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# *N*-Substituted Bis(tetrazol-5-yl)Diazenes: Synthesis, Spectra, X-ray Molecular and Crystal Structures, and Quantum-Chemical DFT Calculations

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ABSTRACT: *N-Substituted bis(tetrazol-5-yl)diazenes (substituents are 1-$CH_3$ (**3a**), 1-Ph (**3b**), 2-$CH_3$ (**3c**), and 2-$^t$Bu (**3d**)) were synthesized by oxidative coupling of corresponding 5-aminotetrazoles. All compounds were characterized with $^1H$ and $^{13}C$ NMR, IR- and UV-spectroscopy, and thermal analysis. Crystal and molecular structures of bis(1-phenyltetrazol-5-yl)diazene (**3b**) and bis(2-tert-butyltetrazol-5-yl)diazene (**3d**) were determined by single crystal X-ray diffraction. Molecules of these compounds are trans-isomers in solid. According to X-Ray data,* **3b** *molecule is S-trans-S-trans conformer, however* **3d** *is S-cis-S-cis one. Quantum-chemical investigation of geometry and relative stability of cis- and trans-isomers and stable conformations of compounds* **3a–d** *was carried out.* © 2010 Wiley Periodicals, Inc. Heteroatom Chem 21:24–35, 2010; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20574

## *INTRODUCTION*

Aromatic azo compounds have a great deal of applications because of a combination of interesting optical and electron properties with good solubility, chemical, and thermal stability. They are known as widespread dyes and pigments [1–3] and studied as liquid crystalline and supramolecular systems [4,5]. Owing to their ability to reversible *trans/cis* isomerization, aryl and hetaryl diazenes are investigated as promising objects for design of advanced materials such as NLO devices and photoresponsive materials [6–8]. The structure of *cis*- and *trans*-isomers and the mechanism of isomerization of diazene and its derivatives, especially azobenzene, have been extensively studied both experimentally [9–12] and using quantum-chemical calculations [13–19]. Azo compounds on the basis of N-containing heterocycles, such as azobispyridine and its analogues with azoimine moiety (N=C—N=N), are intensively studied as ligands capable of forming stable complexes with low-valent metals [20].

Because of the high content of nitrogen, bis(tetrazol-5-yl)diazene (**1**) and its salts (**2**) are investigated as high-energy materials, components of propellants and gas generators [21,22]. N-substituted derivatives **3a–c** are known to be effective antifog and antistain agents and selective desensitizers for silver halide photographic emulsions [23].

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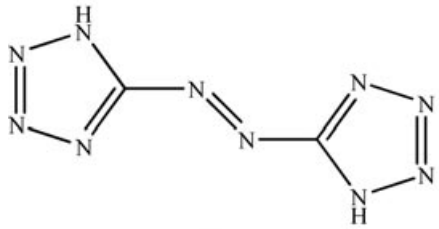
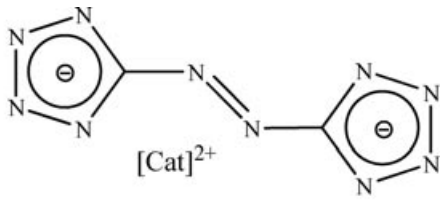


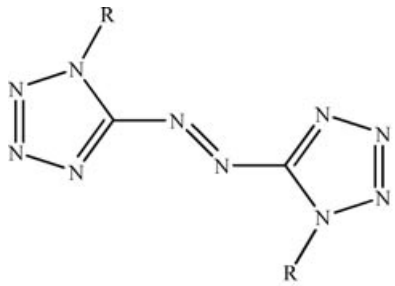
**1**



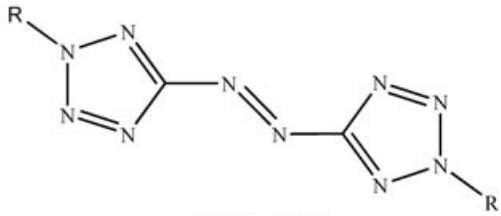

**2**

$[Cat]^{2+}$: metal or organic cation

Bis(1-methyltetrazol-5-yl)diazene (**3a**) [24] and bis(2-methyltetrazol-5-yl)diazene (**3c**) [21] have been structurally characterized and appeared to have *trans* configuration. Preparation of some *cis*-bis-(tetrazol-5-yl)diazenes has been reported, but their assignments to *cis*-isomers have been made only on the basis of UV-spectra [25]. Quantum-chemical calculations of the structure and *cis/trans* isomerism of bis(tetrazol-5-yl)diazenes have not been performed yet. In contrast to azobenzene, besides *cis/trans* isomerism caused by different location of substituents across N=N bond, molecules of N-substituted bis(tetrazol-5-yl)diazenes can form stable S-*cis* and S-*trans* conformations, resulting from rotation of tetrazole cycle around exocyclic C—N bond.



**3a** (R = Me),
**3b** (R = Ph)



**3c** (R = Me),
**3d** (R = $^t$Bu)

In the present paper, devoted to N-substituted bis(tetrazol-5-yl)diazenes, we report the use of a new oxidizing reagent for the synthesis of compounds **3a–d** from corresponding 5-aminotetrazoles, describe their spectroscopic and thermal properties, and discuss the results of quantum-chemical investigation of geometry and relative stability of *cis*- and *trans*-isomers (and stable conformations of these compounds) as well as the data of X-ray diffraction analysis.

## EXPERIMENTAL

### Materials and Methods

5-Amino-1-methyltetrazole (**4a**) [26], 5-amino-1-phenyltetrazole (**4b**) [27], 5-amino-2-methyltetrazole (**4c**) [26], and 5-amino-2-*tert*-butyltetrazole (**4d**) [28] were synthesized as described previously. *N*-bromosuccinimide (NBS) was recrystallized from water. Other reagents and solvents were used as commercially supplied.

$^1$H and $^{13}$C NMR spectra were recorded on a Brucker Avance 400 spectrometer at 298 K using DMSO-$d_6$ as the solvent and TMS as the internal standard. $^1$H-$^{15}$N HMBC NMR spectra were recorded on a Bruker Avance 500 spectrometer operating at 50.69 MHz using DMSO-$d_6$ as the solvent and $MeNO_2$ (0 ppm) as the internal standard. IR spectra of the powdered samples were measured on a Nicolet Thermo Avatar 330 in the range of 4000–400 cm$^{-1}$. UV–vis spectra in the region 200–900 nm were recorded on a Specord M40 spectrometer using acetonitrile as a solvent. Thermal analysis was performed on a Netzsch STA 449 under nitrogen in the range of 30–600°C with heating rate of 10°C min$^{-1}$.

### *General Procedure for the Preparation of Bistetrazolyldiazenes* **3a–d**

0.02 mol (3.56 g) of NBS and 0.1 mmol (12 mg) of azobisisobutyronitrile (AIBN) were added to a solution containing 0.01 mol of *N*-*R*-5-aminotetrazole **4** in 20–25 mL of $CH_3CN$ or $CH_2Cl_2$. The mixture

was stirred under reflux for 4–5 h. Then solvent was removed under vacuum, solid residue was recrystallized from diluted solution of NaOH, and then from ethyl acetate (for **3a**), acetonitrile (for **3b**), or ethanol (for **3c** and **3d**).

**3a:** Yield: 68%. DSC (10°C $min^{-1}$): mp 184°C, 248°C (decomp.) (Lit. 183–184 [25]). IR ($\nu$, $cm^{-1}$): 3044 (w), 3023 (m), 2962 (m), 2923 (w), 1513 (s), 1448 (s), 1406 (w), 1283 (s), 1248 (m), 1185 (s), 1043 (s), 918 (w), 828 (w), 757 (s), 687 (s), 547 (s), 435 (m). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 4.38 (s, $CH_3$). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 159.44 (C5), 35.52 ($CH_3$). $^{15}$N NMR (DMSO-$d_6$, $\delta$, ppm): −153.5 (N1), −3.8 (N2). UV–vis ($CH_3CN$, nm): $\lambda_{max}$ ($\varepsilon$, $M^{-1}$ $dm^{-1}$) = 300 ($7.2 \times 10^4$), 455 ($2.2 \times 10^3$). $C_4H_6N_{10}$ (194.16): C, 24.74; H, 3.11; N, 72.14. Found: C, 24.66; H, 3.07; N, 72.30.

