CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200900034

Disubstituted Azidotetrazoles as Energetic Compounds

Takashi Abe, Young-Hyuk Joo, Guo-Hong Tao, Brendan Twamley, and Jean′ne M. Shreeve*[a]

Abstract: Disubstituted azidotetrazoles are synthesized by the base-catalyzed activation of the C–F bond in the trifluoromethylazo-substituted cyclic and acyclic alkanes. From the reaction of *trans*-1,4-bis(trifluoromethylazo)cyclohexane with four equivalents of NaN_3, *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminocyclohexane was formed in good yield. While, from the similar reaction using *cis/trans*-1,2-bis(trifluoromethylazo)cyclohexane, (5-azido-1*H*-tetrazol-1-yl)-[6-(5-azido-1*H*-tetrazol-1-ylimino)cyclohexenyl]amine was formed as the principal product. The structure of these new disubstituted azidotetrazoles was determined by crystal structure analysis as well as NMR and IR spectroscopy. In a similar fashion, from three trifluoromethylazo-substituted acyclic alkanes, corresponding alkyl-bridged *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)diiminoalkanes were obtained. For example, from 1,2-bis(trifluoromethylazo)ethane, *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diiminoethane was obtained in 75% yield. Heats of formation, detonation pressures, detonation velocities, and impact sensitivities are reported for these new disubstituted azidotetrazoles.

Keywords: azidotetrazoles · C–F activation · energetic materials · heterocycles · high-nitrogen compounds

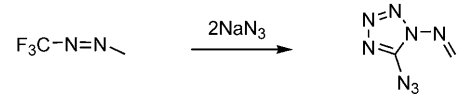
Introduction

The synthesis of energetic heterocyclic compounds has attracted considerable interest in recent years, especially with regard to the syntheses and applications of new members of heterocyclic-based energetic materials.[1] High-nitrogen compounds constitute a unique class of energetic materials. The energy is derived from their high heats of formation rather than from the total heat of combustion. The high heats of formation are directly related to the large number of energetic N–N, N–C, and N–O bonds.[2] Therefore, new methodology for the ready introduction of high-nitrogen groups into the molecule is important for the development of high-energetic compounds. Azidotetrazole is a ligand that has a reduced carbon content relative to nitrogen content. The creation of more high-energy materials can be expected by integrating the N–N bond in the molecule based on the inherent lability of the azidotetrazole. Many papers have dealt with the preparation of azidotetrazoles,[3] for example, nearly 70 years ago, 5-azidotetrazole and sodium 5-azidotetrazolate were prepared by the reaction of cyanogen halide (ClCN or BrCN) with sodium or barium azide and acid.[4] More recently detailed investigations on the synthesis and characterization of 5-azidotetrazoles have been reported.[5]

The blue gas, trifluoronitrosomethane, reacts with various primary amines to give corresponding trifluoromethylazo compounds in good yields.[6] Several reactions of polyfluoroazaalkanes have been reported also.[7] Recently, we have shown that the trifluoromethylazo group (CF_3–N=N–) was transformed into the (5-azido-1*H*-tetrazol-1-yl)imino group in reaction with sodium azide by taking advantage of the activation of the C–F bond (Scheme 1).[8] Based on this new method, high-nitrogen compounds consisting of two or more (5-azido-1*H*-tetrazol-1-yl)imino groups were prepared from compounds that contained one or more CF_3–N=N– group(s).

[a] Dr. T. Abe, Dr. Y.-H. Joo, Dr. G.-H. Tao, Dr. B. Twamley, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
Fax: (+1) 208-885-9146
E-mail: jshreeve@uidaho.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900034.

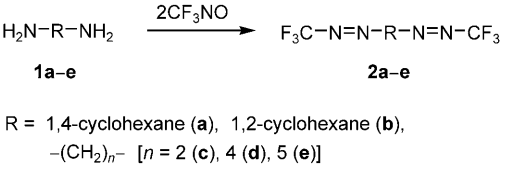


Scheme 1. Transformation of the trifluoromethylazo group into the (5-azido-1*H*-tetrazol-1-yl)imino group

To explore the scope of this reaction, we have extended the study of the synthesis of high-nitrogen compounds beyond those having disubstituted CF_3–N=N– groups, which may provide new high-energetic compounds. The preparation of compounds having disubstituted azidotetrazoles is known, for example, 1,4-bis(5-azido-1*H*-tetrazol-1-yl)benzene was obtained by the reaction of 1,4-(dichloromethyleneamino)benzene with sodium azide where the azidotetrazoles are bonded at the 1,4-positions of the benzene ring.[9] However, by using our new reaction scheme, *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-iminocyclohexane is formed from the reaction of *trans*-1,4-bis(trifluoromethylazo)cyclohexane with sodium azide. This is the first report of compounds that contain disubstituted azidotetrazoles linked to the parent cyclic and/or acyclic alkyl through the imino group. In our current work, we report the preparation of new disubstituted azidotetrazoles, which are more energetic than those of monosubstituted azidotetrazoles.

Results and Discussion

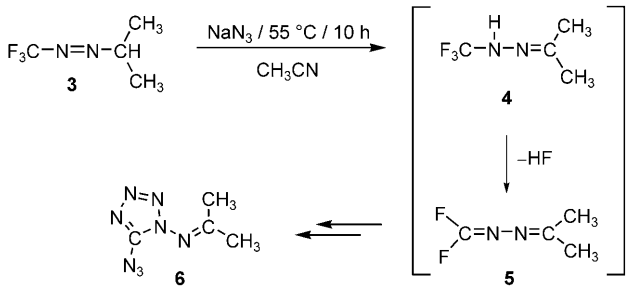
Precursors (**2a–e)** having two trifluoromethylazo groups were prepared by the reaction of diamines (**1a–e**) with trifluoronitrosomethane (Scheme 2). With the exception of



Scheme 2. Preparation of bis(trifluoromethylazo)alkanes.

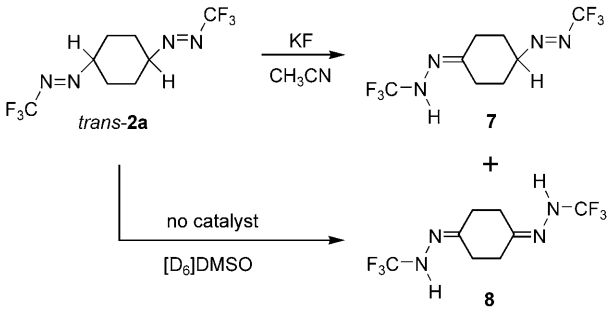
1,2-bis(trifluoromethylazo)ethane (**2c**),[10] all starting materials **2a**, **2b**, **2d**, and **2e** are new compounds. *trans*-1,4-Bis(trifluoromethylazo)cyclohexane (**2a**) is a light brown solid, whereas **2b–e** are green-yellow oily liquids. When compared with bis(trifluoromethylazo)cyclohexanes (**2a**, **2b**) and alkyl(trifluoromethyl)diazenes (alkyl = *n*-C_3H_7, *iso*-C_3H_7, *iso*-C_4H_9, *cyclo*-C_5H_{11}, *cyclo*-C_6H_{13}, *n*-C_8H_{17}),[8] the shelf life of the bis(trifluoromethylazo)alkanes (**2c–e**) is rather low due to the presence of adventitious traces of water. For example, the trifluoromethylazo group of 1,2-bis(trifluoromethylazo)-ethane (**2c**) gradually degrades into the trifluoromethylhydrazono group (CF_3NH–N<) even when stored at −40 °C. When retained at room temperature, decomposition occurs rapidly leading finally to an orange solid. Therefore, these linear bis(trifluoromethylazo)alkanes (**2c–e**) were prepared in methanol solution and reacted with sodium azide without isolation.

