. Analogous reactions with alcohols occur on heating at the boiling point (Scheme 2).

Scheme 2.



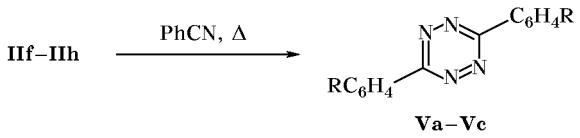
III, Ht = 1-imidazolyl (**a**), 1-benzimidazolyl (**b**), 1-benzotriazolyl (**c**); **IV**, R = Me (**a**), Et (**b**), Pr (**c**).

It is important that the tritylation of alcohols occurs in neutral medium and that secondary hydroxy groups are not involved. The low reactivity of 2-trityltetrazoles toward secondary alcohols is likely to result from steric hindrances in the reagent, created by the triphenylmethyl group. For example, 5-phenyl-2-trityltetrazole does not undergo quaternization by the action of dimethyl sulfate even on heating to 100°C. Less sterically crowded compounds, e.g., 5-substituted 2-*tert*-butyltetrazoles smoothly react with dimethyl sulfate at 60°C [18]. Thus, the use of 2-trityltetrazoles is expected to be most efficient in the protection of O–H bonds in primary alcohols which are insufficiently stable in basic medium.

Studies of thermal transformations of nitrogen-containing heterocycles constitute a promising and extensively developing field in heterocyclic chemistry [19–22]. Beginning with the first Huisgen works, i.e., over a period of more than 40 years, tetrazoles have persistently become the most interesting subjects of these studies. Just the results obtained by studying thermolysis of 2,5-substituted tetrazoles [23, 24] made it possible to formulate a general and fundamental concept of formation of 1,3-dipoles and their participation in 1,3-dipolar cycloaddition and 1,5-electrocyclization processes [25]. From the preparative viewpoint, thermolysis of 2,5-disubstituted tetrazoles is a universal method for preparation of various heterocycles, from pyrazoles, 1,2,4-triazoles, and 1,3,4-oxadiazoles to 3*H*-1,3,4-benzotriazepines [26–28].

The reactivity of 1,3-dipoles generated by thermolysis of 2,5-disubstituted tetrazoles strongly depends on the substituent in position 2 of the heteroring and properties of the reaction medium. The effect of these factors is clearly seen in the thermolysis of 5-substituted 2-trityltetrazoles. Heating of tetrazoles **IIf**–**IIh** in benzonitrile at 150°C leads to formation of the corresponding 3,6-disubstituted 1,2,4,5-tetrazines **Va**–**Vc** in 41–72% yield (Scheme 3).

Scheme 3.



V, R = 4-MeO (**a**), H (**b**), 4-Cl (**c**).

Analogous results were obtained previously [29] while studying thermolysis of 5-phenyltetrazole in mesitylene, as well as on treatment of the same compound with *p*-toluenesulfonyl chloride in pyridine [30]. It should be noted that in the first case the only product was 3,6-diphenyl-1,2,4,5-tetrazine, while in the latter process 3,6-diphenyl-2,3-bis(*p*-tolylsulfonyl)-1,2,4,5-tetrazine was formed in addition to 3,6-diphenyl-1,2,4,5-tetrazine. Presumably, thermal transformations of 5-phenyltetrazole, its *N*-sulfonyl derivatives, and 5-substituted 2-trityltetrazoles follow

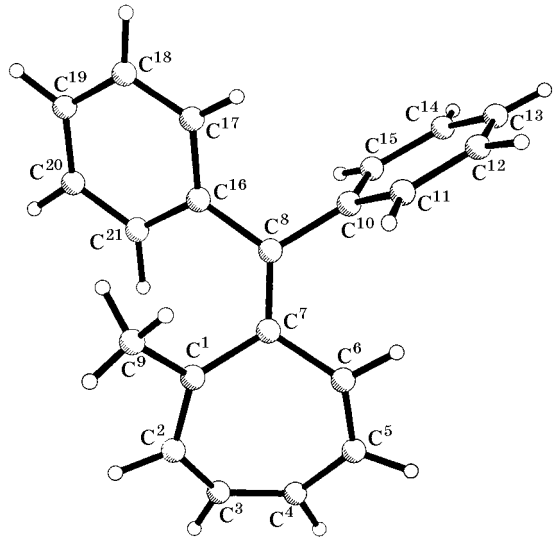


Fig. 1. Structure of the molecule of 1-methyl-8,8-diphenylheptafulvene (**VIa**) according to the X-ray diffraction data.

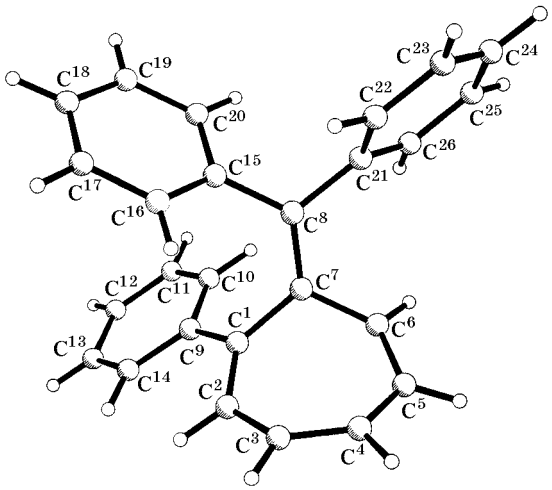


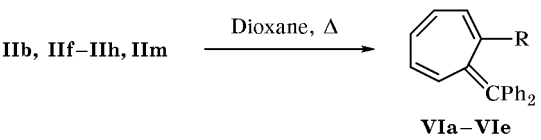
Fig. 2. Structure of the molecule of 1,8,8-triphenylheptafulvene (**VIb**) according to the X-ray diffraction data.

a common mechanism involving intermediate formation of the corresponding 1,3-dipoles, whose dimerization leads to tetrazines.

