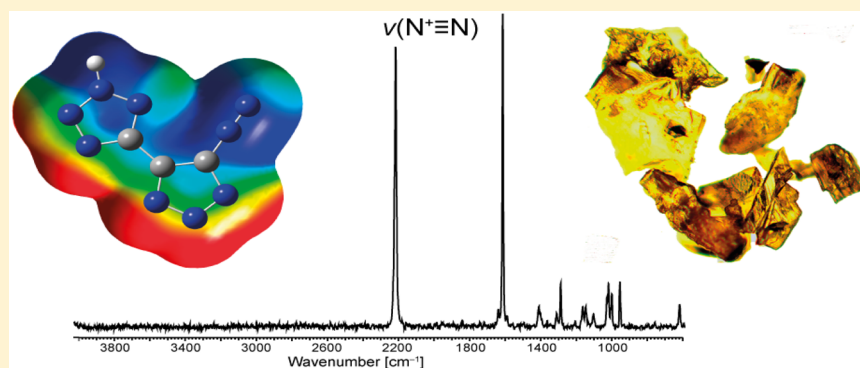# Isolation of a Moderately Stable but Sensitive Zwitterionic Diazonium Tetrazolyl-1,2,3-triazolate

Thomas M. Klapötke,* Burkhard Krumm, and Carolin Pflüger

Department of Chemistry, Ludwig Maximilian University Munich, Butenandtstr. 5-13 (D), 81377 Munich, Germany

S *Supporting Information*

ABSTRACT: An unexpected formation of a diazonium compound was observed by nitration of an amino substituted triazolyl tetrazole with mixed acid. The crystal structure determination revealed a zwitterionic diazonium tetrazolyl-1,2,3-triazolate, whose constitution was supported by NMR and vibrational spectroscopic analysis. The thermal stability and sensitivity toward impact and friction were determined. In contrast, diazotriazoles are rather unstable and are mainly handled in solution and/or low temperatures, which is not the case for this diazonium tetrazolyl-1,2,3-triazolate, being stable at ambient temperature.

Diazoazoles have found wide application as key intermediates in various coupling reactions but also in biological applications.[1] Furthermore, diazonium compounds are important reagents, such as for the conversion into fluoroaromatic compounds according to Balz–Schiemann,[2,3] or for the preparation of azo compounds in the synthetic dye industry.

The formation of diazonium compounds was first reported in 1858 by Griess, who has subsequently discovered various reactions of this compound class.[4,5] The most common method for the synthesis of diazonium compounds is the diazotization of aromatic amines with in situ generated nitrous acid from sodium nitrite and a mineral acid, which was developed in 1875 by Meyer.[5] Several years later, in 1892, the first diazoazole, the highly sensitive diazotetrazole, was synthesized by Thiele, who reported explosions during the synthesis in aqueous solutions at 0 °C.[6] The isolation of 3-diazoindazole by Bamberger in 1899 initiated considerable interest in the properties and reactivity of diazoindoles and diazopyrroles.[7] Furthermore, diazotriazoles, -imidazoles, and -pyrazoles were investigated. Especially, the improvement of techniques for isolation and purification had a great influence in the chemistry of diazoazoles in the second half of the 20th century. On the other hand, diazonium moieties are known to be highly energetic and detonations can be initiated by shock, heat, or exposure to concentrated acids, and therefore, they are often not isolated for safety reasons but directly used in further reactions.[8,9] The stability and reactivity of diazoazoles depend strongly on the mutual influence of the

azole ring and the diazo moiety.[1] Especially, the properties differ according to the azole rings because they range from an electron-rich azole, such as pyrrole, to very electron-deficient azoles, such as tetrazole.

Pyrazole-3-diazonium derivatives are the most extensively studied diazoazoles in regard to stability and reactivity.[10] The more energetic diazo 1,2,3- and 1,2,4-triazoles are much less studied because of their lower stability, and hence difficulties in isolation and safe handling (mainly only in solution) remain challenges.[8] The resonance stabilization of the diazoazoles determines their stability and reactivity due to the delocalization of the negative charge over the azole ring.[1,11] Two crystal structures of diazo 1,2,4-triazoles[12,13] have been reported, showing the zwitterionic character of the diazotriazole in accordance to other diazoazole structures.[14] However, to the best of our knowledge, no crystal structures of diazo-1,2,3-triazoles have been reported so far.