The reaction of *trans*-1,4-bis(trifluoromethylazo)cyclohexane (2a) with NaN_3: The C–F bond of CF_3 group only rarely succumbs to nucleophilic substitution.[11] However, activation of C–F bonds is required for reaction of CF_3–N=N–alkyl to occur. We have found that the initial formation of hydrazono compound **4** from isopropyl(trifluoromethyl)diazene (**3**), which results from a base-catalyzed [1,3]-proton shift from the carbon of the isopropyl group to the nitrogen of the CF_3N< group, is the impetus for the reaction of **3** with sodium azide (Scheme 3).[12] Intermediate **4** transforms



Scheme 3. Synthesis of 5-azido-*N*-(propan-2-ylidene)-1*H*-tetrazole (**6**).

into a reactive difluorocarboimino compound, **5**, followed by reaction with sodium azide to give the azidotetrazole **6**.[8] Similarly, when *trans*-**2a** reacts with sodium azide, the corresponding hydrazono compounds **7** and **8** are considered to be the primary reaction intermediates. This is based on the formation of 1-(trifluoromethylazo)-4-(*N*-trifluoromethylamino)iminocyclohexane (**7**) and 1,4-bis(trifluoromethylhydrazono)-cyclohexane (**8**), which were identified by examining the products obtained from *trans*-**2a** in acetonitrile that contained a catalytic amount of potassium fluoride or by monitoring the behavior of *trans*-**2a** in [D_6]DMSO by ^1H and ^{19}F NMR spectroscopy (see the Supporting Information) (Scheme 4).

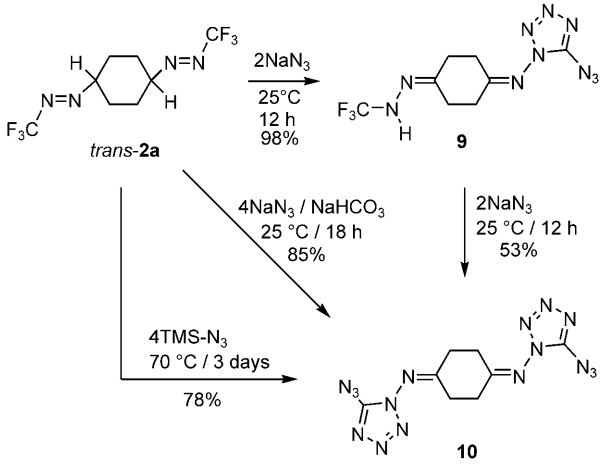


Scheme 4. Isomerization of *trans*-1,4-bis(trifluoromethylazo)cyclohexane (**2a**) into hydrazono compounds **7** and **8**.

Although no apparent change was observed when *trans*-**2a** was held for a week in acetonitrile without base, addition of small quantities of potassium fluoride to the solution caused a change both in ^1H and ^{19}F NMR spectra (Scheme 4). For example, *trans*-**2a** was isomerized into a mixture of mono- and dihydrazono compounds **7** and **8** after being heated at 60 °C for 10 h. In [D_6]DMSO, which is more coordinating (larger donor number DN) than CD_3CN, *trans*-**2a** was isomerized completely into 1,4-bis(trifluoromethyl-

hydrazono)cyclohexane (**8**) after three days at room temperature.

The reaction of *trans*-**2a** with four equivalents of sodium azide in the presence of a base ($NaHCO_3$) at room temperature proceeded smoothly to give a turbid light brown solution (Scheme 5). Workup of this solution gave a white

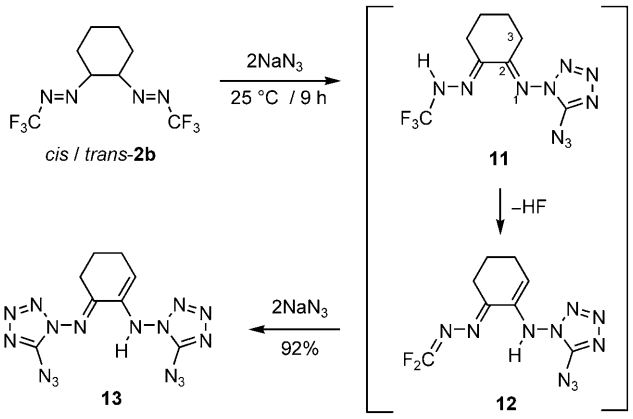


Scheme 5. Synthesis of (5-azido-1*H*-tetrazol-l-yl)-[4-trifluoromethylhydrazonocyclohexylidene]amine (**9**) and *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminocyclohexane (**10**).

powder, which was identified as *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminocyclohexane (**10**) in 85% yield. The structure was determined by single-crystal X-ray crystallography; a thermal ellipsoid plot is given in Figure 1.[13a] The infrared spectrum of **10** shows two characteristic strong bands at 1542 and 2171 cm^{-1} (asymmetric $-N{=}C<$ and $-N_3$ stretching bands, respectively), which are normally observed for azidotetrazoles bonded through the imino group ($-N{=}C<$).[8]

Different products were obtained from the reaction of *trans*-**2a** with sodium azide depending on the molar ratio (*trans*-**2a**/NaN_3) used. This suggests a stepwise reaction mode for the two $CF_3{-}N{=}N{-}$ groups of *trans*-**2a** with sodium azide. When *trans*-**2a** was allowed to react with two equivalents of sodium azide (one half of the stoichiometric amount required), only one of the two $CF_3{-}N{=}N{-}$ groups reacted to give (5-azido-1*H*-tetrazol-1-yl)-[4-(trifluoromethylhydrazono)cyclohexylidene]amine (**9**) selectively, which was isolated and characterized. The ^1H and ^{19}F NMR spectra of **9** are rather complex due to the presence of two different imino groups bonded at the 1- and 4-positions of cyclohexane. However, the presence of the $CF_3(NH){-}$ group in **9** was confidently confirmed on this basis. The ^1H NMR spectra displayed three quartets centered at $\delta = 6.02$ [$^3J(H,F) = 6.2$ Hz], 6.12 [$^3J(H,F) = 6.2$ Hz], and 6.27 ppm [$^3J(H,F) = 6.2$ Hz] in a ratio of 1:0.5:0.2, which are assigned to the $=N{-}NH(CF_3)$ group. While, in the ^{19}F NMR, a set of three doublets was observed due to $=N{-}NH(CF_3)$ group at $\delta = -63.27$ [$^3J(H,F) = 6.2$ Hz], -63.16 [$^3J(H,F) = 6.2$ Hz], and -63.07 ppm [$^3J(H,F) = 6.2$ Hz] in a ratio of 0.2:0.5:1 (see the Supporting Information). Subsequent reaction of **9** with an additional two equivalents of sodium azide gave *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminocyclohexane (**10**) in 53% yield. Access to **10** from *trans*-**2a** was also possible by utilizing trimethylsilylazide, although rather harsh reaction conditions (70°C, three days) were required vis-à-vis the reaction with sodium azide. However, the yield of **10** is considerably higher (78%).