**3b:** Yield: 45%. DSC (10°C $min^{-1}$): 240°C (decomp.) (Lit. 225–227 [23]). IR ($\nu$, $cm^{-1}$): 3184 (w), 3102 (m), 3072 (m), 3044 (w), 1593 (s), 1498 (s), 1475 (s), 1442 (s), 1322 (m), 1283 (s), 1178 (s), 1142 (s), 1074 (s), 1023 (s), 996 (s), 925 (m), 844 (w), 763 (s), 732 (s), 687 (s), 596 (s), 507 (s), 460 (m). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 7.81 (d, 2H, $CH_{arom}$), 7.66 (m, 3H, $CH_{arom}$). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 158.47 (C5), 132.5, 130.48, 129.22, 124.73 ($C_6H_5$). UV–vis ($CH_3CN$, nm): $\lambda_{max}$ ($\varepsilon$, $M^{-1}$ $dm^{-1}$) = 300 ($1.2 \times 10^5$), 455 ($3.2 \times 10^3$). $C_{14}H_{10}N_{10}$ (318.30): C, 52.83; H, 3.17; N, 44.01. Found: C, 52.96; H, 3.11; N, 44.16.

**3c:** Yield: 65%. DSC (10°C $min^{-1}$): mp 163°C, 181°C (decomp.) (Lit. 170–172 [25]). IR ($\nu$, $cm^{-1}$): 3049 (w), 2957 (w), 2920 (w), 1534 (w), 1486 (s), 1448 (s), 1422 (m), 1380 (s), 1348 (s), 1271 (w), 1197 (m), 1094 (m), 1036 (m), 895 (w), 861 (w), 778 (vs), 690 (w), 649 (m), 571 (m). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 4.55 (s, $CH_3$). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 171.0 (C5), 40.4 ($CH_3$). $^{15}$N NMR (DMSO-$d_6$, $\delta$, ppm): −76.8 (N1), −96.6 (N2), 4.2 (N3), −54.1 (N4). UV–vis ($CH_3CN$, nm): $\lambda_{max}$ ($\varepsilon$, $M^{-1}$ $dm^{-1}$) = 290 ($1.1 \times 10^5$), 425 ($3.8 \times 10^3$). $C_4H_6N_{10}$ (194.16): C, 24.74; H, 3.11; N, 72.14. Found: C, 24.82; H, 3.03; N, 72.10.

**3d:** Yield: 59%. DSC (10°C $min^{-1}$): 187°C (decomp.). IR ($\nu$, $cm^{-1}$): 2990 (s), 2941 (m), 2879 (w), 1458 (s), 1399 (m), 1375 (s), 1304 (s), 1273 (m), 1238 (m), 1217 (m), 1190 (s), 1147 (m), 1076 (w), 1029 (m), 934 (w), 870 (w), 822 (m), 775 (m), 749 (m), 600 (m), 566 (m), 503 (w), 466 (w). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 1.79 (s, $CH_3$). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 170.9 (C5), 65.7 ($\underline{C}Me_3$), 28.7 ($CH_3$). $^{15}$N NMR (DMSO-$d_6$, $\delta$, ppm): −69.9 (N2). UV–vis ($CH_3CN$, nm): $\lambda_{max}$ ($\varepsilon$, $M^{-1}$ $dm^{-1}$) = 290 ($1.9 \times 10^5$), 425 ($4.4 \times 10^3$). $C_{10}H_{18}N_{10}$ (278.32): C, 43.15; H, 6.52; N, 50.33. Found: C, 43.33; H, 6.65; N, 50.17.

### *Crystal Structure Determination*

Single crystal X-ray data for **3b** and **3d** were collected at room temperature on a Nicolet *R*3m diffractometer (graphite-monochromated Mo $K_\alpha$ radiation, $\omega$–$2\theta$ scans). The structures were solved by direct methods using program SIR2004 [29]. Refinement on $F^2$ was carried out by full-matrix least-squares technique as implemented in SHELXL-97 [30]. Anisotropic displacement parameters were used for all non-hydrogen atoms. The H atoms were located from difference maps and refined using "riding" model. Crystal data and refinement details are given in Table 1.

### *Molecular Orbital Calculations*

Molecular orbital calculations have been carried out using the density functional theory B3LYP method [31]. Geometries of all investigated structures were optimized with 6-31G* basis set. Our previous investigations [32] showed that this computational level provided good agreement of the calculated geometries of tetrazole derivatives with the experimental data. The validity of the DFT B3LYP method for studying geometry and isomerism of diazene [13], azobenzene [14,16–19], and similar molecular systems was also shown.

To obtain the stable conformations, arising as a result of rotation of tetrazole cycle around exocyclic C—N bond, for the *trans*-isomers of the compounds, the potential energy surface (PES) was generated by scanning one of N=N—C—N dihedral angle from 0.0° to 180.0°. Obtained structures, corresponding to minima on the PES, were then fully optimized without any symmetry restrictions and zero-point vibrational energies (ZPVE) were calculated with unscaled frequencies for obtained structures. To find total energies ($E$), single-point energy calculations were performed with 6-31+G** basis set.

The solvent effects on the geometrical parameters and relative stabilities of isomers of investigated bis(tetrazol-5-yl)diazenes were evaluated using the polarized continuum model (PCM) [33] with the default parameters for water. The PCM energies ($E_{PCM}$) were calculated at B3LYP/6-31+G** level using geometries optimized for isolated structures.

To compare the relative stability of abovementioned isomers in gas phase and in aqueous solution, the ZPVE corrected energies ($E_0$) and Gibbs energies in solution ($G_s$) were calculated for each species using the following equations:

$$E_0 = E + \mathrm{ZPVE}$$

$$G_s = E_0 + \Delta_{solv}G$$

where $\Delta_{solv}G$ is the solvation Gibbs energy calculated by a simple formula $\Delta_{solv}G = E_{PCM} - E$.

These values do not involve thermal corrections; however, for each isomer, these corrections are expected to be approximately the same and do not influence on conclusions about relative stability of isomers.

## *RESULTS AND DISCUSSION*

### *Synthesis and Characterization*

Symmetrical bis(hetaryl)azo compounds are usually prepared by the chemical or electrochemical oxidation of hetarylamines [2]. As yield of diazenes depends on the type of oxidizing reagent, choice of the latter is the main problem of the above method. Described methods of synthesis of N-substituted bis(tetrazol-5-yl)diazenes are based on oxidative coupling of corresponding 5-aminotetrazoles and require such specific or inconvenient reagents as chlorine [23], sodium hypochlorite [25], or 1,3-dibromoisocyanuric acid [34]. N-substituted bis(tetrazol-5-yl)diazenes can also be synthesized by alkylation of tetrazole **1**. Particularly, the synthesis of bis(2-methyltetrazol-5-yl)diazene via methylation of highly explosive silver 5,5'-azotetrazolate with small yield has been reported [21].

Bis-(tetrazol-5-yl)diazenes **3a–d** were synthesized by oxidation of appropriate N-substituted 5-aminotetrazoles **4a–d** with widely used and cheap *N*-bromosuccinimide in the presence of AIBN at a ratio **4**:NBS:AIBN = 1:2:0.001. The reaction takes place in $CH_2Cl_2$ or $CH_3CN$ under reflux and gives products in the yields of 45%–70%.

