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Binary CN Compounds

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C_2N_{14}: An Energetic and Highly Sensitive Binary Azidotetrazole[**]

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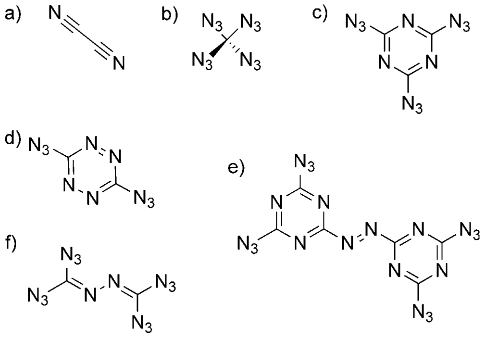
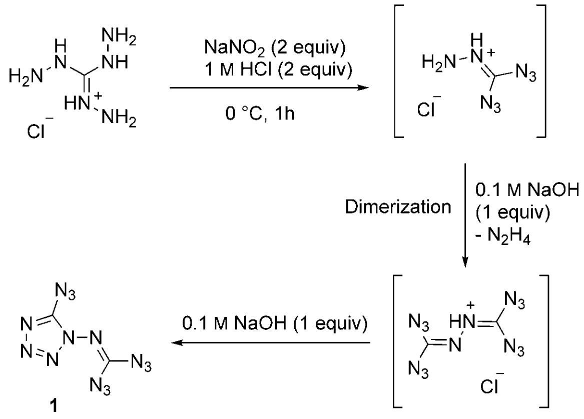
Although binary CN compounds are of great interest, only a few examples are known, which is mostly due to the fact that their chemistry is very challenging. Binary CN compounds exhibit a large variety of characteristics; they can be very harmful owing to their toxicity, such as dicyanogen,[1] and they are thought to be very hard, as calculated for β-C_3N_4,[2] or show graphite-like nanostructures with good electric and catalytic properties, such as mpg-C_3N_4.[3] Furthermore, binary CN compounds composed of azides are highly sensitive towards shock, friction, and electrostatic discharge.

Investigations on these compounds started at the beginning of the 20th century when Ott and Ohse presented C_3N_{12} in 1921 (Scheme 1) as the first binary azido heterocyclic system.[4] Research into heterocyclic azides was recently intensified,[5] as they present very good systems to study highly energetic materials enabled by high positive heats of formation.[5c,6] The high heats of formation derive from the energy input of the azide substituents (70 kJ mol^{-1})[7] and from the large number of energetic N–N and C–N bonds combined in the heterocyclic ring systems. Non-heterocyclic binary CN systems have also attracted much interest, such as tetraazidomethane,[8,5e] which has an extreme sensitivity towards shock and friction, or the open form of the title compound C_2N_{14}, isocyanogentetraazide,[9] which is somewhat less sensitive than the title compound.[10]



Scheme 1. Selected binary CN compounds: a) dicyanogen, b) tetraazidomethane, c) triazidotriazine, d) diazidotetrazine, e) tetraazidoazotriazine (TAAT), and f) C_2N_{14} (open form).

To date, only the open form of C_2N_{14} was known, which can be synthesized by a metathesis reaction of isocyanogentetrabromide with sodium azide.[9] Herein, the synthesis of the closed form of C_2N_{14}, 1-diazidocarbamoyl-5-azidotetrazole (**1**), is presented for the first time, being synthesized by diazotation of triaminoguanidinium chloride in water with two equivalents of sodium nitrite. A suggested mechanism of this reaction is presented in Scheme 2.



Scheme 2. Possible reaction pathway leading to the formation of **1**.

Various attempts using different reaction conditions always yielded **1** as the kinetically stable product, but in different yields. To initiate the dimerization reaction and the following ring-closure reaction,[11] respectively, the acidic reaction solution is brought to pH 8 slowly with 0.1 M sodium hydroxide solution. Basic reaction conditions are very important in this reaction step, otherwise residual sodium nitrite can decompose the azide groups partially, forming amines as byproducts. Compound **1** can be easily isolated by extraction of the reaction solution with diethyl ether followed by a purification step using short-column chromatography with $CHCl_3$ as solvent to remove the decomposition products mentioned above.[12] Compound **1** is obtained as a colorless crystalline solid after recrystallization from diethyl ether, and has a melting point at 78 °C and decomposition starting at 110 °C.

Single crystals of **1** suitable for X-ray diffraction measurements were obtained by recrystallization from diethyl ether. Compound **1** crystallizes in the orthorhombic space group *Pbcn* with a cell volume of 1697.6(2) Å^3 and eight molecules in the unit cell.[13] The bond lengths and angles in the tetrazole rings are in the normal range expected for an azidotetrazole.[14] The N1–N8 bond (1.403(4) Å) only slightly shorter than a formal N–N single bond (1.48 Å),[15] while the N8–C2 bond (1.288(5) Å) is in the range of a C–N double bond (1.22 Å).[15] As shown for 5-azido-1*H*-tetrazole, the azide

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group located on the 5 position lies perfectly within the plane of the tetrazole ring.[5d] The asymmetric unit of **1** is presented in Figure 1.