The reaction of *cis*/*trans*-1,2-bis(trifluoromethylazo)cyclohexane (2b) with NaN_3: When *cis*/*trans*-**2b** was allowed to react with two equivalents of sodium azide in the presence of a base ($NaHCO_3$) at room temperature, the formation of the expected monosubstituted azidotetrazole, (5-azido-1*H*-tetrazol-l-yl)-[2-(trifluoromethylhydrazono)cyclohexylidene]-amine did not occur. However, the reaction of *cis*/*trans*-**2b** with four equivalents of sodium azide under the same reaction conditions gave a light brown solid, (5-azido-1*H*-tetrazole-1-yl)-[6-(5-azido-1*H*-tetrazole-1-yl-imino)cyclohexenyl]-amine (**13**) (Scheme 6). Recrystallization of the product

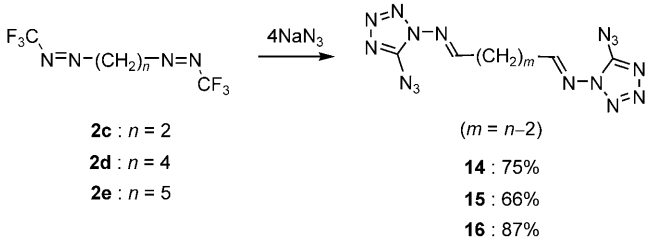


Scheme 6. Synthesis of (5-azido-1*H*-tetrazol-1-yl)-[6-(5-azido-1*H*-imino)-cyclohexenyl]amine (**13**).

from chloroform gave a straw-colored crystalline solid, whose structure was determined by X-ray crystallography; a thermal ellipsoid plot of **13** is given in Figure 2.[13] Due to the inequivalence of the two azidotetrazole groups at the 1,2-positions of the cyclohexane ring of **13**, the asymmetrical stretching bands of the azide groups are found as two strong bands at $\tilde{\nu} = 2151$ and 2166 cm^{-1} in the infrared spectrum. When this reaction was conducted in the absence of a base, the yield of **13** was low (44%) even though the reaction time was four days. It is likely that **13** was derived from an intermediate in which a [1,3]-proton shift from the 3-position of the cyclohexane ring to the imino nitrogen at the 1-position occurred before or concomitantly with the introduction of another azidotetrazole from the monosubstituted azidotetrazole intermediates **11** and **12** to give **13** (Scheme 6).

The reaction of bis(trifluoromethylazo)alkanes 2c–2e with NaN_3: The reaction of **2c** with four equivalents of sodium azide at room temperature under similar conditions proceeded smoothly to give a turbid brown solution from

which a new disubstituted azidotetrazole, *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diimino-ethane (**14**) was isolated as a light brown solid. Following several attempts to optimize this reaction, it was found that lowering the temperature to 0 °C without base ($NaHCO_3$) gave a clean reaction and improved the yield to produce a white powder suspended in solution. This reaction differs from that of *trans*-**2a** in that the behavior of the two trifluoromethylazo groups is identical irrespective of the molar ratio (**2c**/NaN_3). When **2c** was allowed to react with two equivalents of sodium azide under analogous conditions, only **14** was formed in low yield (13 %). Utilizing the same reaction conditions as for **2c**, *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminobutane (**15**) and *N*,*N*′-bis(5-azido-1*H*-tetrazol-1-yl)-1,5-diiminopentane (**16**) were obtained as white or a light brown powders in moderate to good yield, respectively, from the reaction of **2d** and **2e** with sodium azide (Scheme 7). Isolation of single crystals of **14**, **15**, and **16** was not successful.



Scheme 7. Synthesis of alkyl-bridged bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diimine **14**, **15**, and **16**.

Structures: Compounds **10** and **13** were characterized by crystal structure analysis (Table 1). Both structures were solved by using a Bruker SMART APEX diffractometer equipped with a Cryocool Never-Ice low temperature device using $Mo_{K\alpha}$ radiation. The data for compound **10** were rotationally twinned and were successfully deconvoluted byusing CELL_NOW,[24] and refined in the non-standard space group *P*21/*a*. Calculated densities are 1.660 and 1.553 mg m^{-3} for compound **10** and **13**, respectively. The strucutre of compound **10** is shown in Figure 1a with the *para*-oriented azidotetrazole linked to the central alicyclic ring via an imine that is exocyclic to the ring system with N9−C10 = 1.285(2) Å. Each azidotetrazole is twisted back towards the ring and forms a dihedral angle of about 62° to the mean plane of the ring and exocyclic imine nitrogen atoms. The extended structure (Figure 1b) shows that the alicyclic rings stack in the *ab* plane and the azidotetrazole groups point towards each other and are stacked in a stepped fashion. There are no significant intermolecular interactions between the azidotetrazole moieties.

Compound **13** also crystallizes in the monoclinic system, in this case the space group is *P*21/*n*. The data is not twinned and the structure is shown in Figure 2a. In this case, the substitution is *ortho*, but the molecule is no longer symmetric with one of the imines protonated, N9−C10 = 1.307(2) Å, C15−N16 = 1.408(2) Å. The ring now has an endocyclic double bond C14−C15 = 1.345(3) Å. The hydrogen atoms associated with the imine and endocyclic bond positions were located and refined. Although the azido groups are both cofacial, the dihedral angle of each azidotetrazole plane to the

Table 1. Crystallographic data and structure refinement parameters.

	10	**13**
formula	$C_8H_8N_{16}$	$C_8H_8N_{16}$
formula wt	328.30	328.30
space group	*P*21/*a*	*P*21/*n*
exposure [s]	10	20
a [Å]	7.7095(9)	8.7779(11)
b [Å]	8.5955(9)	17.984(2)
c [Å]	9.9351(11)	9.7162(13)
β [°]	93.924(2)	113.755(2)
V [Å^3]	656.83(13)	1403.9(3)
Z	4	4
T [K]	90(2)	90(2)
λ[Å]	0.71073	0.71073
ρ_{calcd} [Mg m^{-3}]	1.660	1.553
(mm^{-1})	0.125	0.117
GF	1.085	1.067
R_1 [$I > 2\sigma(I)$][a]	0.0382	0.0389
wR_2 [$I > 2\sigma(I)$][b]	0.0913	0.0919

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

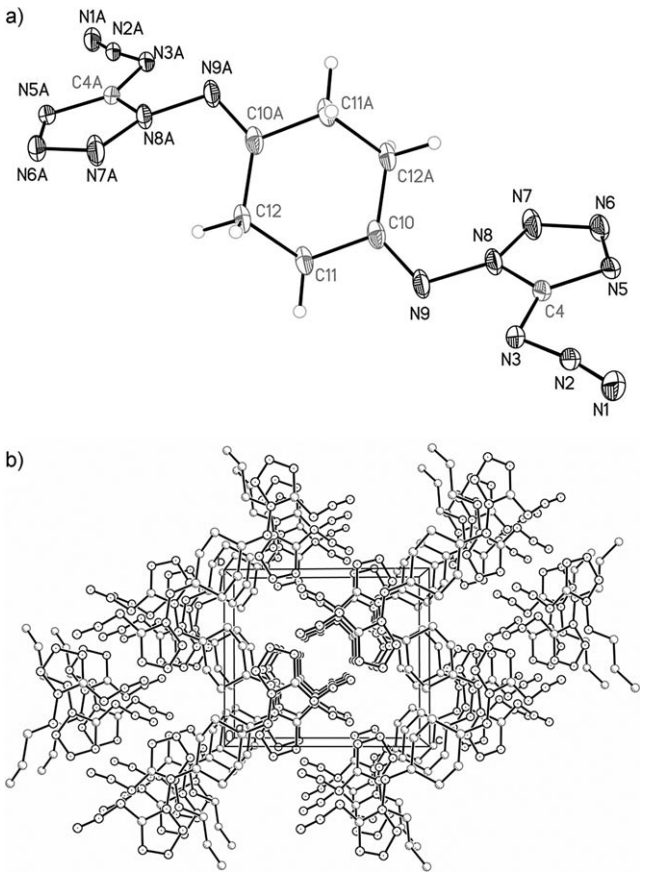


Figure 1. a) Molecular structure of **10** (thermal displacement at 30 % probability). Hydrogen atoms are unlabelled for clarity. b) Packing diagram of **10** with hydrogen atoms omitted for clarity.

