Binary CN Compounds

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Well Known or New? Synthesis and Structure Assignment of Binary C_2N_{14} Compounds Reinvestigated**

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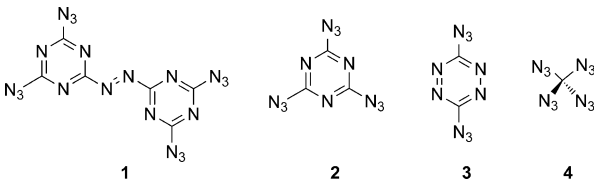
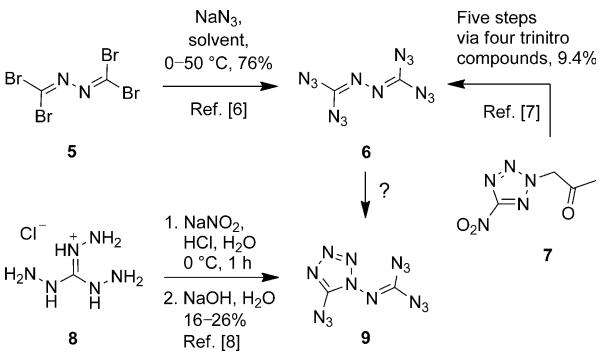
Dedicated to Professor Ernst-Ulrich Würthwein on the occasion of his 65th birthday

Nitrogen-rich organic compounds have gained attention recently because of their high heats of formation and possible applications as highly energetic materials.[1] However, binary CN compounds such as polyazides **1**,[2] **2**,[3] **3**,[4] and **4**[5] are notorious for their extreme sensitivity towards friction and impact (Scheme 1).

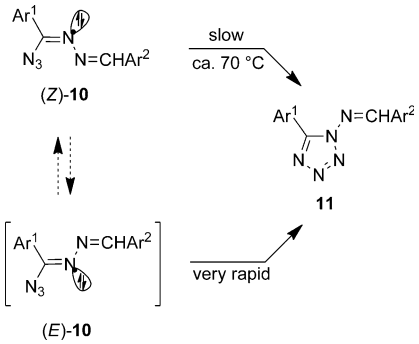


Scheme 1. Polyazides as nitrogen-rich binary CN compounds.

Isocyanogen tetraazide (**6**) was first prepared from the corresponding tetrabromide **5** in 1961 (Scheme 2).[6] At that time, **6** was the most nitrogen-rich organic compound known. Later, **6** was also synthesized by using the multiple-step sequence **7**→**6**.[7] The unique product **6** was characterized by elemental analysis, a melting point of 89 °C,[6] and more recently by a melting point of 76–77 °C as well as by HRMS, EIMS, and IR spectroscopic data.[7] Up to now, however, structural proof by ^{13}C NMR, ^{14}N NMR, and ^{15}N NMR spectra and by single-crystal X-ray diffraction has been lacking. In contrast to this, the isomeric compound **9** was characterized by Klapötke et al. so thoroughly that there is no doubt of the monocyclic tetrazole structure.[8] The C_2N_{14} compound **9**, which shows a melting point of 78 °C, was prepared from salt **8** by nitrosation followed by "dimerization" and ring closure. Surprisingly, the heterocycle **9** seems to be more susceptible toward shock and friction than the tetraazide **6**.[8a] In general, aromatic tetrazoles are less sensitive than covalent azides.[9] It is even more remarkable that **6** does not spontaneously cyclize to yield **9**. Whereas imidoyl azides such as (*Z*)-**10** are well known to undergo slow ring closure only at higher temperatures owing to their unfavorable stereochemistry, the diastereomeric azines (*E*)-**10**, which have a *cis* orientation of the imino lone pair and the azido group, were postulated to form the tetrazoles **11** very rapidly (Scheme 3).[10] Consequently, immediate cyclization of tetraazido-2,3-diazabuta-1,3-diene (**6**) could be expected and this should actually exclude the isolation of this open-chain compound at room temperature.



Scheme 2. Synthesis of the binary C_2N_{14} compounds **6** and **9**.