5-(5-Amino-2H-1,2,3-triazol-4-yl)-1H-tetrazole (**1**) was synthesized in five steps as reported recently by us starting from commercially available benzyl chloride.[15] The nitration of **1** with nitric acid (100%, traces of NO_2) in concentrated sulfuric acid at 5 °C and stirring for 12 h at room temperature did not yield the expected corresponding nitramine ($RNHNO_2$), but

the inner diazonium salt **2** (Scheme 1). This could be due to the presence of NO_2 in the nitration mixture.

Scheme 1. Nitration of 5-(5-Amino-2H-1,2,3-triazol-4-yl)-1H-tetrazole (1) with Mixed Acid To Form the Diazonium 1,2,3-Triazolate (2)
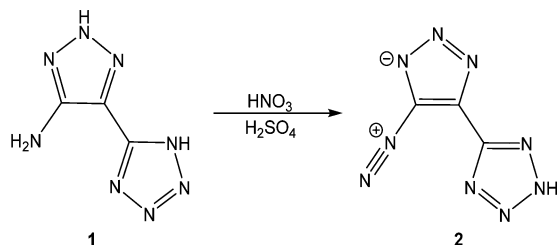
The synthesis of the diazonium salt by direct diazotization in concentrated sulfuric acid using sodium nitrite was not successful. The use of another mineral acid or diluted sulfuric acid was not possible due to the low solubility of the amine **1**.

The formation of the inner diazonium salt 5-diazonium-4-(2H-tetrazol-5-yl)-1,2,3-triazolate (**2**) is proven by its crystal structure showing a deprotonated triazole ring (Figure 1). Selected crystallographic data are summarized in the Supporting Information.
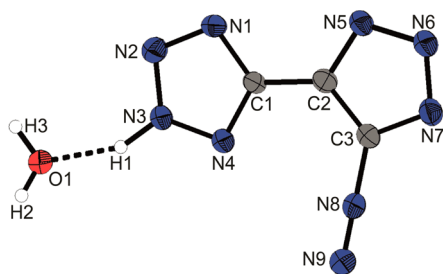

Figure 1. Molecular structure of 5-diazonium-4-(2H-tetrazol-5-yl)-1,2,3-triazolate monohydrate (**2·H₂O**). Thermal ellipsoids are drawn at the 50% probability level.

The triazole and tetrazole rings are twisted by an angle of 8° (∠N5−C2−C1−N4:172.3(2)). The diazonium group N9−N8−C3 is in plane with the triazole ring showing an angle of almost 180° (∠N9−N8−C3:179.9(2)°). The diazonium N8−N9 bond length of 1.096(3) Å is virtually identical to those found in various diazonium cations[14,16,17] and inner diazonium salts[12,18] clearly indicating a N≡N triple bond (1.10 Å[19]). The C3−N8 bond length (1.365(3) Å) is in the range of common C_{sp^2}−N bond lengths (1.34−1.37 Å).[20]

The crystal structure consists of diagonal layers along the *b* axis (Figure 2). The arrangement of the molecules within one layer is supported by hydrogen bonds involving all protons. The heterocyclic proton H1 interacts with the oxygen O1 of the crystal water over a distance of 1.68(3) Å. From each proton of the crystal water, hydrogen bonds are observed to the tetrazole nitrogen N1 and the triazole nitrogen N7, respectively (Table S3).

Furthermore, the diazonium nitrogen N9 shows a dipolar N···N interaction to the tetrazole nitrogen N2 (2.884(3) Å). The layers are connected by weak intermolecular dipolar C···N interactions between C3 and N6 of 3.076(2) Å and a dipolar N···O interaction (N8···O1 2.909(2) Å), which are below the sum of their van der Waals radii.[20]
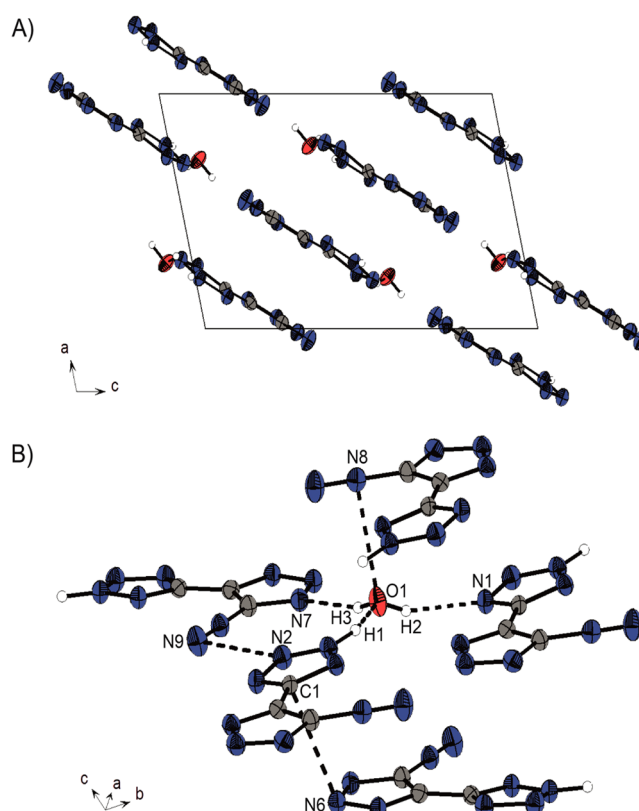
Figure 2. (A) Unit cell of **2·H₂O** along the *b* axis. (B) Interactions within the crystal structure of **2·H₂O**.