Quite surprising results were obtained while studying thermolysis of 2-trityltetrazoles in dodecane at 180°C. Formerly, we proposed that this process leads to formation of the corresponsing *o*-quinodimethanes [17]. Here, the following considerations were taken into account. Thermal transformation of 2-trityltetrazoles is likely to include cleavage of the heteroring and subsequent loss of nitrogen molecule to give 1,3-dipole. The latter undergoes 1,6-electrocyclization to 1,4-dihydrophthalazine. It is known that 1,4-dihydrophthalazines are widely used in the synthesis of *o*-quinodimethanes [31, 32]. Thus there are reasons to believe that thermolysis of 2-trityltetrazoles results in formation of *o*-quinodimethanes. It should be noted that the data of elemental analysis, UV, IR, and ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry for all products obtained by thermolysis of tetrazoles **IIb** and **IIf**–**IIh** do not contradict possible *o*-quinodimetane structures. On the other hand, the thermolysis products are characterized by high thermal stability and low reactivity, e.g., in the cycloaddition with tetracyanoethylene. These properties are inconsistent with the generally accepted views, according to which *o*-quinodimethanes are highly reactive intermediates generated by thermolysis of of benzocyclobutenes, 1,4-dihydrophthalazines, and some other substrates [32]. Although some fairly stable *o*-quinodimethanes have been reported in the recent years [33, 34], these cases are likely to be an exception rather than a rule.

The above discrepancies were eliminated by the results of X-ray diffraction study of the thermolysis products obtained from 5-methyl- and 5-phenyl-2-trityltetrazoles. It was shown that thermal transformation of 5-substituted 2-trityltetrazoles leads not to *o*-quinodimethanes but to isomeric 1-substituted 8,8-diphenylheptafulvenes **VIa**–**VIe** (Scheme 4).

Scheme 4.



VIa–VIe

VI, R = Me (**a**), Ph (**b**), 4-$CH_3OC_6H_4$ (**c**), 4-ClC_6H_4 (**d**), 4-pyridyl (**e**).

The corresponding X-ray diffraction data are given below. Figures 1 and 2 show molecular structures of heptafulvenes **VIa** and **VIb**, and the principal bond lengths and bond angles are presented in Table 1. For comparison, Table 1 also contains published data for 1-isopropyl-8,8-dicyano- and 8,8-dicyano-1,6-dimethylheptafulvenes **VIIa** and **VIIb** [35, 36], which are the closest structural analogs of **VIa** and **VIb**.

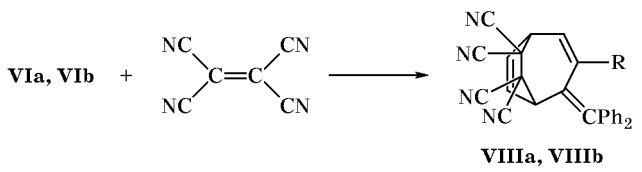
The seven-membered ring in molecules **VIa** and **VIb** has a deep *boat* conformation, whereas the same ring in 8,8-dicyanofulvene is almost planar [37]. The conformations of the different compounds can be compared using the angles α, β, γ, and δ, which are shown in Figs. 3 and 4 and given in Table 2. Analysis of these data indicates that the angle α changes only slightly in going from one structure to another, while

consderable differences are observed in the angle γ, depending on the substituent in position *1*. It attains its maximal value for compound **VIIb** having a phenyl group in that position. By contrast, the angle δ appreciably decreases. The depth of the *boat* along the other axis is characterized by the dihedral angle α. In this case, the maximal deviation from planarity is also typical of structure **VIIb**. The most appreciable differences are observed in the C^1-C^7 and C^7-C^8 bond lengths. The C^1-C^7 bond becomes longer while the exocyclic double $C^7=C^8$ bond becomes shorter as the *boat* depth increases. The reason is increase of the torsion angles C^1–C^7 and C^6–C^7, which reduces the degree of overlap of *p*-orbitals. The bond lengths and angles indicate an insignificant contribution of dipolar structure, which was assumed for unsubstituted 8,8-dicyanoheptafulvene on the basis of its large dipole moment, 7.5 D [37]. The substituents at the exocyclic double bond do not lie in one plane, and the maximal deviation is observed for compound **VIIb**. An analogous effect was noted previously for 8,8-dicyano-1-isopropylheptafulvene [35].

The C^7 and C^8 atoms are characterized by a small degree of pyramidality. The C^7 atom in molecule **VIa** is located above the plane formed by the adjacent carbon atoms (the corresponding deviation is 0.05 Å), whereas the C^8 atom lies in that plane. By contrast, the C^7 atom in **VIb** lies in the plane formed by the neighboring carbon atoms, while C^8 deviates from it by 0.02 Å.