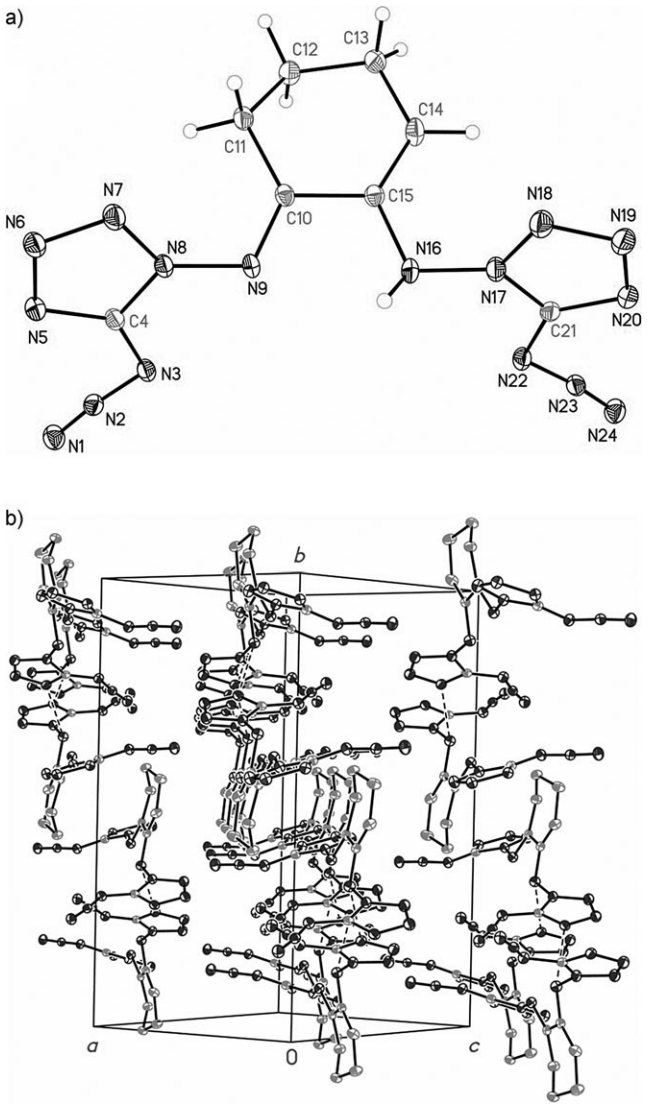


Figure 2. a) Molecular structure of **13** (thermal displacement at 30% probability). Hydrogen atoms are unlabeled for clarity. b) Packing diagram of **13** with hydrogen atoms omitted for clarity. Dashed lines indicate hydrogen bonding. Chains are perpendicular to plane of page.

central ring are slightly different: ring to imine azidotetrazole is about 77° and ring to protonated aminotetrazole is about 70°. The amino group forms an intermolecular interaction, N16–H16···N20i = 2.937(2) Å, (i = symmetry transformation to generate symmetry generated atoms: $x+1/2$, $-y+1/2$, $z+1/2$) tying the extended structure into a double chain as seen in Figure 2b.

Isotopically labeled bis(5-azidotetrazole) ^{15}N-**16** was obtained from $Na^{15}N_3$ and **2e** in acetonitrile. The six ^{15}N NMR signals of ^{15}N-**16**, which are found at $\delta = -297.1$, -143.8, -139.2, -72.6, -26.3, and 4.8 ppm, are observed in the ^{15}N NMR spectrum. (Figure 3) The N_α signal from the azide appears at highest field. The labeled nitrogen N_β was coupled with N_α and N_γ as a doublet of doublets, respectively. The ^{15}N4, ^{15}N2, and ^{15}N3 signals for tetrazole were observed at lowest field. The assignments are given based on the values

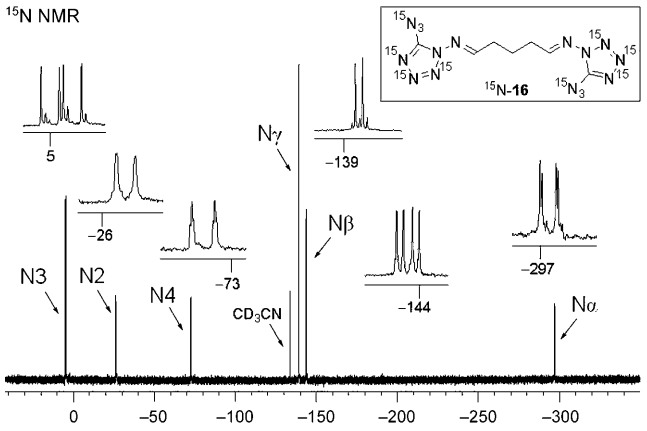


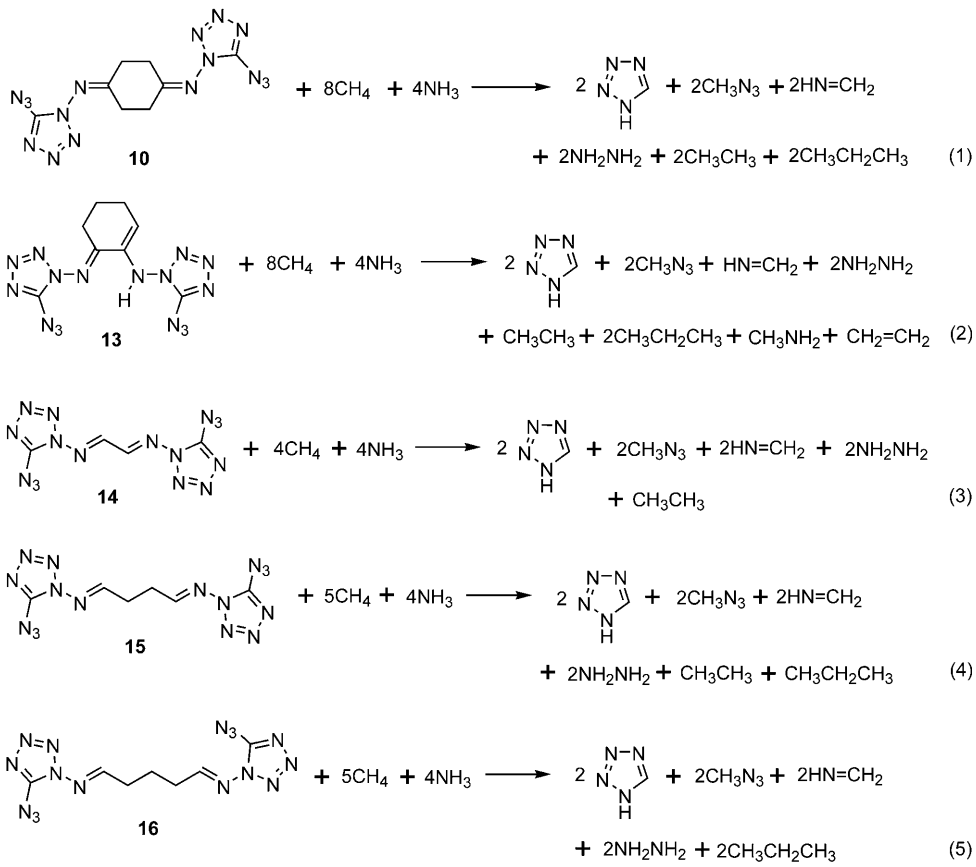
Figure 3. The ^{15}N NMR spectrum of disubstituted ^{15}N-labeled azidotetrazole **16**.