The computed electrostatic potential (ESP) of the molecular surface (Figure 3) clearly shows a large electron-deficient area above the diazonium group and an electron-rich area above the triazole nitrogens thus confirming the zwitterionic structure.

The solubility of **2** only in DMSO-d_6 is sufficiently good to allow thorough NMR characterization, especially the meaningful ^{15}N NMR spectroscopy. However, after a few days in
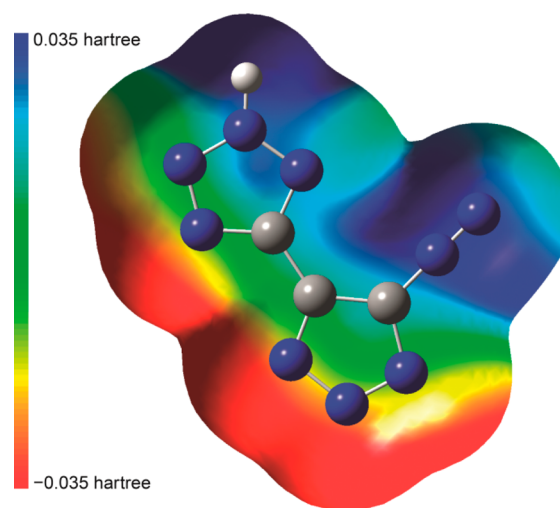

Figure 3. Z-clipped molecular surface electrostatic potential (ESP) of **2** calculated at the B3LYP/6-31G(d,p) level at the 0.001 e/bohr³ hypersurface.[21] The legend for the color range is given on the left, and the range is from −0.035 (red, electron-rich) to 0.035 (blue, electron-deficient) hartrees.
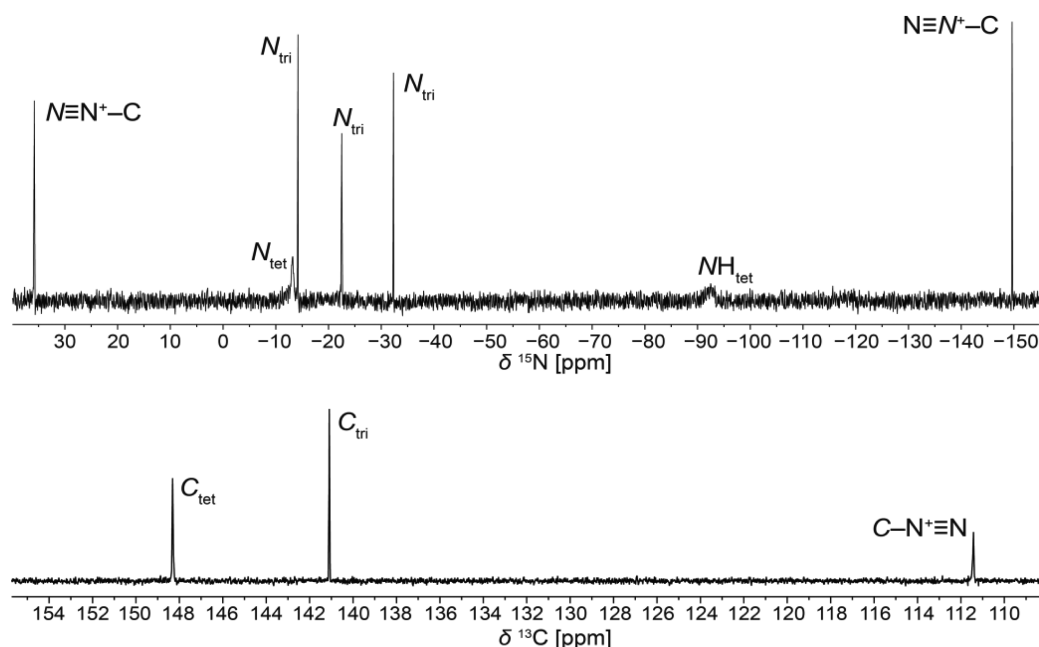
Figure 4. ^{13}C and ^{15}N NMR spectra of 5-diazonium-4-(2H-tetrazol-5-yl)-1,2,3-triazolate (**2**) in DMSO-d_6.