Scheme 3. Ring closure of azido azines **10**.

Herein, we show that the substances isolated in 1961[6] and 2009[7] and claimed to possess the C_2N_{14} structure of **6** are identical with isomeric tetrazole **9** because the ring closure

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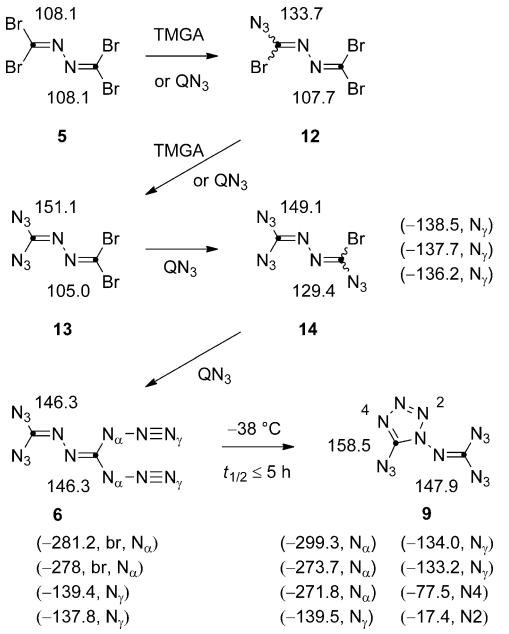
6→**9** is very rapid at room temperature. Nevertheless, we were able for the first time to characterize **6** by NMR spectroscopic methods when the synthesis was performed at low temperature.

After treating tetrabromide **5**[11,12] with sodium azide in aqueous acetone at 0°C and workup as described,[6] we exclusively obtained a highly explosive product which showed two signals ($\delta = 148.0$, 159.5 ppm; see Table 1) in the ^{13}C NMR spectrum. These data are not compatible with the symmetric structure of **6** but nearly identical with the chemical shifts found for Klapötke's compound **9**.[8,13] Thus, we reacted **5** with $Na^{15}N_3$ in analogy to get the 12-fold ^{15}N-labeled product and strongly convincing proof of the structure with the help of ^{15}N NMR spectroscopy. This method indicated nine signals for three different azido groups and three signals that were assigned to a tetrazole unit (Table 1). Our ^{15}N NMR spectroscopic data complement the four broad ^{14}N NMR signals which were observed[8] for compound **9**. Apparently, the tetrazole **9** and not the isomeric tetraazide **6** has been isolated[14] after treatment of **5** with sodium azide. We assumed that the open-chain compound **6** is a short-lived intermediate that rapidly undergoes cyclization to generate **9**.

We confirmed this hypothesis by reacting **5** with an excess of tetramethylguanidinium azide (TMGA) in $CDCl_3$ or with highly soluble hexadecyltributylphosphonium azide (QN_3)[15] in CD_2Cl_2 at low temperatures (−56 to −45°C) and monitoring the reaction progress with the aid of ^{13}C NMR spectroscopy (Scheme 4). The successive transformation of **5** into the less-symmetrical substitution products **12**, **13**, and **14** was observed. Only a single diastereomer was detected in the cases of **12** and **14**. In the temperature range of −45 to −38°C, the increase of a single ^{13}C NMR signal at $\delta = 146.3$ ppm indicated the formation of the symmetrical tetraazide **6**. Further increase of the temperature (−38 to −25°C) led exclusively to the final product **9**. By using ^{13}C NMR spectroscopy, we were able to roughly estimate the half-life of **6** to be $t_{1/2} \leq 5$ h at −38°C although completion of the substitution step **14**→**6** was always accompanied by partial ring closure **6**→**9**. The latter process seems to be irreversible because not even traces of **6** can be detected by ^{13}C NMR spectroscopy[16] during analysis of a solution of the C_2N_{14} compound at room temperature. When such a solution of **9** is cooled, no equilibrium is evident in which **6** can be found.