Compounds **3a–d** were obtained as bright-colored stable crystalline powders and characterized by means of NMR, IR- and UV-spectroscopy, complex thermal analysis, and elemental analysis. Properties of diazenes **3a–c** are identical to those described in the literature. Compound **3d** was synthesized for the first time. The structures of the diazenes **3b** and **3d** were established with X-ray analysis.

The $^1H$ and $^{13}C$ NMR spectra of compounds **3a–d** show signals corresponding to the resonances of substituents. Besides in the $^{13}C$ NMR spectra, the resonances of the tetrazole ring carbon atoms are found at ca. 159 ppm for 1-substituted diazenes **3a** and **3b**, and at ca. 171 ppm for 2-substituted derivatives **3c** and **3d**, which is in agreement with common values for 1,5- and 2,5-substituted tetrazoles [35]. Taking into an account a low sensitivity of $^{15}N$ nuclei and a low solubility of investigated diazenes in most common solvents, $^{15}N$ NMR spectra were analyzed using the 2D HMBC technique. Unfortunately, not all nitrogen atoms of **3** appeared as signals in the $^1H$-$^{15}N$ 2D NMR spectra. In particular, signals of the azo group were not detected for all compounds. The observed signals were assigned to the heteroring nitrogen atoms based on the literature data [35].

The UV–vis absorption spectra of bis(tetrazolyl)diazenes **3a–d** were measured in acetonitrile. There are two absorption maxima in the spectrum of each compound. The main maxima corresponding to $\pi$–$\pi^*$ transitions of the aromatic system are observed in the UV region (290–300 nm). The bands in visible region (425–455 nm) correspond to $n$–$\pi^*$ transitions. The spectra of 2-substituted diazenes **3c** and **3d** are very similar, with maxima lying at

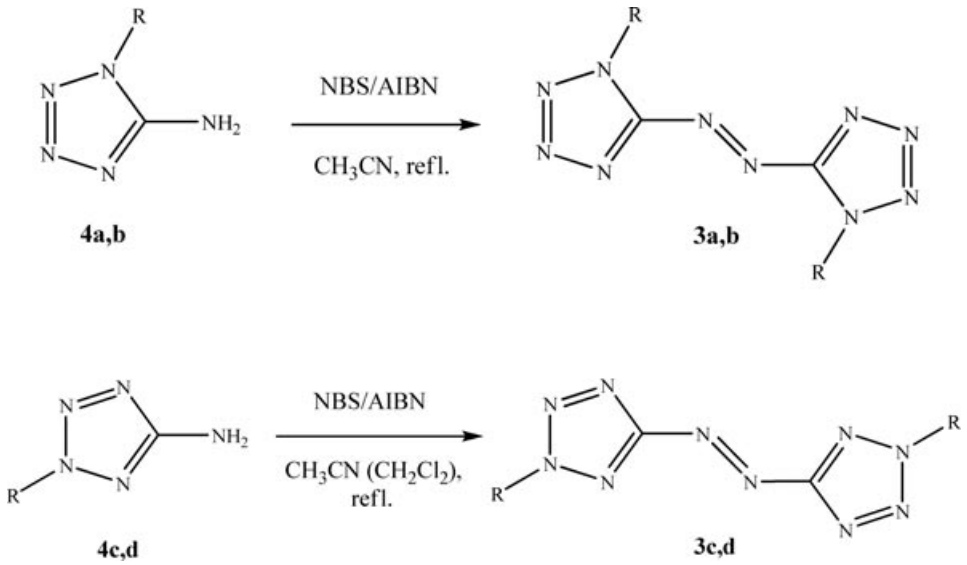


**TABLE 1** Crystal Data and Structure Refinement Details for **3b** and **3d**

| Compound | **3b** | **3d** |
|---|---|---|
| Empirical formula | $C_{14}H_{10}N_{10}$ | $C_{10}H_{18}N_{10}$ |
| Formula weight | 318.32 | 278.34 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ |
| Unit cell dimensions: | | |
| $a$, Å | 6.2128(19) | 6.3278(13) |
| $b$, Å | 13.078(3) | 12.675(3) |
| $c$,Å | 9.192(2) | 9.4429(19) |
| $\beta$,deg | 105.22(2) | 97.201(16) |
| $V$, Å$^3$ | 720.7(3) | 751.4(3) |
| Z | 2 | 2 |
| Density (calculated), Mg m$^{-3}$ | 1.467 | 1.230 |
| Absorption coefficient, mm$^{-1}$ | 0.101 | 0.086 |
| Crystal size, mm$^3$ | 0.38 × 0.32 × 0.28 | 0.40 × 0.20 × 0.20 |
| Theta range for data collection, deg | 2.77–30.06 | 2.70–27.56 |
| Reflections collected | 2291 | 1893 |
| Independent reflections | 2118 [$R$(int) = 0.0230] | 1742 [$R$(int) = 0.0365] |
| Data/restraints/parameters | 2118/0/129 | 1742/39/126 |
| Goodness-of-fit on $F^2$ | 1.032 | 1.035 |
| Final $R$ indices $R_1/wR_2$ [$I > 2\sigma(I)$] | 0.0441/0.1072 | 0.0439/0.1195 |
| $R$ indices $R_1/wR_2$ (all data) | 0.0662/0.1218 | 0.0695/0.1401 |

290 and 425 nm. 1-Substituted diazenes are more bathochromic (300 and 455 nm), while two bands partially overlapping.

Interestingly, in [25], where synthesis of both *trans*- and *cis*-isomers of diazene **3a** was described for the first time, absorption maximum at 301 nm was assigned to *cis*-isomer with m.p. 183–184°C, whereas *trans*-isomer with m.p. 164°C was found to absorb at 370 nm. However, according to the X-ray analysis [24], compound **3a,** with m.p. 183–184°C and $\lambda_{max} = 300$ nm, has *trans*-geometry.

Synthesized compounds were also characterized in solids by IR spectroscopy. The assignments were done using a frequency analysis for optimized structures (see the Computational Study section). All vibrations could be divided into four groups: (1) vibrations predominantly involving the substituent, (2) involving the tetrazole ring, (3) involving the azo-bridge, and (4) vibrations of the mixed nature in which substituent and(or) tetrazole ring and(or) azo-bridge vibrate in concerted way. The regions of 2900–3100 cm$^{-1}$ ($\nu(CH)_{alkyl}$) and nearly 1600 cm$^{-1}$ ($\nu(CC)_{aryl}$) are characterized by the primary contribution of the first group vibrations. The region of 1000–1500 cm$^{-1}$ is characterized by the primary contributions of in-plane vibrations of the tetrazole ring that are strongly coupled with the $\delta(CH_3)$ vibrations of the methyl group. In-plane and out-of-plane bendings of the C5—$N_a$=$N_a$ angle and the C5—$N_a$=$N_a$—C5 torsion vibrations are occurred in the region of 450–900 cm$^{-1}$ (where $N_a$ is a nitrogen atom of azo-bridge). The out-of-plane bendings of the tetrazole ring have occurred at nearly 700 cm$^{-1}$. Our study also indicates that $\nu(N_a{=}N_a)$ vibration is not active in the IR spectra of the studied compounds.

Curves of complex thermal analysis (TG-DSC) of bis(tetrazolyl)diazenes **3a–d** are given in Figs. 1–4. These compounds are much more thermally stable than unsubstituted 5,5′-azotetrazole **1** decomposing at room temperature in a few seconds [21]. 2-Substituted diazenes **3c** and **3d** decompose above 160°C in two exothermic steps (Figs. 3 and 4). 1-Substituted diazenes **3a** and **3b** are even more stable decomposing in one exothermic step with maxima at 240 and 249°C (Figs. 1 and 2). Diazenes **3a** and **3c** additionally show endothermic peaks corresponding to melting at 184 and 163°C, respectively.