DMSO-d_6 a color change from yellow via orange to finally red indicates significant decomposition.

In the ^{1}H NMR spectrum at 6.5 ppm the broadened resonance of the acidic proton of the tetrazole ring is observed. In the ^{13}C NMR spectrum (Figure 4, bottom) the tetrazole carbon resonance is shifted to lower field (148.3 ppm) in comparison to the carbon resonances of the triazole ring. The resonance signal of the triazole carbon atom attached to the tetrazole is observed at 141.1 ppm, whereas the resonance signal of the diazonium bonded carbon is shifted to higher field and broadened (111.5 ppm). This large upfield shift in comparison to other triazole carbon atoms is characteristic for the *ipso* carbon atom of the diazo group.[1] In the proton-coupled ^{15}N NMR spectrum all seven nitrogen resonances are observed (Figure 4, top).

For the tetrazole, only two signals are observed, due to the proton exchange in DMSO-d_6, one signal of the protonated nitrogen at −92.5 ppm (NH) and one of the nonprotonated nitrogen at −13.0 ppm. Both resonances are nicely identified by the broadened appearance due to the direct coupling to hydrogen, respectively over two bonds. A definite assignment of the location of the tetrazole hydrogen atom is not possible, because in solution the NH_{tet} can be found at position 1 or 2 of the tetrazole ring. The resonances of the triazole unit cannot be unambiguously assigned with regard to the specific position of the 1,2,3-triazole. The resonance signal of the positive charged diazonium nitrogen is found at higher field (−149.6 ppm) in the ^{15}N NMR (proven also by the appearance of one visible resonance in the ^{14}N NMR spectrum, which has to be assigned to the positively charged nitrogen at the same position). The terminal diazonium nitrogen atom is unusually detected at low field at +35.8 ppm. The few existing ^{15}N NMR data for diazonium salts report resonances at around −60 ppm for the terminal nitrogen, whereas that of the positively charged nitrogen appears within a narrow range around −150 ppm.[22] The ^{15}N NMR resonances for the terminal nitrogen in diazoalkanes of the type RR′C=N=N seem to be rather flexible, but some exhibit resonances in the range of +60 to +30

ppm,[23] depending on the substituents, and, thus, are in the same region as the observed terminal nitrogen resonance in **2**.

In the IR and Raman spectra of **2** the characteristic valence vibration of the diazonium N≡N bond is observed in the expected region as strong bands at 2206 and 2210 cm^{-1}, respectively.

The loss of the crystal water molecule is observed at 90 °C over a broad temperature range, and directly afterward **2** decomposes. The diazonium salt **2** is thermally stable up to 141 °C, which is comparable to other diazonium 1,2,3-triazoles such as 4-diazonium-1,2,3-triazolate-5-carboxamide (175 °C) and 4-diazonium-1,2,3-triazolate-5-(phenyl)methanone (134 °C).[9,24]

Furthermore, the mechanical sensitivity to impact and friction were determined and classified according to the UN recommendations for the transport of dangerous goods.[25] The diazonium compound **2** is classified as very sensitive to impact (<1 J) and friction (40 N). However, it is less sensitive than 3-diazo- and 4-diazotriazoles, which are light and shock sensitive and explode when scratched.[1]

The inner diazonium salt 5-diazonium-4-(2H-tetrazol-5-yl)-1,2,3-triazolate (**2**) was isolated from the reaction mixture of 5-(5-amino-1,2,3-triazol-4-yl)tetrazole (**1**) in mixed acid. The zwitterionic structure with the delocalized negative charge at the triazole ring was confirmed by single-crystal X-ray analysis. NMR spectroscopic investigation reveals an unusual low-field shift of the terminal nitrogen of the diazonium unit. The diazonium triazolate **2** is very sensitive to outer stimuli such as impact and friction and is thermally rather stable. Therefore, this diazonium compound **2** seems to be a promising diazonium material for further chemistry, such as cycloadditions with dipolarophiles, which could lead to a variety of new C,N-heterocycles.