Our results show that both electronic and steric factors should be taken into account in order to interpret structural parameters and reactivity of substituted 8,8-diphenylheptafulvenes. According to Komatsu *et al.* [38], [4+2]-cycloaddition of 8,8-diphenylheptafulvene to tetracyanoethylene in benzene at 20°C in 4.5 h gives the corresponding product in 62% yield. The reactions of 1-methyl-8,8-diphenylheptafulvene (**VIa**) and 1,8,8-triphenylheptafulvene (**VIb**) with tetracyanoethylene under the same conditions gave only 54 and 65% of the corresponding cycloadducts in 30 days (Scheme 5).

Scheme 5.



VIIIa, VIIIb

VIII, R = Me (**a**), Ph (**b**).

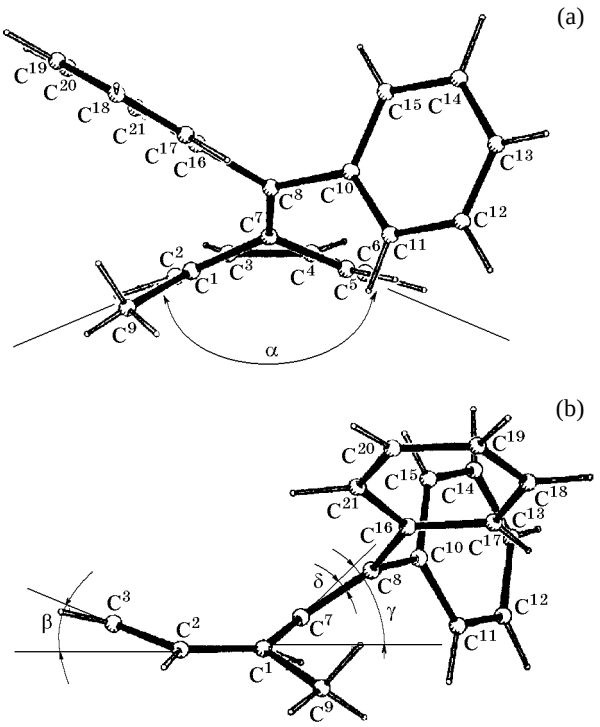


Fig. 3. Projections of the molecule of 1-methyl-8,8-diphenylheptafulvene (**VIb**) with respect to different planes: (a) angle α and (b) angles β, γ, and δ.

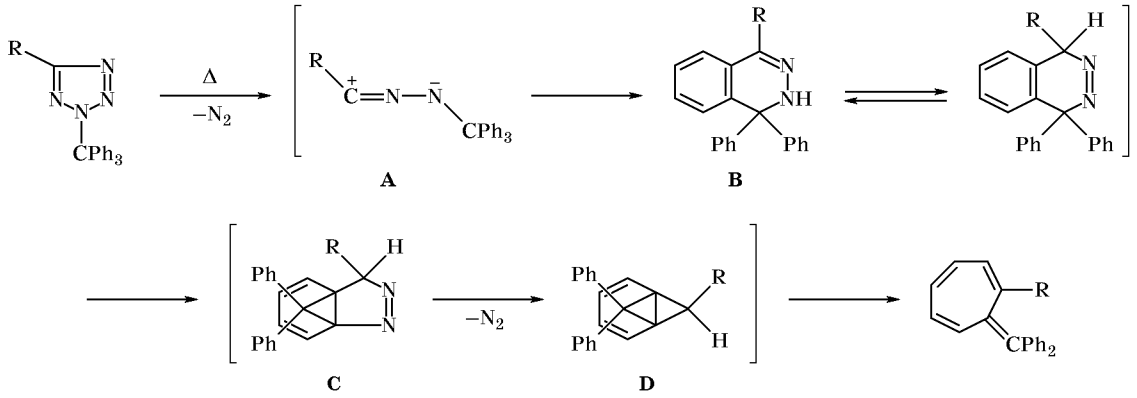
Thus, detailed analysis of our present experimental data and available information on the thermolysis of 2,5-disubstituted tetrazoles and on the method for preparation of 1,3,5-cycloheptatrienes allowed us to propose a probable mechanism of thermal transformations of 5-substituted 2-trityltetrazoles into 1-substituted 8,8-diphenylheptafulvenes (Scheme 6). In the first stage, cleavage of the tetrazole ring occurs with loss of nitrogen molecule to give 1,3-dipole **A**. Its 1,6-electrocyclization yields 1,4-dihydrophthalazine **B**. The key stage in the further transformations is the conversion of 1,4-dihydrophthalazine **B** into 3,4-dihydro-3*H*-pyrazole **C**. The latter gives rise to final 8,8-diphenylheptafulvene through intermediate **D**, following the known scheme [39, 40].

To conclude, it should be noted that thermolysis of 5-substituted 2-trityltetrazoles may be regarded as a new method for preparation of difficultly accessible 1-substituted 8,8-diphenylheptafulvenes.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr. The IR spectrum of **VIb** was taken on a Perkin–Elmer Spectrum BX-1000 instrument. The electron spectrum of **VIb** was measured on

Scheme 6.



a Perkin Elmer Lambda 40 spectrophotometer. The mass spectra (70 eV) were run on an MKh-1321 mass spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-200 instrument in DMSO-d_6 (compounds **IIa**–**IIm**, **IIIa**, **Va**–**Vc**, **VIa**, **VIc**, **VIe**, and **VIIIa**) or $CDCl_3$ (**VIb**, **VId**, and **VIIIb**).