## *Molecular and Crystal Structure*

Molecules of both investigated compounds, **3b** and **3d**, are centrosymmetric, with inversion centers lying in the middle of $N_a$=$N_a$ bonds (Figs. 5 and 6). Similar molecular symmetry was found in previously studied compound **3c** [21], whereas molecules of **3a** have no symmetry in the crystal [24]. Considering *cis–trans* isomerism of diazenes, molecules of all compounds **3a–d** are *trans*-isomers in solid. According to X-ray data, **3a**, **3b**, and **3c** molecules are S-*trans*-S-*trans* conformers, however **3d** is S-*cis*-S-*cis* conformer. Some bond lengths and angles are given in Table 2. Note that, in the crystal structure

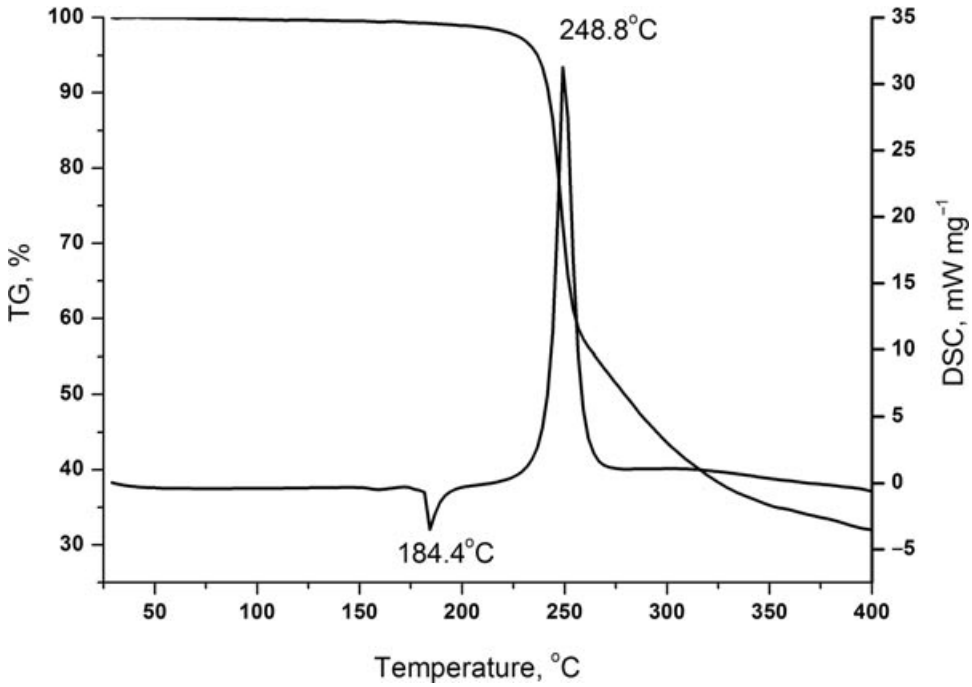



**FIGURE 1** Curves of complex thermal analysis of **3a**.

of **3d**, the *tert*-butyl groups are disordered over two positions with approximately equal occupancies.

In **3d**, there are $\pi$–$\pi$ interactions between the tetrazole rings, forming polymeric chains running along the *b* axis (see Supplementary Material Fig. 1S). More complicated $\pi$–$\pi$ interaction system takes place in the crystal structure of **3b**. Besides the above $\pi$–$\pi$ interactions, there are also those between the benzene rings as well as between the benzene and the tetrazole rings, giving three-dimensional polymeric structure (Supplementary Material Fig. 2S).

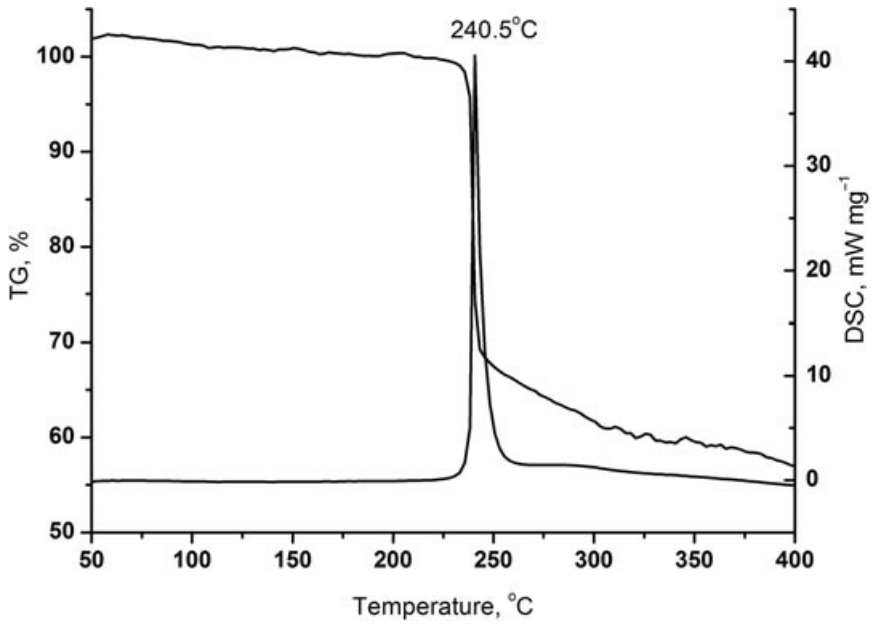



**FIGURE 2** Curves of complex thermal analysis of **3b**.

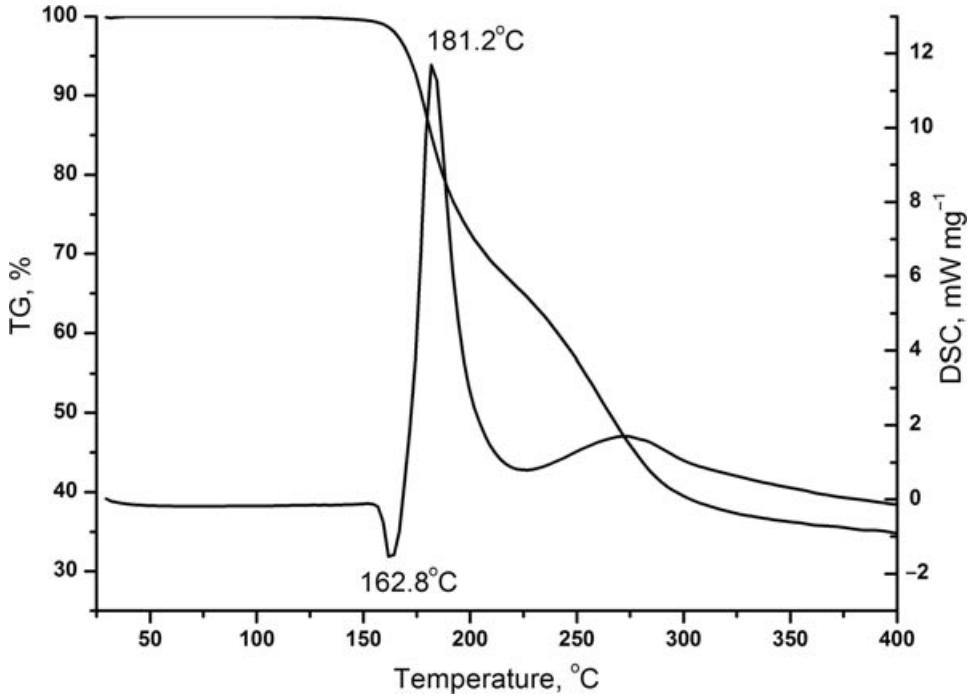



**FIGURE 3** Curves of complex thermal analysis of **3c**.

When comparing experimental and calculated geometries of studied bis(tetrazol-5-yl)diazenes, it is necessary to take into account that the experimental data refer to solids whereas calculated values relate to isolated molecules. In view of this, we investigated influence of medium on structural parameters of studied bis(tetrazol-5-yl)diazenes. For this purpose, we carried out geometry optimization