Scheme 4. ^{13}C NMR and ^{15}N NMR (in brackets) δ values of **5** and its products after treatment with TMGA/$CDCl_3$, QN_3/CD_2Cl_2, or $Q^{15}N{=}N{=}^{15}N/CD_2Cl_2$ at −56 to −35°C. ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$ (−50°C for **5**, **12**, and **13**) or CD_2Cl_2 (−45°C/**14**, −38°C/**6**, −35°C/**9**). ^{15}N NMR spectra were measured at 40.5 MHz in CD_2Cl_2 (−45°C/**14** or −50°C for **6** and **9**) with $MeNO_2$ as external standard.

When **5** was analogously treated with $Q^{15}N{=}N{=}^{15}N$ (49% ^{15}N labeling in both positions)[15,17] in CD_2Cl_2, the substitution reactions could also be monitored by ^{15}N NMR spectroscopy. The signals of intermediate **14** indicated three nonequivalent azido groups whereas only two different azido units were exclusively found in the case of **6** (Scheme 4). At higher temperatures, the latter compound underwent rapid ring closure to yield [$^{15}N_8$]-**9** (Table 1).

Our results demonstrate that the open-chain compound **6** is an elusive species, which already undergoes very fast cyclization at −20°C to afford **9**. Thus, we were not able to run NMR spectra of **6** at 0°C. Consequently, the substances that were isolated at room temperature after treatment of **5** with sodium azide or as final product from the reaction sequence

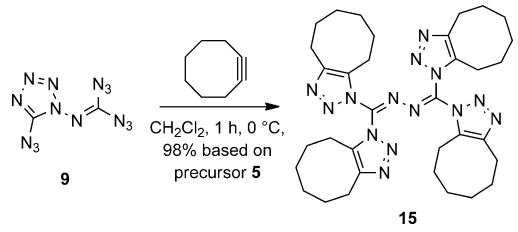
Table 1: Selected NMR spectroscopic data for **9**, [$^{15}N_8$]-**9**, and [$^{15}N_{12}$]-**9** prepared from **5** and NaN_3, $Na^{15}N{=}N{=}^{15}N$, and $Na^{15}N_3$, respectively.[a]

9	^{13}C NMR:	$\delta = 147.77$ (s, $(N_3)_2C{=}N$), 157.71 (s, tetrazole)
	^{13}C NMR:[b]	$\delta = 148.00$ (s, $(N_3)_2C{=}N$), 159.46 (s, tetrazole)
[$^{15}N_8$]-**9**	^{15}N NMR:	$\delta = -300.11$ (s, N_α), −274.55 (s, N_α), −272.73 (s, N_α), −139.37 (s, N_γ), −133.68 (s, N_γ), −133.21 (s, N_γ), −77.06 (s, tetrazole N4), −16.74 (s, tetrazole N2)
[$^{15}N_{12}$]-**9**	^{15}N NMR:	$\delta = -300.18$ (dd, $^1J_{N\alpha N\beta} = 14.6$ Hz, $J = 0.6$ Hz, N_α), −274.78 (ddt, $^1J_{N\alpha N\beta} = 15.6$ Hz, $J = 1.2$ Hz, $J = 0.8$ Hz, N_α), −272.96 ("dm", $^1J_{N\alpha N\beta} = 15.9$ Hz, N_α), −150.70 (dd, $^1J_{N\beta N\alpha} = 15.5$ Hz, $^1J_{N\beta N\gamma} = 5.9$ Hz, N_β), −150.45 (ddd, $^1J_{N\beta N\alpha} = 15.9$ Hz, $^1J_{N\beta N\gamma} = 6.2$ Hz, $J = 1.3$ Hz, N_β), −145.85 (dd, $^1J_{N\beta N\alpha} = 14.5$ Hz, $^1J_{N\beta N\gamma} = 6.5$ Hz, N_β), −139.35 (d, $^1J_{N\gamma N\beta} = 6.5$ Hz, N_γ), −133.72 (dd, $^1J_{N\gamma N\beta} = 5.9$ Hz, $^2J_{N\gamma N\alpha} = 1.1$ Hz, N_γ), −133.30 (dd, $^1J_{N\gamma N\beta} = 6.2$ Hz, $^2J_{N\gamma N\alpha} = 0.7$ Hz, N_γ), −77.15 (ddd, $^1J_{N4N3} = 20.3$ Hz, $J = 1.3$ Hz, $J = 0.4$ Hz, tetrazole N4), −16.89 (d, $^1J_{N2N3} = 16.2$ Hz, tetrazole N2), 3.01 (dd, $^1J_{N3N4} = 20.4$ Hz, $^1J_{N3N2} = 16.2$ Hz, tetrazole N3)