of the chemical shifts of substituted azidotetrazoles on comparison with the literature.[8]

Properties: Being different from energetic compounds having an azidotetrazole which tended to form super-cooled liquids,[8] these disubstituted azidotetrazoles are solids and exhibit poor solubility in common solvents. They do not melt but decompose violently at 162–185 °C. Impact sensitivity tests were carried out using a BAM Fallhammer method.[14] The disubstituted azidotetrazoles blowup on impact at 1 J for **10** and **13** and 0.5 J for **14**–**16**, respectively, and thus they are very sensitive energetic materials which may have some promise as primaries. To avoid the hazard due to high shock sensitivity, densities were not measured for **14**–**16** by using a pycnometer. Their densities were calculated by using an empirical method.[15]

Theoretical study: Computations were performed by using the Gaussian 03 (Revision D.01) suite of programs.[16] The geometric optimization and the frequency analyses are carried out at the level of Becke three Lee–Yan–Parr (B3LYP) parameters up to 6-31+G(d,p) basis sets.[17] All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The enthalpy of reaction ($\Delta H_r^\circ{}_{298}$) is obtained by combining the MP_2/6-311++G**[18] energy difference for the reaction, the scaled zero-point energies, and other thermal factors. The heats of formation of the products were determined by using the method of isodesmic reactions (Scheme 8).[19] The heats of formation for compounds **10**, **13**, **14**, **15**, and **16** were calculated and are summarized in Table 2. All disubstituted azidotetrazoles exhibit high positive heats of formation per mole with **13** having the highest value (1683.1 kJ mol^{-1}). Their heats of formation per unit mass are higher than the corresponding structurally similar monosubstituted azidotetrazoles.[8] Due to its lower molecular weight, **14** has the highest heat of formation per unit mass (6.13 kJ g^{-1}).

The detonation pressures (P) and velocities (D) of the disubstituted azidotetrazoles were calculated based on traditional Chapman–Jouget thermodynamic detonation theory



Scheme 8. Isodesmic reactions used for calculation of disubstituted azidotetrazoles.

Table 2. Decomposition points (T_d), density, heats of formation ($\Delta_f H°$), and detonation pressure (P) and detonation velocity (D) of the energetic materials.

Compd	T_d[a] [°C]	Density [g cm^{-3}]	$\Delta_f H°$[d] [kJ mol^{-1}, kJ g^{-1}]	P[e] [GPa]	D[e] [m s^{-1}]	IS[f] [J]
10	185	1.63[b]	1586.7, 4.83	21.9	7793	<1.0
13	154	1.65[b]	1683.1, 5.13	23.2	7980	<1.0
14	185	(1.70)[c]	1679.8, 6.13	27.9	8614	<0.5
15	168	(1.59)[c]	1625.2, 5.38	23.5	7950	<0.5
16	162	(1.56)[c]	1602.9, 5.07	22.5	7750	<0.5

[a] DSC under nitrogen gas, 10 °C min^{-1}. [b] Gas pycnometer (25 °C). [c] Calculated. Ref. [16]. [d] Calculated in Gaussian 03. [e] Calculated by Cheetah 5.0. [f] Impact sensitivity (BAM Fallhammer).

using Cheetah 5.0.[20] The heats of formation in the condensed phase are calculated by using 83.68 kJ mol^{-1} as the enthalpy of sublimation for each compound.[21] These new azidotetrazoles exhibit higher detonation values than TNT (P = 20 GPa, D = 6900 m s^{-1}).

Conclusions

A straightforward synthetic procedure for new high-nitrogen compounds containing disubstituted azidotetrazoles starting from cyclic and/or acyclic alkyl-bridged bis(trifluoromethylazo) groups has been established. The ability of the trifluoromethylazo group to undergo reaction by activating the C–F bond, when an H atom exists at the carbon of the alkyl group, contributes greatly to its synthetic value. The new type of high-energetic compounds were fully characterized and shown to be highly energetic.

Experimental Section

Caution: For handling these energetic materials, small scale and best safety practices (leather gloves, face shield) are strongly encouraged in undertaking preparation of compounds **10**, **13**, **14**, **15**, and **16**. Compound **14** is extremely shock sensitive (IS <0.5). These compounds should not be contacted with metal.

General methods: ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Avance nuclear magnetic resonance spectrometer operating at 300.1, 282.4, and 75.5 MHz, respectively, using $CDCl_3$, CD_3CN, and [D_6]DMSO as solvent. The ^{15}N NMR spectra were recorded on a 500 MHz Bruker Avance nuclear magnetic resonance spectrometer operating at 50.7 MHz. Chemical shifts: ^{1}H and ^{13}C are reported relative to Me_4Si; ^{19}F relative to $CFCl_3$; ^{15}N relative to external CH_3NO_2. The melting and decomposition points were obtained on a differential scanning calorimeter at a scan rate of 10 °C min^{-1}. Densities of solids were obtained at room temperature by employing a Micromeritics Accupyc1330 gas pycnometer. Electrospray MS was obtained by protonating the product using formic acid. Elemental analyses were determined by using an Exeter CE-440 elemental analyzer.

X-ray crystallography: Crystals of **10** and **13** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[22] Data were collected at low temperatures using a Bruker/Siemens SMART APEX instrument ($Mo_{K\alpha}$ radiation, λ = 0.71073 Å) equipped with a Cryocool NeverIce low temperature device. Data were measured by using omega scans of 0.3° per frame for various exposures, and a full sphere of data was collected in each case. A total of 2400 frames was collected with final resolutions of 0.83 Å. Cell parameters were retrieved by using SMART[23] software and refined by using SAINTPlus[24] on all observed reflections. The data were rotationally twinned for **10** and were deconvoluted by using CELL_NOW[25] giving a two-component twin relationship: 180° rotation about the reciprocal axis 0.499, −0.001, 1.000. The matrix used to relate the second orientation to the first domain is:

Each cell component was refined by using SAINTPlus[24] on all observed reflections. Absorption corrections were applied by using TWINABS for **10** and SADABS for **13**.[26] Data reduction and correction for Lp and decay were performed by using the SAINTPlus software. Structures were solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package.[27] Each structure was solved by analysis of systematic absences. All non-hydrogen atoms were refined

−0.389	0.001	0.693
−0.002	−1.000	−0.001
1.224	0.000	0.389

anisotropically. No decomposition was observed during data collection. Details of the data collection and refinement are given in Table 1.