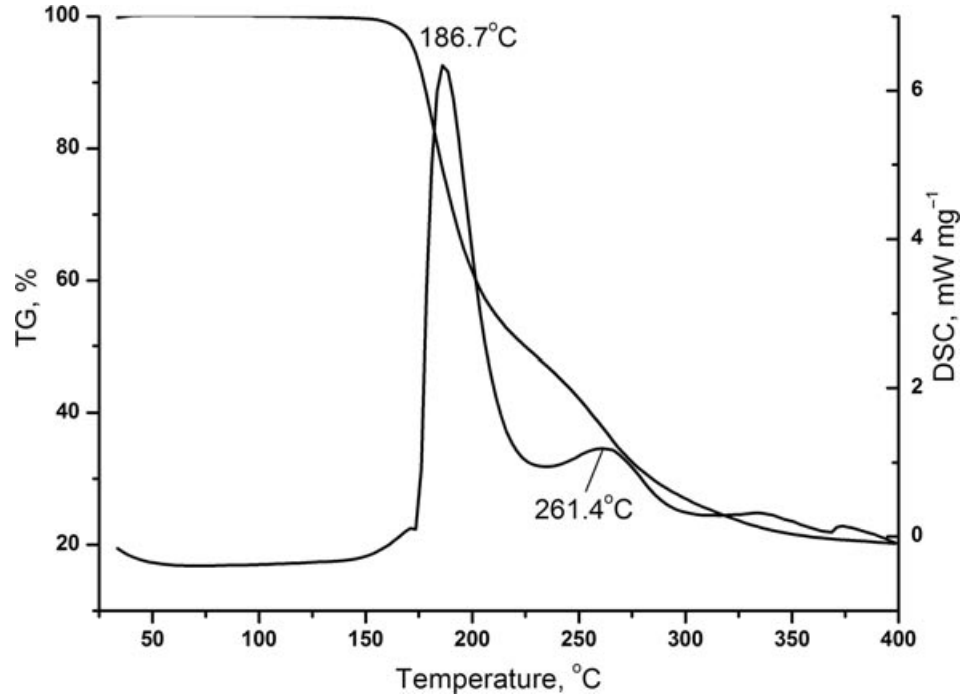



**FIGURE 4** Curves of complex thermal analysis of **3d**.

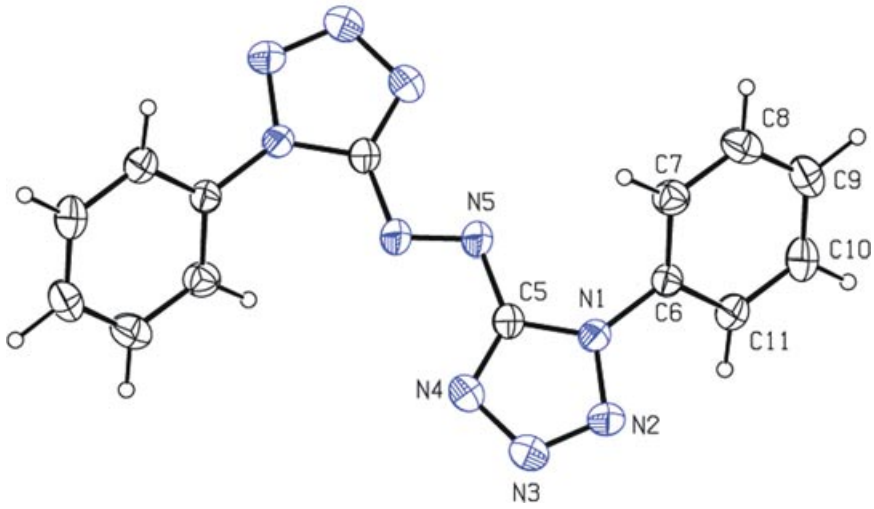



**FIGURE 5** Molecular structure of **3b**.

of their molecules in aqueous solution (the continuum model). This model does not allow studying the influence of specific interactions in crystal on the structural parameters. The results of calculations and experimental data are given in Table 2. The structural parameters, optimized within continuum model, do not differ substantially from those calculated for isolated molecules. Calculated geometry of C5—$N_a$=$N_a$—C5 fragment and tetrazole ring bond lengths of isolated molecules of 1-substituted bis(tetrazol-5-yl)diazenes (B3LYP/6-31G*) are in a good agreement with experimental ones, except for N4—C5 and N1—C5. For 2-substituted compounds, calculated values of valence and torsion angles are still in a good agreement with experimental ones, but agreement between calculated and experimental bond lengths is substantially worse. For investigated molecules in solid the C5—$N_a$=$N_a$—C5 fragment is practically planar, which agrees with the results of DFT calculations for isolated molecules and molecules in polar medium. According to the X-ray data, in molecules **t3a**, **t3b**, and **t3d** the tetrazole rings are slightly rotated relative to the plane C5—$N_a$=$N_a$, whereas **t3c** has a planar structure.

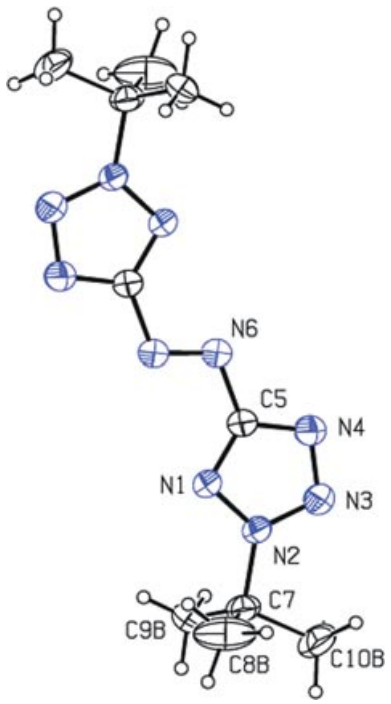



**FIGURE 6** Molecular structure of **3d**. Disorder of the *tert*-butyl groups is not shown.

## *Cis–Trans Isomerism and Conformations*

The molecular structures of stable conformations of isolated **t3a** molecule, optimized at B3LYP/6-31G* level are shown in Fig. 7. For *trans*-isomers of investigated compounds, there are three stable conformations differing by the rotation angles $\phi_1$ and $\phi_2$ of the tetrazole rings around exocyclic C—N bonds (Fig. 7). For **t3a**, **t3c**, and **t3d** molecules, these stable conformations are planar, when the most favorable conditions for conjugation between the $\pi$-systems of the tetrazole ring and the $N_a$=$N_a$ group are achieved, whereas in stable conformations of **t3b** tetrazole rings are slightly rotated relative to the plane C5—$N_a$=$N_a$ (Table 3). The barriers corresponding to transformations S-*trans*-S-*trans*-**t3a** → S-*cis*-S-*trans*-**t3a**, S-*cis*-S-*trans*-**t3a** → S-*trans*-S-*trans*-**t3a**, S-*cis*-S-*trans*-**t3a** → S-*cis*-S-*cis*-**t3a**, and S-*cis*-S-*cis*-**t3a** → S-*cis*-S-*trans*-**t3a**, calculated at