Crystals of compound **VIa**, suitable for X-ray analysis, were obtained by recrystallization from 2-propanol. Pink prisms, mp 114–115°C, crystal habit $0.46 \times 0.10 \times 0.06$. The unit cell parameters and reflection intensities were measured on an Enraf–Nonius CAD-4 diffractometer (MoK_α-irradiation, $\theta/2\theta$ scanning). Tetragonal crystals: a = 32.493(5), c = 5.844(1) Å; V = 6170.1(17) Å^3; d_{calc} = 1.164 g/cm^3; space group $I4_1/a$; Z = 16. The structure was solved by the direct method; R = 0.025, R_w = 0.058 [from 1672 reflections with $I > 2\sigma(I)$]. A correction for X-ray absorption by the sample (0.066 cm^{-1}) was introduced.

Crystals of **VIb** were obtained by recrystallization from acetonitrile. Yellow prisms, mp 106–108°C, crystal habit $0.56 \times 0.40 \times 0.20$. Triclinic crystals: a = 6.2680(10), b = 8.444(2), c = 17.677 Å; α = 93.48, β = 98.88(3), γ = 93.51(3)°; V = 920.3(3) Å^3, d_{calc} = 1.164 g/cm^3; space group $P\bar{1}$; Z = 2. The structure was solved by the direct method: R = 0.0291, R_w = 0.0739 [from 2198 reflections with $I > 2\sigma(I)$]. A correction for X-ray absorption by the sample (0.066 cm^{-1}) was introduced.

2-Trityltetrazole (IIa). A mixture of 2.5 mmol of 5-phenyltetrazole, 0.2 mmol of tetrabutylammonium bromide, 10 ml of 10% aqueous sodium hydroxide, and 10 ml of chloroform was stirred for 15 min at 20°C. A solution of 3 mmol of triphenylmethyl

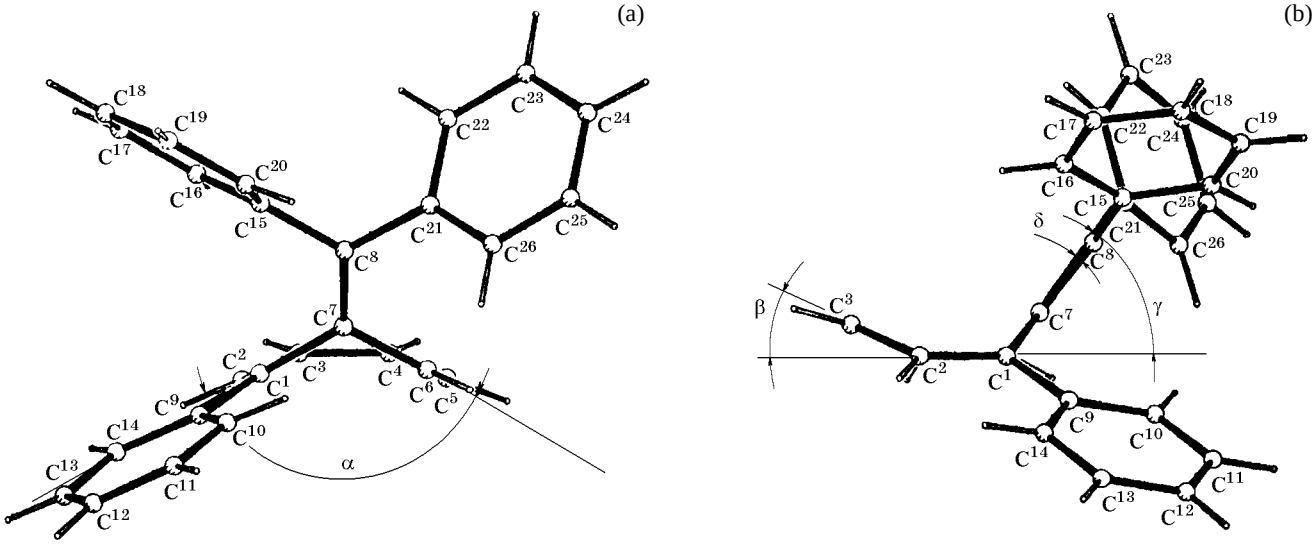


Fig. 4. Projections of the molecule of 1,8,8-triphenylheptafulvene (**VIb**) with respect to different planes: (a) angle α and (b) angles β, γ, and δ.

chloride in 20 ml of chloroform was added, and the mixture was stirred for 4 h at 20°C. The organic phase was separated, washed with 5 ml of 10% aqueous sodium hydroxide and water (2 × 10 ml), dried over sodium sulfate, and evaporated to dryness. Yield 0.53 g (67%), mp 212°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 930, 960, 1010, 1020, 1040, 1090, 1140, 1150, 1170, 1190, 1280, 1330, 1390, 1450, 1500, 1600, 2940, 3040, 3080. ^{1}H NMR spectrum, δ, ppm: 6.90–7.40 m (15H, H_{arom}), 8.90 s (1H, CH). Found, %: C 76.51; H 5.28; N 17.61. $C_{20}H_{16}N_4$. Calculated, %: C 76.92; H 5.13; N 17.95.