■ EXPERIMENTAL SECTION

General Information. All reagents and solvents were used as received. The decomposition point was measured with a DSC with a heating rate of 5 °C min^{-1}. The NMR spectra were recorded with a 400 MHz instrument ([1]H 399.8 MHz, [13]C 100.5 MHz, [14]N 28.9 MHz, and [15]N 40.6 MHz) at ambient temperature. Chemical shifts are

quoted in parts per million with respect to TMS (^{1}H, ^{13}C) and nitromethane (^{14}N, ^{15}N). Infrared (IR) spectra were measured with an ATR device. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), and "weak" (w). Raman spectra were recorded in glass tubes with Nd:YAG laser excitation up to 300 mW (at 1064 nm) in the range between 200 and 4000 cm^{-1}. The intensities are reported as percentages of the most intense peak and are given in parentheses. Sensitivity data were determined using a BAM drophammer and a BAM friction tester.[26,27] The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN from OZM Research. Single-crystal X-ray diffraction was performed with Mo K$_\alpha$ radiation (λ = 0.71073). The data collection was realized by using CRYSALISPRO software.[28] The structure was solved by direct methods (SIR-92) implemented in the program package WINGX[29] and finally checked using PLATON.[30] All H atoms were located from a Fourier map and refined isotropically, with U_{iso}(H) = 1.2U_{eq}(N,O). Diamond[31] plots are shown with thermal ellipsoids at the 50% probability level. Crystallographic data for the reported structures in this contribution have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers (CCDC 1465295). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Synthesis. *CAUTION! This diazonium compound is an energetic compound with very high sensitivity to various stimuli. While no issues in the synthesis and handling of this material were encountered, proper protective measures (face shield, ear protection, body armor, Kevlar gloves and earthed equipment) as well as a plastic spatula, should be used all the time.*

5-Diazonium-4-(2H-tetrazol-5-yl)-1,2,3-triazolate (2). 5-(5-Amino-1,2,3-triazol-4-yl)tetrazole (**1**) (388 mg, 2.55 mmol) was dissolved in concentrated H_2SO_4 (2.5 mL). The yellow solution was cooled to 0 °C, and 0.4 mL of HNO_3 (100%) was added in small portions and stirred for 2 h at 0 °C. Then the mixture was allowed to slowly warm up to room temperature and stirred overnight. The mixture was poured onto ice (10 g) and stored at 4 °C to obtain yellow crystals of **2**·H_2O (102 mg, 22%).

DSC (5 °C min^{-1}): T_{dehyd} = 90 °C, T_{dec} = 141 °C. ^{1}H NMR (DMSO-d_6, 399.8 MHz) δ: 6.5 (vbr, NH, H_2O) ppm. ^{13}C{^{1}H} NMR (DMSO-d_6, 100.5 MHz) δ: 148.3 (C_{tet}), 141.1 (C_{tri}), 111.5 (br, CN_2^+) ppm. ^{14}N NMR (DMSO-d_6, 28.9 MHz) δ: −150 ($N^+\equiv$N) ppm. ^{15}N NMR (DMSO-d_6, 40.6 MHz): δ = 35.8 (C$N^+\equiv N$), −13.0 (N_{tet}), −14.2/−22.5/−32.3 (N_{tri}), −92.5 (NH_{tet}), −149.6 (C$N^+\equiv$N) ppm. IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3433 (m), 3342 (w), 3230 (w), 3019 (w), 2833 (w), 2730 (w), 2640 (w), 2353 (vw), 2206 (vs), 1867 (vw), 1724 (vw), 1612 (w), 1499 (w), 1464 (vw), 1400 (w), 1365 (vw), 1351 (vw), 1312 (s), 1289 (m), 1246 (vw), 1209 (m), 1166 (m), 1147 (m), 1125 (w), 1074 (w), 1037 (vs), 1004 (m), 981 (w), 958 (m), 937 (m), 903 (w), 826 (vw), 764 (vw), 727 (vw), 685 (vw), 673 (vw). Raman (1064 nm, 300 mW, cm^{-1}): $\tilde{\nu}$ = 2210 (90), 1638 (6), 1613 (100), 1589 (4), 1412 (7), 1404 (6), 1396 (4), 1366 (3), 1312 (5) 1290 (15), 1209 (3), 1168 (7), 1151 (7), 1137 (3), 1107 (5), 1033 (10), 1024 (15), 1005 (11), 960 (15), 765 (2), 628 (8), 578 (4), 505 (3), 428 (3), 385 (5), 377 (7), 207 (13). MS (DCI+): m/e: 273.2 (3) [$C_6H_4N_{14}^+$], 138.1 (9) [$C_3H_3N_7^+$]. Anal. Calcd for C_3HN_9·H_2O: C, 19.89; H, 1.67; N, 69.60. Found C, 19.77; H, 2.20; N, 65.91. Sensitivity (grain size: < 100 μm): IS: < 1 J; FS: 40 N; ESD: 40 mJ.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01098.