Preparation of *trans*-1,4-bis(trifluoromethylazo)cyclohexane (2a): CF_3NO (3 mmol) was condensed by PVT techniques at −196 °C into a 50 mL Schlenk tube with a Teflon stopcock that contained *trans*-1,4-diaminocyclohexane (**1a**; 0.16 g, 1.4 mmol) in methanol (1.0 mL). The reaction mixture was allowed to warm from −78 °C to room temperature overnight while stirring. After the reaction, the solid material was dissolved in CH_3CN, and the solvent (CH_3OH, CH_3CN) was removed by rotary evaporator to give **2a** as a light brown solid. Yield: 0.29 g, 77 %; m.p. 87 °C; ^{1}H NMR ($CDCl_3$): δ = 3.97 (br. s, 2H; CH), 2.12–2.21 (m, 4H; CH_2), 1.91–2.01 ppm (m, 4H; CH_2); ^{19}F NMR ($CDCl_3$): δ = −74.9 ppm (s, CF_3); ^{13}C NMR ($CDCl_3$): δ = 119.8 (q, J(C,F) = 275 Hz, CF_3), 75.2, 27.5 ppm; elemental analysis calcd (%) for $C_8H_{10}N_4F_6$ (276.2): C 34.78, H 3.65, N 20.29; found: C 34.56, H 3.57, N 20.01.

Preparation of *cis*/*trans*-1,2-bis(trifluoromethylazo)cyclohexane (2b): The reaction mixture of *cis*/*trans*-1,2-diaminocyclohexane (**1b**; 0.16 g, 1.4 mmol) and CF_3NO (3 mmol) in methanol (1.0 mL) was allowed to warm from −78 °C to room temperature overnight while stirring. After the reaction, brine (2 mL) and concentrated HCl (one drop) were added. The lower layer was separated to give **2b** as a yellow-green oil. Yield: 0.268 g, 69 % (*cis*/*trans* mixture); ^{1}H NMR ($CDCl_3$): δ = 4.46–4.56 (m, 2H), 4.36–4.38 (m, 2H), 1.54–2.29 ppm (m, 16H). ^{19}F NMR ($CDCl_3$): δ = −74.29 (s, CF_3), −74.16 ppm (s, CF_3); MS (EI): *m/z* (%): 180 (13) [$C_7H_{11}F_3N_2^+$], 179 (100) [$M^+ - CF_3N{=}N$], 151 (27) [$C_5H_6F_3N_2^+$], 94 (15) [$C_6H_8N^+$], 82 (12) [$C_6H_{10}^+$], 81 (68) [$C_6H_9^+$], 69 (100) [CF_3^+], 67 (42) [$C_5H_7^+$]; MS (Cl): *m/z* (%): calcd for $C_8H_{11}N_4F_6$ (pseudo molecular ion [$M^+ + H$]), 277.0888; found; 277.0866.

Preparation of 1,2-bis(trifluoromethylazo)ethane (2c):[10] The reaction mixture of 1,2-diaminoethane (**1c**; 0.066 g, 1.1 mmol) and CF_3NO (2.5 mmol) in methanol (0.75 mL) was allowed to warm from −196 to −78 °C, and then held at 0 °C for 2 h. After recovering unreacted CF_3NO in vacuo while immersing the reactor in a cold bath (−98 °C), the reaction mixture was used for the further reaction immediately. All of **1c** was consumed and the formation of **2c** was confirmed by ^{1}H and ^{19}F NMR spectroscopy. ^{1}H NMR ($CDCl_3$) (in methanol solution): δ = 4.78 ppm (s, CH_2); ^{19}F NMR ($CDCl_3$) (in methanol solution): δ = −74.26 ppm (s, CF_3).

Preparation of 1,4-bis(trifluoromethylazo)butane (2d): Prepared as for **2c** and obtained from 1,4-diaminobutane (**1d**; 0.052 g, 0.59 mmol) in methanol (0.75 mL). ^{1}H NMR ($CDCl_3$) (in methanol solution): δ = 4.17 (m, 4H; CH_2), 2.02 ppm (m, 4H; CH_2); ^{19}F NMR ($CDCl_3$) (in methanol solution): δ = −74.19 ppm (s, CF_3).

Preparation of 1,5- bis(trifluoromethylazo)pentane (2e): Prepared as for **2c** and obtained from 1,5-diaminopentane (**1e**; 0.047 g, 0.46 mmol) in methanol (0.75 mL). ^{1}H NMR ($CDCl_3$) (in methanol solution): δ = 4.13 (tq, ^3J(H,H) = 7.0 Hz, ^5J(H,F) = 1.6 Hz, 4H; CH_2), 1.97 (m, ^3J(H,H) = 7.0–7.9 Hz, 4H; CH_2), 1.49 ppm (m, 2H; CH_2); ^{19}F NMR ($CDCl_3$) (in methanol solution): δ = −74.19 ppm (s, CF_3).

Reaction of *trans*-1,4-bis(trifluoromethylazo)cyclohexane (2a): i) With four equivalents of NaN_3 to give **10**: Into a 50 mL flask were placed *trans*-**2a** (0.127 g, 0.46 mmol) in acetonitrile (5 mL), $NaHCO_3$ (0.08 g), and NaN_3 (0.139 g, 2.14 mmol). After stirring the reaction mixture at room temperature for 18 h, a turbid light brown liquid was obtained. The solution was filtered, washed with water (3 × 1 mL), and dried to give *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-iminocyclohexane (**10**). Suitable crystals for single-crystal X-ray structure determination were obtained from chloroform. White powder; yield: 0.129 g, 85 %; T_d 185 °C; ^{1}H NMR ($CDCl_3$): δ = 2.96–3.27 ppm (m, 8H; CH_2); ^{13}C NMR (CD_3CN): δ = 179.6, 150.4, 31.6, 29.4 ppm; IR (KBr): $\tilde{\nu}$ = 1094, 1236, 1294, 1536, 1542 (s; $_{as}$(C=N)), 2172 (s; $_{as}$(N_3)), 1636 cm^{-1}; elemental analysis calcd (%) for $C_8H_8N_{16}$ (328.3): C 29.27; H 2.46; N 68.27; found: C 30.66, H 2.69, N 61.11 (exploded during analysis).

ii) With two equivalents of NaN_3 to give **9**: Into a 50 mL flask was placed **2a** (0.115 g, 0.42 mmol) in acetonitrile (3 mL), and NaN_3 (0.055 g, 0.85 mmol). The solution was stirred at room temperature overnight. After the reaction, the solvent was removed to give a light brown solid. The solid mixture was dissolved in dry acetone (3 mL) and filtered. Evaporation of the solvent left a light brown solid, which was washed with water (3 × 1 mL) to give (5-azido-1*H*-tetrazol-1-yl)-[4-trifluoromethylhydrazono)cyclohexylidene]amine (**9**). This compound is a mixture of three isomers in a ratio of 0.2:0.5:1. Light brown solid; Yield: 0.132 g, 98 %: T_d 116 °C; ^{1} H NMR ($CDCl_3$): δ = 6.27 (q, ^3J(H,F) = 6.0 Hz, NH), 6.12 (q, ^3J-(H,F) = 5.8 Hz, NH), 6.02 (q, ^3J(H,F) = 6.1 Hz, NH), 2.43–3.30 ppm (m, 8H; CH_2); ^{19}F NMR ($CDCl_3$): δ = - 63.07 (d, ^3J(H,F) = 6.2 Hz; CF_3), −63.16 (d, ^3J(H,F) = 6.2 Hz; CF_3), −63.27 (d, ^3J(H,F) = 6.2 Hz, CF_3), −74.19 ppm; IR (liq. film): $\tilde{\nu}$ = 906, 1113, 1198, 1267, 1317, 1485, 1537 (s; $_{as}$(C=N)), 2158 (s; $_{as}$(N_3)), 2921, 2971 cm^{-1}; elemental analysis calcd (%) for $C_8H_9N_{10}F_3$ (302.2): C 31.79, H 3.00, N 46.35; found: C 31.52, H 3.17, N 33.40 (exploded during analysis).

iii) With four equivalents of $(CH_3)_3SiN_3$ to give **10**: Analogously, into a 50 mL flask was placed **2a** (0.124 g, 0.45 mmol) in acetonitrile (5 mL), and $TMSN_3$. (0.239 g, 2.1 mmol). The reaction mixture was stirred at room temperature for 24 h, and then at 67–70 °C for three days. The reaction was monitored by ^{1}H and ^{19}F NMR spectroscopy. After completion, the solvent was removed to give a brown powder (0.113 g), which was identified as **10** by spectroscopic analysis (IR and ^{1}H NMR). Yield 78 %.