Tetrazoles **IIb**–**IIm** were synthesized by a similar procedure.

5-Methyl-2-trityltetrazole (IIb). Yield 60%, mp 178°C [11] (from ethyl acetate). IR spectrum, ν, cm^{-1}: 890, 910, 930, 1010, 1030, 1040, 1090, 1170, 1190, 1290, 1330, 1360, 1390, 1450, 1500, 1520, 1600, 2970, 3040, 3070. ^{1}H NMR spectrum, δ, ppm: 3.10 s (3H, CH_3), 6.90–7.20 m (6H, H_{arom}), 7.30–7.45 m (9H, H_{arom}).

5-Benzyl-2-trityltetrazole (IIc). Yield 56%, mp 154°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1005, 1025, 1040, 1095, 1160, 1195, 1290, 1340, 1390, 1460, 1500, 1610, 2860, 2940, 3050, 3080. ^{1}H NMR spectrum, δ, ppm: 4.60 s (2H, CH_2), 7.00–7.50 m (20H, H_{arom}). Found, %: C 80.50; H 5.54; N 13.96. $C_{27}H_{22}N_4$. Calculated, %: C 80.60; H 5.47; N 13.93.

5-(1-Phenylpropyl)-2-trityltetrazole (IId). Yield 24%, mp 110°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 890, 910, 940, 1005, 1050, 1070, 1095, 1160, 1195, 1240, 1290, 1390, 1450, 1500, 1605, 2890, 2950, 2980, 3040, 3080. ^{1}H NMR spectrum, δ, ppm: 0.70–0.90 m (3H, CH_3), 1.90–2.30 m (2H, CH_2), 4.20–4.30 t (1H, CH), 6.90–7.50 m (20H, H_{arom}). Found, %: C 81.05; H 5.97; N 13.10. $C_{29}H_{26}N_4$. Calculated, %: C 80.93; H 6.05; N 13.02.

5-Phenoxymethyl-2-trityltetrazole (IIe). Yield 58%, mp 145°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 880, 920, 940, 990, 1010, 1030, 1040, 1080, 1150, 1160, 1185, 1195, 1220, 1240, 1270, 1300, 1330, 1360, 1405, 1450, 1500, 1600, 2850, 2930, 2970, 3040, 3090. ^{1}H NMR spectrum, δ, ppm: 5.45 s (2H, CH_2), 6.90–7.40 m (20H, H_{arom}). Found, %: C 77.65; H 5.31; N 13.49. $C_{27}H_{22}N_4O$. Calculated, %: C 77.51; H 5.26; N 13.40.

5-(4-Methoxyphenyl)-2-trityltetrazole (IIf). Yield 55%, mp 186°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1000, 1040, 1070, 1100, 1150, 1170, 1190, 1230, 1280, 1300, 1330, 1390, 1450, 1500, 1580, 1600, 2900, 2950, 2990, 3050. ^{1}H NMR spectrum, δ, ppm: 3.82 s (3H, CH_3O), 6.95–7.40 m (17H, H_{arom}), 8.00 m (2H, H_{arom}). Found, %: C 77.56; H 5.48; N 13.44. $C_{27}H_{22}N_4O$. Calculated, %: C 77.51; H 5.26; N 13.40.

5-Phenyl-2-trityltetrazole (IIg). Yield 93%, mp 155–156°C (from butyl acetate); published data

Table 1. Principal bond lengths *d* and bond angles ω in molecules **VIa**, **VIb**, **VIIa**, and **VIIb**

Parameter	**VIa**	**VIb**	**VIIa**	**VIIb**
Bond	*d*, Å			
C^1-C^2	1.348 (6)	1.346 (2)	1.361 (9)	1.342 (8)
C^2-C^3	1.425 (7)	1.440 (2)	1.443 (12)	1.420 (8)
C^3-C^4	1.329 (6)	1.339 (3)	1.347 (15)	1.338 (8)
C^4-C^5	1.432 (6)	1.431 (3)	1.426 (14)	1.410 (8)
C^5-C^6	1.339 (5)	1.341 (3)	1.343 (11)	1.335 (7)
C^6-C^7	1.466 (5)	1.478 (2)	1.474 (9)	1.460 (8)
C^7-C^1	1.477 (6)	1.494 (2)	1.471 (8)	1.470 (7)
C^7-C^8	1.347 (5)	1.342 (2)	1.367 (8)	1.361 (8)
C^1-C^9	1.522 (7)	1.489 (2)	1.535 (8)	1.507 (11)
Angle	ω, deg			
$C^2C^1C^7$	124.4 (4)	118.84 (14)	122.8 (5)	121.8 (5)
$C^2C^1C^9$	117.7 (5)	121.60 (14)	119.9 (5)	120.9 (6)
$C^7C^1C^9$	117.7 (5)	119.53 (12)	117.3 (5)	117.2 (5)
$C^1C^2C^3$	128.2 (5)	127.66 (16)	130.3 (7)	129.5 (5)
$C^4C^3C^2$	127.1 (6)	126.26 (19)	125.4 (9)	125.2 (5)
$C^3C^4C^5$	126.1 (5)	126.12 (17)	127.4 (10)	127.1 (5)
$C^6C^5C^4$	126.9 (5)	125.28 (18)	127.4 (8)	128.3 (5)
$C^5C^6C^7$	127.2 (5)	122.84 (17)	126.7 (7)	123.2 (5)
$C^8C^7C^6$	121.5 (4)	122.72 (13)	118.6 (5)	122.6 (4)
$C^8C^7C^1$	123.5 (4)	124.28 (13)	123.2 (5)	122.0 (4)
$C^6C^7C^1$	114.5 (4)	112.99 (12)	117.8 (5)	115.2 (4)