**TABLE 2** Experimental[a] and Calculated Bond Lengths (Å) and Angles (deg) in Molecules of N-Substituted Bis(tetrazol-5-yl)diazenes

| | S-*trans*-S-*trans*-**t3a** | | | S-*trans*-S-*trans*-**t3b** | | | S-*trans*-S-*trans*-**t3c** | | | S-*cis*-S-*cis*-**t3d** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Bond/Angle | Gas | Solution | X-Ray [21][b] | Gas | Solution | X-Ray | Gas | Solution | X-Ray [19a] | Gas | Solution | X-Ray |
| N1—C5 | 1.358 | 1.355 | 1.339/1.336 | 1.366 | 1.361 | 1.348 | 1.337 | 1.337 | 1.324 | 1.339 | 1.338 | 1.320 |
| N1—N2 | 1.337 | 1.334 | 1.334/1.331 | 1.349 | 1.344 | 1.346 | 1.319 | 1.318 | 1.321 | 1.320 | 1.320 | 1.325 |
| N2—N3 | 1.312 | 1.312 | 1.306/1.304 | 1.305 | 1.307 | 1.302 | 1.345 | 1.338 | 1.321 | 1.342 | 1.337 | 1.322 |
| N3—N4 | 1.343 | 1.341 | 1.346/1.343 | 1.342 | 1.342 | 1.353 | 1.302 | 1.306 | 1.322 | 1.307 | 1.310 | 1.317 |
| N4—C5 | 1.330 | 1.331 | 1.320/1.320 | 1.329 | 1.330 | 1.317 | 1.364 | 1.360 | 1.343 | 1.358 | 1.355 | 1.332 |
| $N_a$=$N_a$ | 1.263 | 1.262 | 1.253 | 1.265 | 1.264 | 1.252 | 1.261 | 1.261 | 1.256 | 1.261 | 1.262 | 1.235 |
| C5—$N_a$ | 1.387 | 1.389 | 1.398/1.401 | 1.386 | 1.389 | 1.403 | 1.397 | 1.395 | 1.411 | 1.398 | 1.396 | 1.424 |
| C5—$N_a$=$N_a$ | 114.0 | 113.8 | 112.3/112.5 | 113.5 | 113.4 | 112.2 | 113.4 | 113.6 | 112.2 | 113.6 | 114.0 | 112.4 |
| N1—C5—$N_a$ | 119.3 | 119.8 | 119.6/119.6 | 121.0 | 120.6 | 119.9 | 118.8 | 118.9 | 118.4 | 128.2 | 128.3 | 127.5 |
| N4—C5—$N_a$=$N_a$ | 0.0 | 0.0 | 10.7/14.4 | 9.0 | −11.5 | 2.2 | 0.0 | 0.0 | 4.5 | 180.0 | 180.0 | 179.5 |
| C5-$N_a$=$N_a$−C5 | 180.0 | 180.0 | −178.0 | 180 | 180 | 180 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |

[a]S.D. of experimental bond lengths and angles do not exceed 0.002 Å and 0.2°, respectively.
[b]There are two tetrazole rings in the asymmetric unit of compound **3a**.

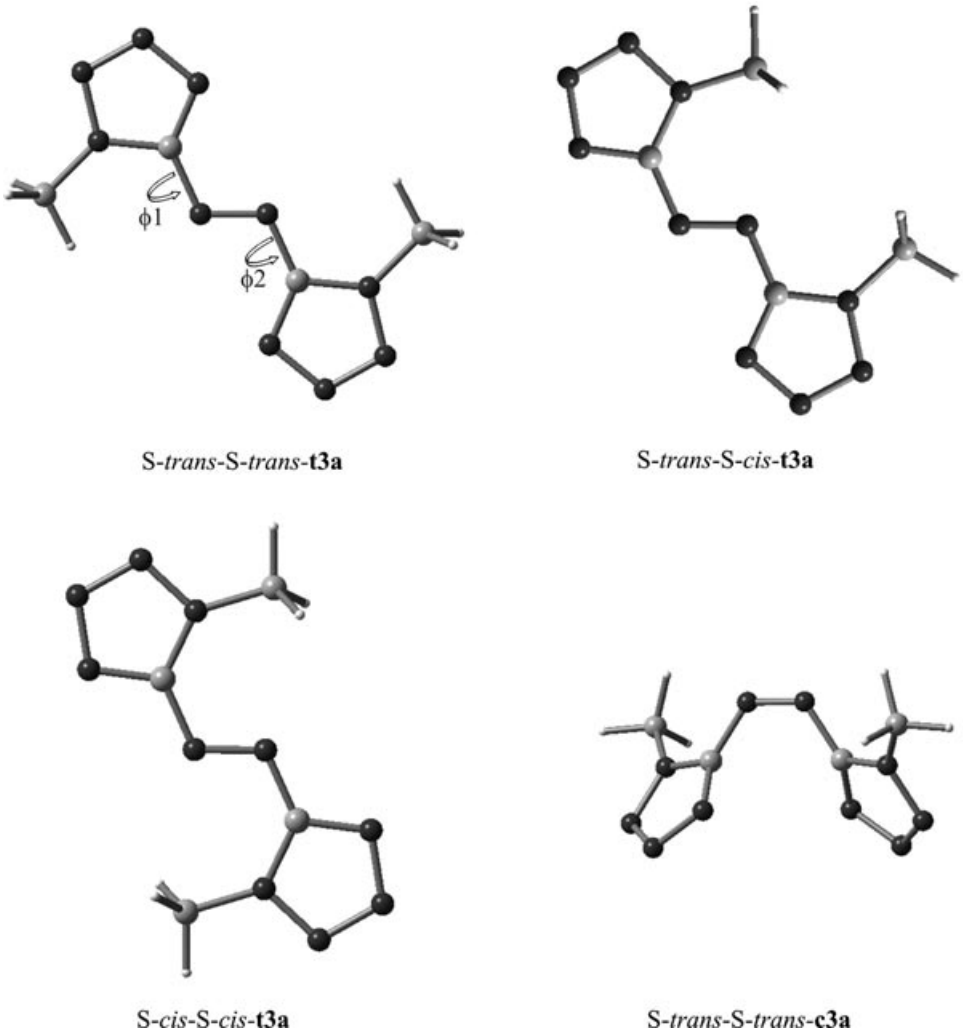



**FIGURE 7** Structures of stable conformations of isolated **t3a** and **c3a** molecules, optimized with B3LYP/6–31G* level.

**TABLE 3** Calculated Bond Lengths (Å), Angles (deg), and Relative ZPVE-Corrected Energies $\Delta E_0$ (kJ mol$^{-1}$) for Isolated Molecules and Relative Gibbs Energies in Solution $\Delta G_s$ (kJ mol$^{-1}$) of Isomers of N-Substituted Bis(tetrazol-5-yl)diazenes