Reaction of (5-azido-1*H*-tetrazol-1-yl)-[4-trifluoromethylhydrazono)cyclohexylidene]amine (9) with two equivalents of NaN_3: Into a 50 mL flask was placed **9** (0.115 g, 0.38 mmol) in acetonitrile (3 mL), and NaN_3 (0.067 g, 1.00 mmol). The solution was stirred at room temperature overnight and was removed to give a brown solid. The solid was washed with water (3 × 1 mL) to give a light brown powder (0.066 g) which was found to be **10** by spectroscopic analysis (IR and ^{1}H NMR). Yield 53 %.

Reaction of *cis*/*trans*-1,2-bis(trifluoromethylazo)cyclohexane (2b) with four equivalents of NaN_3: Into a 50 mL flask was placed **2b** (0.270 g, 0.98 mmol) in acetonitrile (8 mL), $NaHCO_3$ (0.164 g), and NaN_3 (0.270 g, 4.16 mmol). After stirring the reaction mixture for 9 h at room temperature, a turbid red wine solution was obtained. The solution was filtered, the residue washed with water (3 × 1 mL), and dried to give a light pink solid (0.114 g) (Product A). Evaporation of the filtrate left a red wine colored solid (0.163 g), which was washed with acetonitrile (3 × 1 mL), to leave a light brown solid (0.123 g) (Product B). The compound which could be dissolved in acetonitrile easily was investigated by MS (FAB; thioglycerol). The main component has a moleculr weight of 219 which corresponded to $C_7H_9N_9$ {[3-(5-azido-1*H*-tetrazol-1-yl)imino]-2-aminocyclohexene-1}. Products A and B were found to be identical based on IR spectroscopy. The structure was determined to be (5-azido-1*H*-tetrazole-1-yl)-[6-(5-azido-1*H*-tetrazole-1-yl-imino)cyclohexenyl]amine (**13**) by X ray crystallography using crystals obtained by recrystallization from chloroform. Light brown solid: yield; 0.237 g, 75 %: T_d 161 °C; ^{1}H NMR ($CDCl_3$): δ = 7.92 (s, NH), 5.66 (t, ^3J = 4.9 Hz, 1H), 2.91 (t, ^3J = 6.2 Hz), 2.34 (td, ^1J = 6.0 Hz, ^2J = 4.9 Hz), 1.84 ppm (quin, J = 6.2 Hz); ^{13}C NMR (CD_3CN): δ = 168.2, 152.1, 149.0, 135.6, 123.6, 27.7, 23.2, 21.0 ppm; IR (KBr): $\tilde{\nu}$ = 2166, 2151 (s; $_{as}$(N_3)), 1643, 1564, 1533 (s; $_{as}$(C=N)), 1310, 1290, 1236, 1094 cm^{-1}; elemental analysis calcd (%) for $C_8H_8N_{16}$ (328.3): C 29.27, H 2.46, N 68.27; found: C 30.98, H 2.51, N 65.10 (exploded during analysis).

Reaction of 1,2-bis(trifluoromethylazo)ethane (2c) with NaN_3: i) With four equivalents to give **14**: Into a 50 mL flask was placed a solution of **2c** in MeOH (0.75 mL), which was prepared from the reaction of **1c** (0.070 g, 1.18 mmol) with CF_3NO, acetonitrile (3 mL), and NaN_3 (0.330 g, 5.08 mmol). The solution was stirred at 0 °C for 24 h. After the reaction, the mixture was filtered. The solid was washed with water (3 × 1 mL), and dried to give *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,2-diiminoethane (**14**) as a white powder. Yield: 0.245 g, 75 %; ^{1}H NMR ($CDCl_3$,): δ = 8.99 ppm (s,

>CH–); ^{13}C NMR (CD_3CN): δ = 153.8, 152.1 ppm; MS (electrospray): $C_4H_2N_{16}$, 274.7 [M^+]; IR (KBr): $\tilde{\nu}$ = 962, 1082, 1165, 1325, 1427, 1442, 1540 (s; $_{as}$(C=N)), 2174 cm^{-1} (s; $_{as}$(N_3)). ii) With two equivalents of NaN_3 to give **14**: Similarly, into a 50 mL flask was placed a solution of **2c** in MeOH (0.75 mL), which was prepared by the reaction of **1c** (0.069 g, 1.14 mmol) with CF_3NO, acetonitrile (3 mL), and NaN_3 (0.147 g, 2.28 mmol). The solution was stirred at 0 °C for 24 h to give a turbid yellow solution. After the reaction, the mixture was filtered, washed with water (3×1 mL) and dried to give **14** (0.042 g, 0.15 mmol) as a white powder. Yield 13 %.

Reaction of 1,4-bis(trifluoromethylazo)butane (2d) with four equivalents of NaN_3: *N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,4-diiminobutane (**15**): White powder; Yield: 0.118 g, 66 %; ^{1}H NMR ($CDCl_3$): δ = 8.74 (m, 1H; CH), 2.97 ppm (m, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 164.2, 149.9, 28.7 ppm; MS (electrospray): $C_6H_6N_{16}$, 302.9 [M^+]; IR (KBr): $\tilde{\nu}$ = 2176 (s; $_{as}$(N_3)), 1543 (s; $_{as}$(C=N)), 1450, 1359, 1242, 1176 cm^{-1}.

Reaction of 1,5-bis(trifluoromethylazo)pentane (2e) with four equivalents of NaN_3:*N,N′*-bis(5-azido-1*H*-tetrazol-1-yl)-1,5-diiminopentane (**16**): White powder; Yield: 0.126 g, 87 %; ^{1}H NMR ($CDCl_3$): δ = 8.68 (t, ^3J = 5.0 Hz, 2H; CH), 2.69 (td, ^3J = 5.3 Hz, ^3J = 5.0 Hz, 4H; CH_2), 2.06 ppm (quin, ^3J = 7.3 Hz, 2H; CH_2); ^{13}C NMR ($CDCl_3$): δ = 151.2, 149.8, 165.6, 118.1, 32.6, 21.3 ppm; IR (KBr): $\tilde{\nu}$ = 1171, 1243, 1359, 1451, 1559 (s; $_{as}$(C=N), 2163 (s; $_{as}$(N_3)), 2180 cm^{-1}.

Reaction of 1,5-bis(trifluoromethylazo)pentane (2e) with four equivalents of $Na^{15}N_3$: Into a 50 mL flask was placed a solution of **2e** in MeOH (0.5 mL), which was prepared by the reaction of **1e** (0.019 g, 0.18 mmol), acetonitrile (2.5 mL), and $Na^{15}N_3$ (45.5 mg, 0.67 mmol). The solution was stirred at 0 °C for 12 h, and then at room temperature for two days. After the reaction, the solution was filtered to give a ^{15}N-labeled azidotetrazole ^{15}N-**16**: White solid; yield: 0.045 g (0.14 mmol). Yield 77 %.