Table 2. Dihedral angles α, β, γ, and δ[a] in molecules **VIa**, **VIb**, **VIIa**, and **VIIb**

Comp. no.	α	β	γ	δ
VIa	134.4	20.9	39.1	6.1
VIb	125.2	24.8	51.0	0.6
VIIa	137.9	19.5	37.3	5.6
VIIb	131.9	20.1	45.3	4.0

[a] See Figs. 3 and 4.

[10]: mp 158–160°C. IR spectrum, ν, cm^{-1}: 930, 1005, 1030, 1050, 1160, 1195, 1285, 1330, 1380, 1455, 1480, 1500, 1605, 2870, 2930, 3050, 3075. ^1H NMR spectrum, δ, ppm: 7.08–7.48 m (18H, H_{arom}), 8.03 m (2H, H_{arom}).

5-(4-Chlorophenyl)-2-trityltetrazole (IIh). Yield 51%, mp 187°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1010, 1020, 1040, 1100, 1160, 1200, 1270, 1330, 1420, 1450, 1500, 1610, 2860, 2940, 3030, 3070. ^1H NMR spectrum, δ, ppm: 7.10–7.50 m (15H, H_{arom}), 8.20 m (4H, H_{arom}). Found, %: C 74.08; H 4.46; N 13.35. $C_{26}H_{19}ClN_4$. Calculated, %: C 73.85; H 4.50; N 13.25.

5-(4-Nitrophenyl)-2-trityltetrazole (IIi). Yield 43%, mp 203°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1005, 1020, 1040, 1090, 1120, 1170, 1200, 1230, 1280, 1330, 1360, 1450, 1500, 1530, 1610, 2900, 2950, 2990, 3050. ^1H NMR spectrum, δ, ppm: 7.10–7.50 m (17H, H_{arom}), 8.10 m (2H, H_{arom}). Found, %: C 72.02; H 4.25; N 16.19. $C_{26}H_{19}N_5O_2$. Calculated, %: C 72.05; H 4.39; N 16.17.

5-Methylthio-2-trityltetrazole (IIj). Yield 60%, mp 139°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 940, 1005, 1030, 1040, 1060, 1090, 1150, 1170, 1190, 1220, 1285, 1300, 1390, 1450, 1500, 1590, 1605, 2860, 2949, 3040, 3070. ^1H NMR spectrum, δ, ppm: 2.64 s (3H, CH_3), 6.95–7.40 m (15H, H_{arom}). Found, %: C 70.35; H 5.16; N 15.66. $C_{21}H_{18}N_4S$. Calculated, %: C 70.39; H 5.01; N 15.64.

5-Phenylthio-2-trityltetrazole (IIk). Yield 42%, mp 122°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 920, 940, 1010, 1040, 1070, 1100, 1150, 1170, 1190, 1230, 1280, 1300, 1330, 1390, 1450, 1500, 1580, 1600, 2900, 2950, 2990, 3050. ^1H NMR spectrum, δ, ppm: 7.00–7.42 m (20H, H_{arom}). Found, %: C 74.39; H 4.56; N 13.36. $C_{26}H_{20}N_4S$. Calculated, %: C 74.28; H 4.76; N 13.30.

5-(3-Pyridyl)-2-trityltetrazole (IIl). Yield 40%, mp 167°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 880, 915, 1010, 1030, 1095, 1160, 1195, 1285, 1340, 1420, 1455, 1500, 1610, 2870, 2940, 3050, 3080. ^1H NMR spectrum, δ, ppm: 7.00–7.60 m (17H, H_{arom}), 8.30–8.50 m (1H, pyridine), 8.60–8.70 d (1H, pyridine), 9.10–9.30 s (1H, pyridine). Found, %: C 77.15; H 4.93; N 17.93. $C_{25}H_{19}N_5$. Calculated, %: C 77.12; H 4.88; N 17.99.

5-(4-Pyridyl)-2-trityltetrazole (IIm). Yield 69%, mp 201°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 910, 950, 1000, 1010, 1050, 1095, 1160, 1195, 1215, 1290, 1330, 1370, 1430, 1450, 1500, 1540, 1620, 2870, 2940, 3050, 3080. ^1H NMR spectrum, δ, ppm: 7.00–7.50 m (15H, H_{arom}), 7.90–8.10 m (2H, pyridine), 8.70–8.90 m (2H, pyridine). Found, %: C 77.19; H 4.92; N 17.89. $C_{25}H_{19}N_5$. Calculated, %: C 77.12; H 4.88; N 17.99.

1-Tritylimidazole (IIIa). A mixture of 0.2 mmol of imidazole, 0.2 mmol of 5-phenyl-2-trityltetrazole, and 0.3 mmol of NaOH in 10 ml of acetonitrile was heated for 10 h under reflux (80°C). After cooling, the precipitate was filtered off, and the filtrate was evaporated to dryness. Yield 0.45 g (72%), mp 212–215°C (from ethyl acetate); published data [41]: mp 210–212°C.

