Synthesis and X-ray Structure Determination of *tert*-Butylhydrazinium Azide and *N,N,N*-Trimethylhydrazinium Azide

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tert-Butylhydrazinium azide $[t\mathrm{BuNH_2NH_2}]^+[\mathrm{N_3}]^-$ (**1**) was prepared in a high yield reaction from *tert*-butylhydrazine and HN_3. *N,N,N*-Trimethylhydrazinium azide $[\mathrm{NH_2N(CH_3)_3}]^+[\mathrm{N_3}]^-$ (**2**) was prepared from the reaction of silver azide with *N,N,N*-trimethylhydraziniumiodide. Both were characterized by X-ray structural analysis, IR, Raman, and multinuclear (^{1}H, ^{13}C, ^{14}N) NMR spectroscopy.

Introduction

Hydrazinium azide, first reported by Curtius in 1891,[1a] is a powerful explosive that produces only nitrogen, hydrogen, and ammonia after explosion.[1b]

During the last 8 years, significant advances have been made in the area of inorganic azides, as indicated by the number of recent reviews covering various aspects of the subject.[2a–c] In contrast to the chemistry of many hydrazinium salts, which has been extensively explored in the last 30 years,[3][4] detailed studies into the chemistry of ionic hydrazinium azides have only recently come to fruition.[5a,b] We have recently become interested in the preparation of hydrazinium azides and their possible application as high-energy-density materials (*HEDM*) for military use.[6][7] The low melting point and the high volatility of hydrazine azide prevent its use. In order to increase the melting point and to decrease the volatility, organic substituents were attached to hydrazine. The first attempt in this direction was the synthesis of *N,N*-dimethylhydrazinium azide,[8] which proved to be more volatile than hydrazinium azide. The goal for the current research was to find a hydrazinium azide derivative that has a higher melting point and is less volatile than hydrazinium azide.

Results and Discussion

Anhydrous *tert*-butylhydrazine reacts at 0°C with a solution of hydrazoic acid in ether to form *tert*-butylhydrazinium azide **1** (Equation 1). Hydrazoic acid must be used in excess to prevent the formation of an adduct of **1** with *tert*-butylhydrazine.

$$t\mathrm{BuNHNH_2} + \mathrm{HN_3} \xrightarrow{\mathrm{Et_2O}} [t\mathrm{BuNH_2NH_2}]^+[\mathrm{N_3}]^- \qquad (1)$$

The vibrational spectra show the characteristic absorptions of an ionic azide at 2037 cm^{-1} (ν_{as}, IR) and 1340 cm^{-1} (ν_s, Raman). The ^{1}H-NMR spectrum contains a broad signal at $\delta = 7.26$, which is characteristic for a hydrazinium ion. The ^{14}N-NMR spectrum shows two signals at $\delta = -134$ and -277, corresponding to the terminal azide nitrogen atom and the the central azide nitrogen atom respectively. No ^{14}N-NMR resonance was detected for the hydrazinium ion. This effect is observed with other ammonia and hydrazine compounds.[9]

Crystals of **1** are orthorhombic with space group P_{bcm} and $Z = 4$ molecules in the unit cell. The bond lengths and angles of the *tert*-butylhydrazinium ion, as indicated in Figure 1, are in accordance with the bond lengths and angles of known compounds.[10][11] The N−C bond length is in compliance with the literature data for this kind of molecule. The bond length is with 1.52 Å slightly longer than the N−C bond length of primary carbon atoms due to the bulky substituent. The bond length and angles of the azide ion are also in agreement with the literature data.[12] As can be seen in Figure 1, the azide anions are linked to the hydrazinium ions through hydrogen bonding between the terminal azide nitrogens and both nitrogen atoms of the *tert*-butylhydrazinium ion. In total there are four hydrogen bonds per azide anion (two per terminalazide nitrogen). One terminal azide nitrogen is connected through each of ist to hydrogen bonds to the protonated nitrogen atom of the hydrazinium ion. These two bonds have a length of 1.91 Å. The other terminal azide nitrogen is analogously connected to the non-protonated nitrogen of the *tert*-butylhydrazinium ion. These two bonds are longer, with a length of 2.25 Å.

This results in a highly symmetric crystal structure. The azide ions form layers, which are sandwiched between two different layers of hydrazinium ions.

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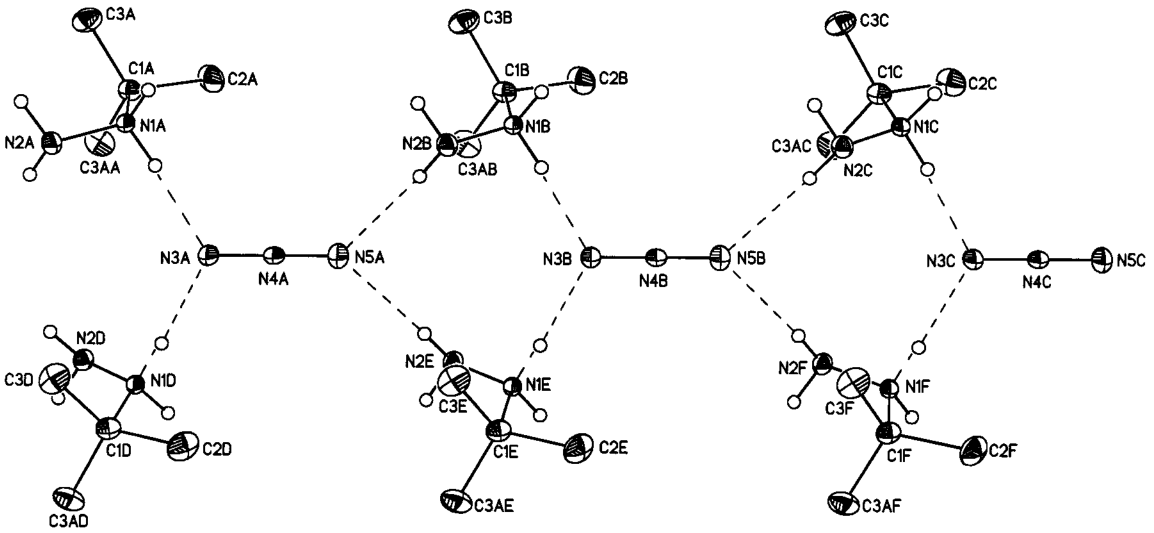