Acknowledgements

The authors gratefully acknowledge the support of AGFOSR (F49620–03–1–0209), NSF (CHE0315275), and ONR (N00014–02–1–0600). The Bruker (Siemens)SMART APEX diffraction facility was established at the University of Idaho with the assistance of the NSF-EPSCoR program and the M. J. Murdock Charitable Trust, Vancouver, WA.

[1] a) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem.* **2006**, *118*, 3664–3682; *Angew. Chem. Int. Ed.* **2006**, *45*, 3584–3601; b) G. Steinhauser, T. M. Klapötke, *Angew. Chem.* **2008**, *120*, 3376–3394; *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347; c) R. P. Singh, H. Gao, R. D. Verma, D. T. Meshri, J. M. Shreeve in *High Energy Density Materials* (Ed.: T. M. Klapötke), Springer, Heidelberg, **2007**, pp. 35–83; d) T. M. Klapötke in *High Energy Density Materials* (Ed.: T. M. Klapötke), Springer, Heidelberg, **2007**, pp. 85–122; e) R. N. Butler in *Comprehensive Heterocyclic Chemistry II. A Review of the Literature 1982–1985, Vol. 4* (Eds.: A. R. Katritzky, C. W. Rees, E. F. Scriven), Pergamon, New York, **1996**, pp. 897–904.

[2] a) M. A. Hiskey, D. E. Chavez, D. L. Naud, S. F. Son, H. L. Berghout, C. A. Bolme, *Proc. Int. Pyrotech. Semin.* **2000**, *27*, 3–14; b) T. M. Klapötke, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2008**, 4055–4062.

[3] a) J. C. Kauer, W. A. Sheppard, *J. Org. Chem.* **1967**, *32*, 3580–3592; b) J. A. C. Alves, R. A. W. Johnstone, *Synth. Commun.* **1997**, *27*, 2645–2650.

[4] W. Friederich, K. Flick, US 2179783, **1939** [*Chem. Abstr.* **1940**, *34*, 11610].

[5] a) A. Hammerl, T. M. Klapötke, *Inorg. Chem.* **2002**, *41*, 906–912; b) A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, G. Holl, *Propellants Explos. Pyrotech.* **2003**, *28*, 165–173; c) A. Hammerl, T. M. Klapötke, P. Mayer, J. J. Weigand, *Propellants Explos. Pyrotech.* **2005**, *30*, 17–26; J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1051–1057.

[6] a) S. P. Makarov, A. Y. Yakubovich, V. A. Ginsburg, A. S. Filatov, M. A. Englin, N. F. Privezentseva, T. Y. Nikiforova, *Dokl. Akad. Nauk SSSR* **1961**, *141*, 357–360; b) A. H. Dinwoodie, R. N. Haszeldine, *J. Chem. Soc.* **1965**, 2266–2268; c) S. P. Makarov, A. S. Filatov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1967**, *37*, 158–163; d) A. S. Filatov, S. P. Makarov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1967**, *37*, 837–841; e) S. P. Makarov, A. Y. Yakubovich, A. S. Filatov, M. A. E′nglin, T. Y. Nikiforova, *Zh. Obshch. Khim.* **1968**, *38*, 709–715; f) V. A. Ginsburg, M. N. Vasil′eva, *Zh. Org. Khim.* **1973**, *9*, 2028–2031; g) A. Sekiya, T. Umemoto, *Chem. Lett.* **1982**, 1519–1520; h) T. Umemoto, O. Miyano, *J. Fluorine Chem.* **1983**, *22*, 91–94; i) A. Sekiya, T. Umemoto, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2962–2964; j) G. Bolte, A. Haas, *J. Fluorine Chem.* **1984**, *26*, 69–76.

[7] a) V. A. Ginsburg, A. Y. Yakubovich, A. S. Filatov, V. A. Shpanskii, E. S. Vlasova, G. E. Zelenin, L. F. Sergienko, L. L. Martynova, S. P. Makarov, *Dokl. Akad. Nauk SSSR* **1962**, *142*, 88–91; b) V. A. Ginsburg, A. Y. Yakubovich, A. S. Filatov, G. E. Zelenin, S. P. Makarov, V. A. Shpanskii, G. P. Kotel′nikova, L. F. Sergienko, L. L. Martynova, *Dokl. Akad. Nauk SSSR* **1962**, *142*, 354–357; c) A. S. Filatov, S. P. Makarov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1968**, *38*, 33–35; d) A. S. Filatov, S. P. Makarov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1968**, *38*, 35–38; e) A. S. Filatov, S. P. Makarov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1968**, *38*, 40–42; f) A. S. Filatov, S. P. Makarov, A. Y. Yakubovich, *Zh. Obshch. Khim.* **1968**, *38*, 247–249; g) P. S. Engel, W.-X. Wu, *J. Org. Chem.* **1990**, *55*, 1503–1505.

[8] T. Abe, G.-H. Tao, Y.-H. Joo, Y. Huang, B. Twamley, J. M. Shreeve, *Angew. Chem.* **2008**, *120*, 7195–7198; *Angew. Chem. Int. Ed.* **2008**, *47*, 7087–7090.

[9] This compound has been reported to be extremely shock sensitive and explodes on rubbing with spatula. See ref. [3a].

[10] It is reported that **2c** was successfully isolated and distilled (b. p. 99 °C). See ref. [6d].

[11] B. J. Liddle, J. R. Gardinier, *J. Org. Chem.* **2007**, *72*, 9794–9797, and references therein.

[12] It is reported that some aliphatic trifluoromethylazocarboxylic acids rearrange to trifluoromethylhydrazonocarboxylic acid by a proton shift during distillation. See ref. [6f].

[13] CCDC-710866 (**10**) and CCDC-710867 (**13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data center via www.ccdc.cam.ac.uk/data_request/cif.

[14] Reichel & Partner GmbH, http://www.reichel-partner.de/.

[15] C. Ye, J. M. Shreeve, *J. Phys. Chem. A* **2007**, *111*, 1456–1461.

[16] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[17] R. G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press; New York, **1989**.

[18] a) C. M. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622; b) J. A. Pople, J. S. Binkely, R. Seeger, *Int. J. Quantum Chem.* **1976**, *10*, 1–19.

[19] a) H. Gao, C. Ye, C. M. Piekarski, J. M. Shreeve, *J. Phys. Chem. C* **2007**, *111*, 10718–10732; b) M. W. Schmidt, M. S. Gordon, J. A. Boatz, *J. Phys. Chem. A* **2005**, *109*, 7285–7295.

[20] S. Bastea, L. E. Fried, K. R. Glaesemann, W. M. Howard, P. C. Souers, P. A. Vitello, Cheetah 5.0 User's manual, Lawrence Livermore National Laboratory, **2007**.
[21] C. Ye, G. L. Gard, R. W. Winter, R. G. Syvret, B. Twamley, J. M. Shreeve, *Org. Lett.* **2007**, *9*, 3841–3844.
[22] H. Hope, *Prog. Inorg. Chem.* **1994**, *41*, 1–20.
[23] SMART, version 5.632, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, **2005**.
[24] SAINTPlus, version 7.23a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, **2004**.
[25] CELL_NOW, G. M. Sheldrick, **2002**.
[26] SADABS, version 2007/4 and TWINABS, version 2007/5, empirical absorption correction programs, G. M., Sheldrick, Bruker AXS Inc., Madison, WI, **2007**.
[27] SHELXTL, version 6.14, Structure Determination Software Suite, G. M. Sheldrick, Bruker AXS Inc., Madison, WI, **2004**.

Received: January 7, 2009
Published online: February 26, 2009