Compounds **IIIb** and **IIIc** were synthesized in a similar way.

1-Tritylbenzotriazole (IIIb). Yield 47%, mp 216–218°C (from ethyl acetate); published data [41]: mp 214–216°C.

1-Tritylbenzimidazole (IIIc). Yield 89%, mp 181–182°C (from ethyl acetate). ^1H NMR spectrum, δ, ppm: 6.40–6.50 d (1H, CH), 6.75–6.90 t (1H, H_{arom}), 7.05–7.45 m (16H, H_{arom}), 7.60–7.70 d (1H, H_{arom}), 7.80–7.90 s (1H, H_{arom}). Found, %: C 86.59; H 5.49; N 7.57. $C_{26}H_{20}N_2$. Calculated, %: C 86.67; H 5.55; N 7.77.

Methyl triphenylmethyl ether (IVa). 5-Phenyl-2-trityltetrazole, 0.13 mmol, was dissolved in 15 ml of methanol, and the solution was heated for 3 h under reflux. The mixture was diluted with 10 ml of 10% aqueous sodium hydroxide and allowed to settle down, and the precipitate was filtered off. Yield 1.4 g (71%), mp 82°C (from 2-propanol) [42].

Ethyl triphenylmethyl ether (IVb). 5-Phenyl-2-trityltetrazole, 0.13 mmol, was dissolved in 15 ml of ethanol, and the solution was heated for 4 h under reflux. The mixture was diluted with 10 ml of 10% aqueous sodium hydroxide and allowed to settle down, and the precipitate was filtered off. Yield 45%, mp 76°C (from 2-propanol) [42].

Propyl triphenylmethyl ether (IVc). 5-Phenyl-2-trityltetrazole, 0.13 mmol, was dissolved in 15 ml of 1-propanol, and the solution was heated for 18 h under reflux. The mixture was diluted with 10 ml of 10% aqueous sodium hydroxide and allowed to settle down, and the precipitate was filtered off. Yield 36%, mp 54°C (from 2-propanol) [42].

3,6-Diphenyl-1,2,4,5-tetrazine (Va). A mixture of 2.6 mmol of 5-phenyl-2-trityltetrazole and 10 ml of benzonitrile was heated for 5–7 h at 150°C. The mixture was then evaporated to dryness, and the solid tarry residue was treated with petroleum ether

(3 × 10 ml). Yield 0.2 g (65%), violet crystals with mp 189°C (from DMF) [43]. IR spectrum, ν, cm^{-1}: 810, 820, 900, 990, 930, 1030, 1070, 1090, 1150, 1370, 1440, 1470, 1570, 2965, 3130. ^1H NMR spectrum, δ, ppm: 7.50–7.80 m (3H, H_{arom}), 8.55–8.70 d (2H, H_{arom}). Found, %: C 71.94; H 4.15; N 23.84. $C_{14}H_{10}N_4$. Calculated, %: C 71.79; H 4.27; N 23.93.

3,6-Bis(4-chlorophenyl)-1,2,4,5-tetrazine (Vb). A mixture of 2.4 mmol of 5-(4-chlorophenyl)-2-trityltetrazole and 10 ml of benzonitrile was heated for 5–7 h at 150°C. After cooling, the violet solid was filtered off. Yield 0.26 g (77%), violet crystals with mp 303°C (from DMF). IR spectrum, ν, cm^{-1}: 810, 830, 910, 990, 930, 1010, 1060, 1090, 1150, 1370, 1440, 1470, 1570, 2980, 3110. ^1H NMR spectrum, δ, ppm: 7.65–7.80 d (2H, H_{arom}), 8.5–8.65 d (2H, H_{arom}). Found, %: C 55.63; H 2.57; Cl 23.22; N 18.73. $C_{14}H_8ClN_4$. Calculated, %: C 55.45; H 2.64; Cl 23.43: N 18.82.

3,6-Bis(4-methoxyphenyl)-1,2,4,5-tetrazine (Vc) was obtained in a similar way. Yield 41%, mp 250°C (from DMF) [43]. IR spectrum, ν, cm^{-1}: 835, 910, 1020, 1050, 1100, 1110, 1170, 1250, 1295, 1385, 1510, 1590, 2860, 2950, 2990. ^1H NMR spectrum, δ, ppm: 3.95–4.05 s (6H, CH_3), 7.10–7.30 d (2H, H_{arom}), 8.45–8.55 d (2H, H_{arom}). Found, %: C 65.41; H 14.71; N 18.97. $C_{16}H_{14}N_4O_2$. Calculated, %: C 65.31; H 14.76; N 19.05.

1-Methyl-8,8-diphenylheptafulvene (VIa). A mixture of 3 mmol of 5-methyl-2-trityltetrazole and 10 ml of dodecane was heated for 3 h at 170–180°C. After cooling, the yellow precipitate was filtered off. Yield 0.63 g (76%), mp 116°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 700, 760, 780, 800, 850, 930, 980, 1030, 1080, 1450, 1500, 1610, 2860, 2930, 3030. ^1H NMR spectrum, δ, ppm: 1.70 s (3H, CH_3), 5.80–6.50 m (5H, CH, H_{arom}), 7.00–7.40 m (10H, H_{arom}). Found, %: C 93.30; H 6.78. M^+ 270. $C_{21}H_{18}$. Calculated, %: C 93.33; H 6.67. *M* 270.