| | $N_a$=$N_a$ | C5—$N_a$ | C5—$N_a$=$N_a$ | N1—C5—$N_a$ | N4—C5—$N_a$=$N_a$ | C5—$N_a$=$N_a$—C5 | $\Delta E_0$ | $\Delta G_s$[a] |
|---|---|---|---|---|---|---|---|---|
| S-*trans*-S-*trans*-**t3a** | 1.263 | 1.387 | 114.0 | 119.3 | 0.0 | 180.0 | 0.0 | 0.0 |
| S-*cis*-S-*trans*-**t3a**[b] | 1.267 | 1.385(1.391) | 114.5(113.8) | 130.6(119.5) | 180.0(0.0) | 180.0 | 17.7 | −1.5 |
| S-*cis*-S-*cis*-**t3a** | 1.268 | 1.386 | 114.3 | 130.2 | 180.0 | 180.0 | 3.7 | 1.2 |
| S-*trans*-S-*trans*-**c3a** | 1.255 | 1.402 | 122.1 | 121.0 | −44.2 | −14.5 | 42.1 | 48.5 |
| S-*trans*-S-*trans*-**t3b**[c] | 1.265 | 1.386 | 113.5 | 121.0 | 9.0 | 180.0 | 0.0 | 0.0 |
| S-*cis*-S-*trans*-**t3b** | 1.264 | 1.393(1.390) | 113.8(113.8) | 130.3(121.0) | 154.7(−22.5) | 176.4 | 17.6 | 9.7 |
| S-*cis*-S-*cis*-**t3b** | 1.262 | 1.389 | 115.5 | 131.8 | −165.8 | −177.4 | 20.3 | 15.7 |
| S-*trans*-S-*trans*-**c3b** | 1.254 | 1.405(1.406) | 121.5(120.8) | 122.3(124.5) | −48.5(−48.5) | −16.1 | 37.8 | 44.0 |
| S-*trans*-S-*trans*-**t3c** | 1.261 | 1.397 | 113.4 | 118.8 | 0.0 | 180.0 | 0.0 | 0.0 |
| S-*cis*-S-*trans*-**3c** | 1.261 | 1.398(1.397) | 113.5(113.5) | 128.2(118.8) | 180.0(0.0) | 180.0 | −3.1 | −3.6 |
| S-*cis*-S-*cis*-**t3c** | 1.261 | 1.398 | 113.6 | 128.2 | 180.0 | 180.0 | 1.4 | 1.8 |
| S-*trans*-S-*trans*-**c3c** | 1.252 | 1.413 | 122.2 | 120.6 | 125.8 | 12.5 | 42.0 | 54.9 |
| S-*cis*-S-*trans*-**c3c** | 1.251 | 1.413(1.414) | 123.1(122.8) | 125.9(119.9) | −147.4 | 11.5 | 46.9 | 56.9 |
| S-*cis*-S-*cis*-**c3c** | 1.250 | 1.414 | 123.2 | 125.8 | −147.2 | 11.4 | 51.8 | 59.9 |
| S-*trans*-S-*trans*-**t3d** | 1.261 | 1.398 | 113.4 | 118.8 | 0.0 | 180.0 | 0.0 | 0.0 |
| S-*cis*-S-*trans*-**t3d** | 1.261 | 1.398(1.398) | 113.5(113.5) | 128.1(118.8) | 180.0(0.0) | 180.0 | 1.1 | 1.2 |
| S-*cis*-S-*cis*-**t3d** | 1.261 | 1.398 | 113.6 | 128.2 | 180.0 | 180.0 | 0.2 | 2.2 |
| S-*trans*-S-*trans*-**c3d** | 1.252 | 1.413 | 122.1 | 120.6 | 43.0 | 12.3 | 41.0 | 55.9 |
| S-*cis*-S-*trans*-**c3d** | 1.251 | 1.413(1.414) | 123.0(122.9) | 125.9(119.8) | −147.4 | 11.3 | 46.6 | 60.8 |
| S-*cis*-S-*cis*-**c3d** | 1.249 | 1.416 | 122.9 | 125.6 | −147.5 | 12.0 | 51.9 | 61.0 |

[a]Calculated at (PCM)B3LYP/6-31+G**//B3LYP/6-31G* level.
[b]Values in parentheses correspond to second tetrazole ring.
[c]All values correspond to the most stable conformer.

B3LYP/6-31G* level as energy differences between the maxima and minima on PES without ZPVE corrections, are 34.9, 18.7, 18.4, and 32.7 kJ mol$^{-1}$, respectively. The barrier corresponding to transformation S-*trans*-S-*trans*-**t3a** → S-*cis*-S-*trans*-**t3a** (35 kJ mol$^{-1}$) is somewhat greater than this one calculated for 2*R*-5-vinyltetrazoles (about 20 kJ mol$^{-1}$) [36] and azobenzene (about 25 kJ mol$^{-1}$) [19] molecules. But it is not obligatory that conjugation between $\pi$-systems of the tetrazole ring and the $N_a$=$N_a$ group in the **t3a** molecule is greater than similar conjugation in 2*R*-5-vinyltetrazoles and azobenzene molecules. So, the barrier to internal rotation in systems with conjugated bonds depends, apart from the conjugation energy, on such factors as steric interactions, hyperconjugation effects, and so on. It was shown [15] that calculations at the MP2/6-31+G* level lead to the distorted (nonplanar) structure of *trans*-azobenzene, which is different from DFT calculations with various basis sets. So, we calculated the PES along dihedral angle $\phi_1$ of the **t3a** molecule at MP2/6-31+G* and B3LYP/6-31+G* levels (Fig. 8). We found that for B3LYP calculations addition of the diffuse functions did not influence significantly on the structure of stable conformations, their relative energies, and the height of the barrier to internal rotation. At MP2/6-31+G* level the minima on the PES correspond to nonplanar conformations of the **t3a** molecule, which is different from B3LYP calculations. But MP2 calculations indicate that the energy variation in regions $\phi_1 = -10^\circ$ to $10^\circ$ and $-160^\circ$ to $160^\circ$ is very small, and the energy barriers separating two equivalent nonplanar structures are only 0.2 and 0.5 kJ mol$^{-1}$, respectively (Fig. 8).

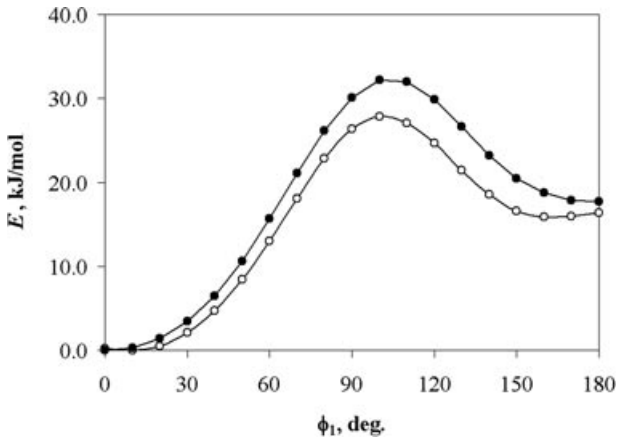



**FIGURE 8** PESs along dihedral angle $\phi_1$ of isolated **t3a** molecule, calculated at B3LYP/6-31+G* (●), and MP2/6-31+G* (○) levels. $\phi_1 = 0^\circ$ corresponds to S-*trans*-S-*trans*-**t3a**, and $\phi_1 = 180^\circ$ corresponds to S-*trans*-S-*cis*-**t3a**. The energies are given relative to S-*trans*-S-*trans*-**t3a** conformer.

All stable conformations of *cis*-isomers of studied compounds have nonplanar structure (Table 3). Minima on PES corresponding to S-*cis*-S-*trans* and

S-*cis*-S-*cis* conformations of *cis*-isomers had been found only for 2-substituted tetrazole derivatives. *Cis*-isomers of studied compounds have shorter $N_a$=$N_a$ bond and longer C5—$N_a$ bond than these ones in trans-isomers (Table 3). It is in agreement with the partial loss of conjugation between the $\pi$-systems of the tetrazole ring and the $N_a$=$N_a$ group due to non-planarity of the molecules of *cis*-isomers. In the gas-phase and in polar medium, *trans*-isomers of studied compounds are substantially more stable than *cis*-isomers (Table 3). It is in agreement with the fact that molecules of bis(tetrazol-5-yl)diazenes exist as *trans*-isomers in obtained crystals. Energies of different stable conformations of molecules of *trans*-isomers are practically the same in gas and in polar medium (Table 3), which agrees with the fact that molecules of *trans*-isomers can exist in different conformations in crystal (**t3a**, **t3b**, and **t3c** molecules have S-*trans*-S-*trans*-conformation and **t3d** has S-*cis*-S-*cis*-conformation).

## *CONCLUSION*

N-substituted bis(tetrazol-5-yl)diazenes were obtained by oxidative coupling of corresponding 5-aminotetrazoles with readily available reagent, *N*-bromsuccinimide. Single crystal X-ray diffraction data of bis(tetrazol-5-yl)diazenes showed *trans*-configuration around diazene N=N bond. Molecules of 1-monosubstituted bis(tetrazol-5-yl)diazenes have S-*trans*-S-*trans* conformation, whereas conformation of molecules of 2-isomers in crystal depends on nature of substituent. Bis(2-*tert*-butyltetrazol-5-yl)diazene exists as S-*cis*-S-*cis* conformer, whereas bis(2-methyltetrazol-5-yl)diazene exists as S-*trans*-S-*trans* conformer. Calculated geometries and relative stability of conformations of bis(tetrazol-5-yl)diazenes are in good agreement with the experimental data.