The carbamoyl diazide group in **1** itself is twisted out of the plane of the tetrazole ring (N1,N2,N3,N4,C1) by 66.12° relative to the plane formed by N12, C2, N9, and N8. This twist within the molecule results in the buildup of 2D chains along the *c* axis which show a zigzag conformation with an angle of 113.22° (Supporting Information, Figure S4).

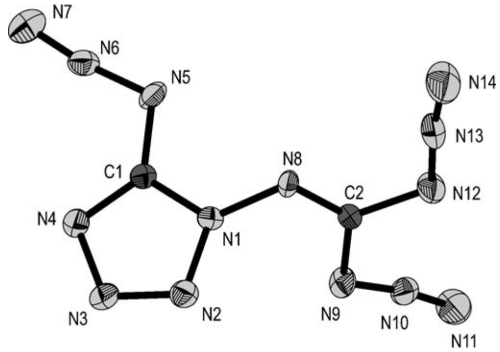

Figure 1. ORTEP representation of **1**. Thermal ellipsoids are set at 50% probability. Selected crystallographic data: orthorhombic, *Pbcn*; $Z=8$, $a=18.1289(1)$, $b=8.2128(7)$, $c=11.4021(9)$ Å, $\alpha=\beta=\gamma=90°$, $V=1697.6(2)$ Å^3.

Calculations of the electrostatic potential at the B3LYP/cc-pVDZ level of theory[16] in the gas phase show a clear charge distribution within **1**, which is reflected in the structure. The positive charge is located on the azide moieties, with N_β exhibiting the highest positive charge compared to N_α and N_γ. The negative charge is mainly located on the N4, N3, and N2 nitrogen atoms of the tetrazole ring, hence exhibiting a large inhomogeneity in the charge distribution (Supporting Information, Figure S5).

Short contacts are found between terminal nitrogen atoms N11 and N13 (3.125(6) Å) and between N7 and N3 (3.047(5) Å), which are much shorter than the sum of van der Waals radii for nitrogen atoms ($2r_w(N)=3.2$ Å).[15] The bonding situation is shown in Figure 2. A very rare bonding situation can be observed in which the structure is formed exclusively by interactions between partially charged nitrogen atoms.

The 2D chains are stacked along the *b* axis with a distance of 5.993 Å between coplanar chains (every second chain, chains in between are rotated by 180°; Figure 3). The very dense packing is represented by a high density of $\rho=1.723\,\mathrm{g\,cm^{-3}}$. The chains are connected through short N–N contacts, namely N9···N3 at 3.051 Å and N9···N2 at 3.001 Å, also showing very strong electrostatic interactions between negatively and positively charged nitrogen atoms.[17]

IR and Raman spectra of **1** were recorded in the solid state. For safety reasons, only a small number of crystals were measured (the compound decomposes explosively upon irradiation by a Nd:YAG laser with an intensity of only 150 mW!). The IR frequencies were also calculated using the B3LYP/cc-pVDZ level of theory and fitted according to Witek and Keiji with a scaling factor of 0.9704.[18] The theoretical values are in good agreement with the experimental data, in which the stretching modes of the azide groups were observed in the region between 2100 and 2200 cm^{-1}. In both Raman and IR spectra, a splitting was observed. Stretching modes of the azide groups are observed at 2179 cm^{-1}, 2165 cm^{-1}, and 2133 cm^{-1} (Raman) and 2175 cm^{-1}, 2155 cm^{-1}, and 2133 cm^{-1} (IR; Figure 4). Even though we performed computational calculations regarding the stretching modes, we cannot clearly distinguish between the stretching modes for each individual azide group because the difference in the wavenumbers is too small. From the calculations of the IR spectra, we were able to see stretching motions of all three azide groups in **1** for each of the frequencies mentioned above. For each IR band however, one azide group shows a much larger stretching motion than the other two. The calculated frequencies and intensities are compiled in the Supporting Information, Table S3.

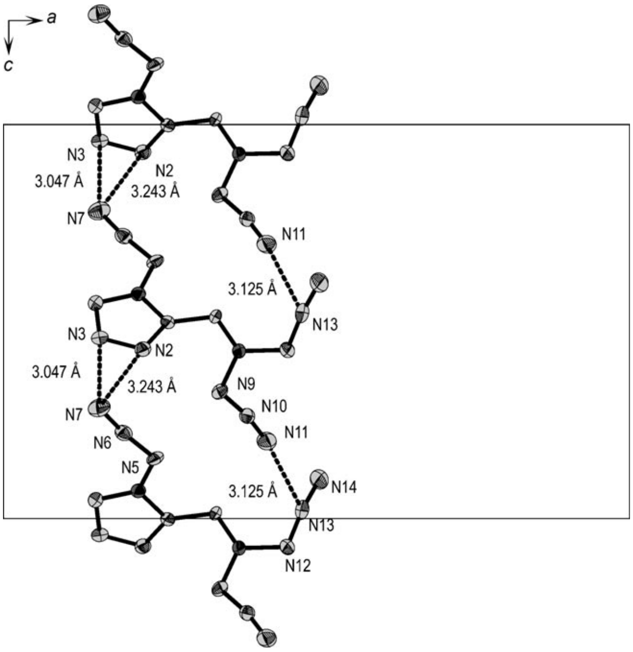

Figure 2. Short N–N contacts, which correspond to electrostatic interactions. Thermal ellipsoids are set at 50% probability.