> Crystallographic data, vibrational spectra, and computational details (PDF)

> Crystallographic data (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tmk@cup.uni-muenchen.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Cirrincione, G.; Almerico, A. M.; Aiello, E.; Dattolo, G. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: 1990; Vol. 8, p 65.

(2) Balz, G.; Schiemann, G. *Ber. Dtsch. Chem. Ges. B* **1927**, *60*, 1186.

(3) Swain, C. G.; Rogers, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 799.

(4) Griess, P. *Ann. Chem. Pharm.* **1858**, *106*, 123.

(5) Wizinger-Aust, R. *Angew. Chem.* **1958**, *70*, 199.

(6) Thiele, J. *Liebigs Ann. Chem.* **1892**, *270*, 1.

(7) Bamberger, E. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 1773.

(8) Hui, H. K. W.; Shechter, H. *Tetrahedron Lett.* **1982**, *23*, 5115.

(9) Shealy, Y. F.; Struck, R. F.; Holum, L. B.; Montgomery, J. A. *J. Org. Chem.* **1961**, *26*, 2396.

(10) Ledenyova, I. V.; Didenko, V. V.; Shikhaliev, K. S. *Chem. Heterocycl. Compd.* **2014**, *50*, 1214.

(11) Tišler, M.; Stanovnik, B. *Chem. Heterocycl. Compd.* **1980**, *16*, 443.

(12) Dippold, A. A.; Klapötke, T. M.; Martin, F. A.; Wiedbrauk, S. *Eur. J. Inorg. Chem.* **2012**, 2429.

(13) Klapötke, T. M.; Nordheider, A.; Stierstorfer, J. *New J. Chem.* **2012**, *36*, 1463.

(14) Brint, R. P.; Coveney, D. J.; Lalor, F. L.; Ferguson, G.; Parvez, M.; Siew, P. Y. *J. Chem. Soc., Perkin Trans. 2* **1985**, 139.

(15) Izsák, D.; Klapötke, T. M.; Pflüger, C. *Dalton Trans.* **2015**, *44*, 17054.

(16) Alcock, N. W.; Greenhough, T. J.; Hirst, D. M.; Kemp, T. J.; Payne, D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 8.

(17) Cygler, M.; Przybylska, M.; Elofson, R. M. *Can. J. Chem.* **1982**, *60*, 2852.

(18) Izsák, D.; Klapötke, T. M.; Preimesser, A.; Stierstorfer, J. *Z. Anorg. Allg. Chem.* **2016**, *642*, 48.

(19) Holleman, A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*, 102nd ed.; de Gruyter: Berlin, 2007.

(20) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin,

K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

(22) Casewit, C.; Roberts, J. D.; Bartsch, R. A. *J. Org. Chem.* **1982**, *47*, 2875.

(23) Berger, S.; Braun, S.; Kalinowski, H.-O. *NMR Spektroskopie von Nichtmetallen Bd 2, ^{15}N-NMR-Spektroskopie*; Thieme: Stuttgart, New York, 1992.

(24) Stadler, D.; Anschütz, W.; Regit, M.; Keller, G.; VanAssche, D.; Fleury, J.-P. *Justus Liebigs Ann. Chem.* **1975**, 2159.

(25) Test methods according to the *UN Manual of Test and Criteria*.

(26) NATO *Standardization Agreement 4489 (STANAG 4489), Explosives, Impact Sensitivity Tests* 1999.

(27) NATO *Standardization Agreement 4487 (STANAG 4487), Explosives, Friction Sensitivity Tests* 2002.

(28) *CrysAlisPro*, Version 1.171.35.11 (release 16.05.2011 CrysAlis171.net); Agilent Technologies: 2011.

(29) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(30) Spek, A. L.; *Platon, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht (NL), 1997.

(31) Brandenburg, K. *Diamond*, 3.2k ed.; Crystal Impact GbR: Berlin, 2014.