[a] ^{13}C NMR and ^{15}N NMR spectra were recorded at 100.6 and 40.5 MHz, respectively, in $CDCl_3$ at room temperature. δ values in ppm. [b] Recorded in [D_6]DMSO.

starting from **7**[6,7] cannot have the structure of **6**. Instead, the formation of the isomeric C_2N_{14} compound **9** is now proved for the substitution of **5** and most likely for the product resulting from **7**.

The structures of binary C_2N_{14} compounds such as **6** and **9** should be directly deduced from their spectroscopic data since subsequent reactions to produce less dangerous derivatives can lead to outcomes that are easily misunderstood. For example, treatment of **9** with an excess of cyclooctyne[18] furnished the cycloadduct **15**, the structure of which was confirmed by NMR data and also by single-crystal X-ray diffraction analysis (Scheme 5, Figure 1). However, **15** is obviously not formed from **6**. We assume that **9** first cycloadds



Scheme 5. Reaction of **9** with cyclooctyne.

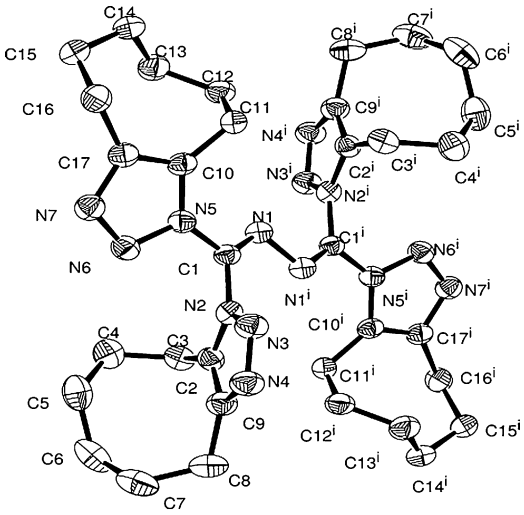


Figure 1. ORTEP view of the molecular structure of **15** (without H atoms) in the solid state, determined by single-crystal X-ray diffraction analysis. Thermal ellipsoids at 50% probability.

three molecules of cyclooctyne. The conversion of electron-releasing azido groups into electron-withdrawing 1*H*-1,2,3-triazol-1-yl units should shift the tetrazole–azidoazomethine equilibrium[9c,19] to liberate the fourth azido function, which reacts with cyclooctyne to produce **15**.

In summary, we have demonstrated that the tetrazole **9** has been known since 1961 although an alternative synthesis reported in 2011 was claimed to be the first route to this C_2N_{14} compound.[8] In 1961[6] and also in 2009,[7] however, it was not recognized that the open-chain tetraazide **6** could not be isolated at ambient temperature because it tends to cyclize very rapidly to give the isomeric substance **9**. Thus, the elusive binary CN compound **6** was characterized now by NMR spectroscopy for the first time.

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[12] We utilized Thiele's three-step sequence with isolation of 1,2-di(tetrazol-5-yl)hydrazine instead of the alternative two-step procedure because the final product **5** was significantly purer.
[13] After consideration of the δ values of **6**, **13**, and **14**, we assigned the ^{13}C NMR signals of **9** in a different way than in Ref. [8].
[14] **Caution!** The azide **9** is extremely explosive and should be handled only in solution if possible (see also Ref. [8]). Thus, the description of the properties of **6** in Ref. [6a] is misleading. For potential hazards in handling hydrazoic acid and organic azides, see: T. Keicher, S. Löbbecke in *Organic Azides: Syntheses and Applications* (Eds.: S. Bräse, K. Banert), Wiley, Chichester, **2010**, pp. 3 – 27.
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