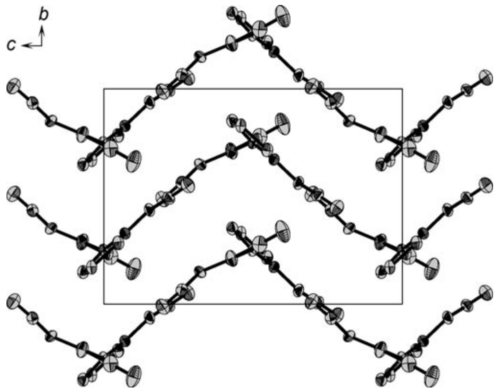

Figure 3. Stacking of 2D chains along the *b* axis. ORTEP representation shown along the *a* axis with ellipsoids set at 50% probability.

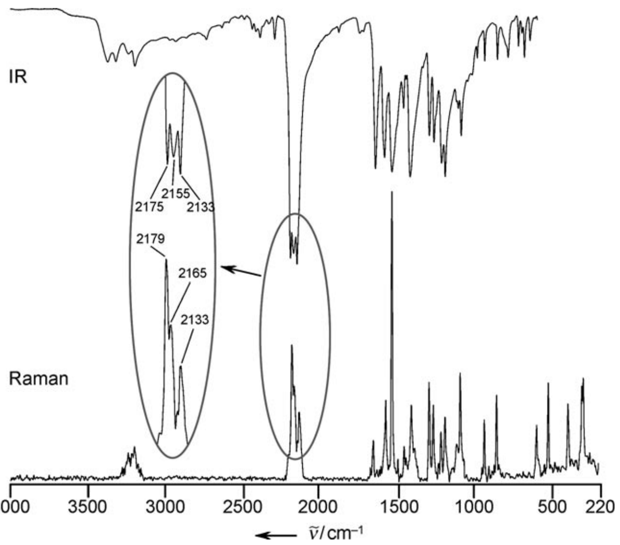

Figure 4. Comparison of the IR and Raman spectra of **1**. The three individual stretching modes for each of the azide groups are identified (expansion shown in the ellipse).

^{13}C and ^{14}N NMR spectroscopy studies reveal clearly assignable peaks for the corresponding carbon or nitrogen atoms. As the carbamoyl diazide group can rotate freely around the N1–N8 bond in solution, only two signals are observed in the ^{14}N spectra regarding the N_β nitrogen atoms of the three azide groups (N6, N10, N13). The N_α signals can be observed, but lead to a very broad signal. The N_γ signals were also observed as a very broad signal, but are overlapped by the two N_β peaks. If the solvent is changed from $CDCl_3$ to [D$_6$]DMSO, only one broader peak can be observed for the three N_β atoms.

The sensitivity of C_2N_{14} is beyond our capabilities of measurement. The smallest possible loadings in shock and friction tests led to explosive decomposition. It must be stated that the shock and friction sensitivity of **1** no doubt lies well under the limits of 0.25 J in impact and 1 N in friction sensitivity that can be experimentally determined (Table 1).

This sensitivity is thought to be due to the enormous inequality in the charge distribution, which is known to be responsible for such an increase in sensitivity.[19] Additionally, owing to the extremely high heat of formation (1495 kJ mol^{-1}), which is higher than most known heats of formation for CN systems,[5c] and the very high nitrogen content of 89.08 %, compound **1** is very powerful and has to be handled with extreme care!

Table 1: Compiled sensitivities, calculated heats of formation, and detonation parameters for **1**.[a]

IS [J]	FS [N]	ρ [g cm^{-3}]	ΔH_f^0 (s) [kJ mol^{-1}]	Q_v [kJ kg^{-1}]	P_{C-J} [kbar]	V_{det} [m s^{-1}]
< 0.25	< 1	1.723	1495	−6855	339	8960

[a] IS = impact sensitivity, FS = friction sensitivity, ΔH_f^0 = heat of formation, Q_v = heat of explosion, P_{C-J} = detonation pressure at the Chapman–Jouguet point, V_{det} = detonation velocity.

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[12] Details of the synthesis and the characterization of compound **1** along with the complete compilation of analytical data are included in the Supporting Information.

[13] A compilation of the crystallographic data can be found in the Supporting Information.

[14] CCDC 693485 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[17] Additional illustrations of the packing scheme of the crystal structure along the *a* and *b* axis are given in the Supporting Information.

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