Heptafulvenes **VIb**–**VIe** were obtained by a similar procedure.

1,8,8-Triphenylheptafulvene (VIb). Yield 68%, mp 107–108°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 755, 859, 907, 1043, 1069, 1352, 1440, 1490, 1559, 1600, 1636, 3013. UV spectrum (ethanol), λ_{max}, nm (log ε): 240.58 (4.18), 268.85 (4.02), 324.28 (3.76). ^1H NMR spectrum, δ, ppm: 6.15 m (1H, CH), 6.42–7.42 m (19H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 125.7, 125.9, 126.1, 126.2, 126.5, 126.8, 127.2, 127.3, 127.5, 127.9, 128.0, 128.7, 129.0, 129.3, 130.1. Found, %: C 94.10; H 5.91. M^+ 332. $C_{26}H_{20}$. Calculated, %: C 93.97; H 6.03. *M* 332.

1-(4-Chlorophenyl)-8,8-diphenylheptafulvene (VIc). Yield 51%, mp 127°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 830, 870, 900, 1010, 1080, 1100, 1360, 1410, 1495, 1610, 1650, 3040, 3080. ^1H NMR spectrum, δ, ppm: 6.15 m (1H, CH), 6.25–7.40 m (18H, H_{arom}). Found, %: C 84.95; H 5.15. M^+ 367. $C_{26}H_{19}Cl$. Calculated, %: C 85.13; H 5.18. *M* 366.5.

1-(4-Methoxyphenyl)-8,8-diphenylheptafulvene (VId). Yield 49%, mp 133°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 830, 870, 900, 1020, 1070, 1100, 1360, 1410, 1460, 1490, 1600, 1640, 3040, 3080. ^1H NMR spectrum, δ, ppm: 3.63 s (3H, CH_3O), 6.10 m (1H, CH), 6.20–7.40 m (18H, H_{arom}). Found, %: C 89.75; H 6.20. $C_{27}H_{22}O$. Calculated, %: C 89.50; H 6.08.

1-(4-Pyridyl)-8,8-diphenylheptafulvene (VIe). Yield 45%, mp 133°C (from 2-propanol). IR spectrum, ν, cm^{-1}: 910, 920, 970, 1000, 1040, 1080, 1160, 1180, 1370, 1420, 1450, 1500, 1600, 3040, 3070, 3090. ^1H NMR spectrum, δ, ppm: 6.05–6.15 m (1H, CH); 6.42–7.42 m (19H, H_{arom}). Found, %: C 90.12; H 5.71; N 4.38. $C_{25}H_{19}N$. Calculated, %: C 90.09; H 5.70; N 4.21.

4-Diphenylmethylene-3-methylbicyclo[3.2.2]-nona-2,6-diene-8,8,9,9-tetracarbonitrile (VIIIa). 1-Methyl-8,8-diphenylheptafulvene, 0.17 mmol, was dissolved in 10 ml of benzene, and a solution of 0.17 mmol of tetracyanoethylene in 10 ml of benzene was added. The mixture was kept for 30 days at room temperature and evaporated, and the residue was treated with petroleum ether. Yield 0.26 g (54%), mp 142–143°C (from EtOH–H_2O). IR spectrum, ν, cm^{-1}: 800, 830, 890, 950, 1000, 1030, 1070, 1160, 1280, 1320, 1370, 1440, 1490, 1570, 1620, 2350, 3050, 3440. ^1H NMR spectrum, δ, ppm: 1.40 s (3H, CH_3), 3.80 t (1H, CH), 4.40 d (1H, CH), 5.75 d (1H, CH), 6.35 t (1H, CH), 6.70 t (1H, CH), 6.90–7.40 m (10H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 24.7, 41.92, 43.65, 46.67, 50.32, 112.31, 112.77, 113.59, 124.91, 127.52, 128.28, 128.36, 128.44, 128.84, 128.97, 129.16, 129.29, 133.18, 138.77, 141.77, 142.25, 148.43. Found, %: C 81.48; H 4.71; N 13.98. $C_{27}H_{18}N_4$. Calculated, %: C 81.41; H 4.52; N 14.07.

4-Diphenylmethylene-3-phenylbicyclo[3.2.2]-nona-2,6-diene-8,8,9,9-tetracarbonitrile (VIIIb) was synthesized in a similar way. Yield 65%, mp 225–226°C (from ethyl acetate). IR spectrum, ν, cm^{-1}: 855, 965, 1030, 1074, 1280, 1440, 1490, 1600, 2250,

3060, 3450, 3650. ^{1}H NMR spectrum, δ, ppm: 4.00 t (1H, CH), 4.65 d (1H, CH), 5.90 d (1H, CH), 6.40 t (1H, CH), 6.70 t (1H, CH), 6.90–7.50 m (15H, H_{arom}). ^{13}C NMR spectrum, δ, ppm: 38.02, 39.27, 42.55, 45.84, 108.01, 108.40, 108.54, 109.34, 121.49, 122.59, 123.22, 123.73, 124.48, 125.03, 125.24, 126.14, 127.92, 137.36, 137.46, 140.47, 146.30. Found, %: C 83.87; H 4.03; N 11.99. $C_{32}H_{20}N_4$. Calculated, %: C 83.48; H 4.35; N 12.17.

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