## *SUPPLEMENTARY DATA*

Further details of crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request. Deposition numbers CCDC 732700 (**3b**) and CCDC 732701 (**3d**).

## *SUPPLEMENTARY MATERIAL*

Figure 1S showing $\pi$–$\pi$ interactions in the crystal structures of **3d** and Figure 2S showing $\pi$–$\pi$ interactions in the crystal structures of **3b** are available from the corresponding author on request.

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## *REFERENCES*

[1] Towns, A. D. Dyes Pigm 1999, 42, 3–28.
[2] Wang, M.; Funabiki, K.; Matsui, M. Dyes Pigm 2003, 57, 77–86.
[3] Seferoglu, Z.; Ertan, N.; Hokelek, T.; Sahin, E. Dyes Pigm 2008, 77, 614–625.
[4] Yeap, G.-Y.; Ong, C.-H.; Takeuchi, D.; Kakeya, M.; Osakada, K.; Mahmood, W. A. K.; Atsuko, O.; Vill, V. J Mol Struct 2008, 882, 1–8.
[5] Dincalp, H.; Toker, F.; Durucasu, I.; Avcıbas, N.; Icli, S. Dyes Pigm 2007, 75, 11–24.
[6] Raposo, M. M. M.; Sousa, A. M. R. C.; Fonseca, A. M. C.; Kirsch, G. Tetrahedron 2005, 61, 8249–8256.
[7] Coelho, P. J.; Carvalho, L. M.; Fonseca, A. M. C.; Raposo, M. M. M. Tetrahedron Lett 2006, 47, 3711–3714.
[8] Raposo, M. M. M.; Ferreira, A. M. F. P.; Belsley, M.; Moura, J. C. V. P. Tetrahedron 2008, 64, 5878–5884.
[9] Traettenberg, M.; Hilmo, I.; Hagen, K. J Mol Struct 1977, 39, 231–239.
[10] Tsuji, T.; Takashima, H.; Takeuchi, H.; Egawa, T.; Konaka, S. J Phys Chem A 2001, 105, 9347–9353.
[11] Bouwstra, J. A.; Schouten, A.; Kroon, J. Acta Cryst C 1983, 39, 112–1123.
[12] Harada, J.; Ogawa, K.; Tomoda, S. Acta Cryst B 1997, 53, 662–672.
[13] Jursic, B. S. Chem Phys Lett 1996, 261, 13–17.
[14] Biswas, N.; Umapathy, S. J Phys Chem A 1997, 101, 5555–5566.
[15] Kurita, N.; Tanaka, S.; Itoh, S. J Phys Chem A 2000, 104, 8114–8120.
[16] Crecca, C. R.; Roitberg, A. E. J Phys Chem A 2006, 110, 8188–8203.
[17] Wang, L.; Wang, X. J Mol Struct (Theochem) 2007, 806, 179–186.
[18] Stepanić, V.; Baranović, G.; Smrečki, V. J Mol Struct 2001, 569, 89–109.
[19] Chen, P. C.; Chieh, Y. C. J Mol Struct (Theochem) 2003, 624, 191–200.
[20] Kaim, W. Coord Chem Rev 2001, 219–221, 463–488.
[21] Hammerl, A.; Holl, G.; Klapötke, T. M.; Mayer, P.; Nöth, H.; Piotrowski, H.; Warchhold, M. Eur J Inorg Chem 2002, 834–845.
[22] (a) Klapötke, T. M.; Sabaté, C. M.; Chem Mater 2008, 20, 3629–3637; (b) Sivabalan, R.; Anniyappan, M.; Pawar, S. J.; Talawar, M. B.; Gore, G. M.; Venugopalan, S.; Gandhe, B. R. J Hazard Mater A 2006, 137, 672–680; (c) Ye, C.; Xiao, J.-C.; Twamley, B.; Shreeve, J. M. Chem Commun 2005, 2750–2752; (d) Anga, H.-G.; Frank, W.; Karaghiosoff, K.; Klapötke, T. M.; Nöth, H.; Sprott, J.; Suter, M.; Vogt, M.; Warchhold, M. Z Anorg Allg Chem 2002, 628, 2901–2906; (e) Hammerl, A.; Klapötke, T. M.; Nöth, H.; Warchhold, M. Inorg Chem 2001, 40, 3570–3575; (f) Tao, G.-H.; Twamley, B.; Shreeve J. M. Inorg Chem 2009, 48, 9918–9923; (g) Klapötke, T. M. In Structure

and Bonding; Klapötke, T. M. (vol. editor), Mingos, D. M. P. (series editor); Vol. 125/2007: High Energy Density Compounds; Springer: Berlin/Heidelberg, 2007; (h) Klapötke, T. M. Chemie der hochenergetischen Materialien; Walter de Gruyter: Berlin, 2009.
[23] Agostino, B.; Luigi, C. German Pat. 2212550, 1974.
[24] Lyakhov, A. S.; Serebryanskaya, T. V.; Gaponik, P. N.; Voitekhovich, S. V.; Ivashkevich, L. S. Acta Cryst C 2006, 62, m223–m226.
[25] Williams, M. M.; McEwan, W. S.; Henry, R. A. J Phys Chem 1957, 61, 261–267.
[26] Ronald, A. H.; William, G. F. J Am Chem Soc 1954, 76, 923–926.
[27] Vorobyov, A. N.; Gaponik, P. N.; Petrov, P. T.; Ivashkevich, O. A. Synthesis 2006, 1307–1312.
[28] Voitekhovich, S. V.; Gaponik, P. N.; Lyakhov, A. S.; Ivashkevich, O. A. Tetrahedron 2008, 64, 8721–8725.
[29] Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori G.; Spagna R. J Appl Cryst 2005, 38, 381–388.
[30] Sheldrick, G. M. Acta Cryst A 2008, 64, 112–122.
[31] Becke, A. D. J Chem Phys 1993, 98, 5648–5652.
[32] (a) Gaponik, P. N.; Voitekhovich, S. V.; Lyakhov, A. S.; Matulis, Vadim E.; Ivashkevich, O. A.; Quesada, M.; Reedijk, J. Inorg Chim Acta 2005, 358, 2549–2557; (b) Gaponik, P. N.; Degtyarik, M. M.; Lyakhov, A. S.; Matulis, Vadim E.; Ivashkevich, O. A.; Quesada, M.; Reedijk, J. Inorg Chim Acta 2005, 358, 3949–3957; (c) Matulis, Vadim E.; Lyakhov, A. S.; Gaponik, P. N.; Voitekhovich, S. V.; Ivashkevich, O. A. J Mol Struct 2003, 649, 309–314; (d) Lyakhov, A. S.; Matulis, Vadim E.; Gaponik, P. N.; Voitekhovich, S. V.; Ivashkevich, O. A. J Mol Struct 2008, 876, 260–267.
[33] Cancès, M. T.; Mennucci, B.; Tomasi, J. J Chem Phys 1997, 107, 3032–3041.
[34] Semenov, S. E.; Churakov, A. M.; Ioffe, S. L.; Vinogradova, E. A.; Zlotin, S. G.; Luk'yanov, O. A. Russ Chem Bull 1991, 40, 1727.
[35] (a) Butler, R. N. In Comprehensive Heterocyclic Chemistry II; Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. (Eds.); Pergamon: Oxford, UK, 1996; Vol. 4. p. 621; (b) Ostrovskii, V. A.; Koldobskii, G. I.; Trifonov, R. E. In Comprehensive Heterocyclic Chemistry III; Katritzky, A. R.; Ramsden, C. A.; Scriven, E. F. V.; Taylor, R. J. K.; Zhdankin V. V. (Eds.); Elsevier: Oxford, UK, 2008; Vol. 6, p. 257.
[36] Ivashkevich, O. A.; Matulis, Vadim E.; Matulis, Vitaly E.; Gaponik, P. N. Russ J Gen Chem 2004, 74, 134–140.