Figure 1. Molecular structure and hydrogen bonds of **1** as ORTEP plot (thermal ellipsoids represent 25% probability); selected bond lengths [Å] and angles [°] of **1**: N(1)−N(2) 1.441(2), N(1)−C(1) 1.522(2), C(1)−C(3/3A) 1.514(2), C(1)−C(2) 1.529(2), N(2)−N(1)−C(1) 107.9(7), N(1)−C(1)−C(2) 104.14(1), C(3/3A)−C(1)−N(1) 108.44(8), C(3/3A)−C(1)−C(2) 111.57(9), N(5)−N(4)−N(3) 180.0.

Synthesis of 2

N,N,N-Trimethylhydrazinium azide **2** is prepared via an ion exchange reaction with silver azide in aqueus solution. After removal of byproducts and water, **2** crystallizes from methanol.

$$[(CH_3)_3NNH_2]^+[I]^- + AgN_3 \xrightarrow[-\,AgI]{H_2O} [(CH_3)_3NNH_2]^+[N_3]^- \qquad (2)$$

As mentioned for **1**, the vibrational spectra show the typical azide absorptions at 2055 cm^{-1} (ν_{as}, IR) and 1327 cm^{-1} (ν_s, Raman). The region around 3200 cm^{-1}, where NH vibrations typically occur, is different from *N,N,N*-trimethylhydrazinium iodide. Otherwise the vibrational spectra, ^{1}H-NMR and ^{13}C-NMR spectra are in agreement with the iodide.[13] The ^{14}N-NMR spectrum shows two signals for the azide ion at $\delta = -133$ (*N*N*N*) and −278 (N*N*N). The two signals of the hydrazinium ion give a very broad signal at $\delta = -306$. The compound has a melting point of 174 °C and is not volatile. **2** is also very hygroscocopic.

Crystal Structure of 2

Bond lengths and angles of **2** are similar to *N,N,N*-trimethylhydrazinium chloride.[14] The major difference is in the structure of the hydrogen bonds between the hydrazinium and the azide ions, explaining the different NH-vibrational bands in the vibrational spectra. The azide ion has four hydrogen bonds to adjacent hydrazinium ions. Each terminal azide nitrogen atom has two short hydrogen bonds to two hydrazinium ions of two different layers (2.20 Å and 2.17 Å). Another hydrazinium ion has two very long hydrogen bonds of 2.92 Å and 2.97 Å to the terminal azide nitrogen atom that has the shorter bond length of 2.17 Å.

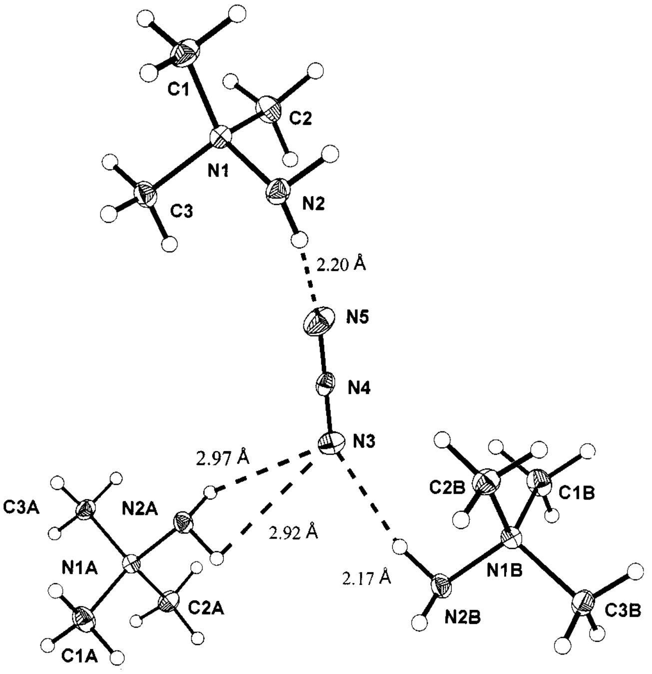

Figure 2. Molecular structure and atom numbering scheme of **2** as ORTEP plot (thermal ellipsoids represent 25% probability); selected bond lengths [Å] and angles [°] of **2**: N(1)−N(2) 1.459(1), N(1)−C(1) 1.489(2), N(1)−C(2) 1.497(2), N(1)−C(3) 1.493(2), N(3)−N(4) 1.180(2), N(4)−N(5) 1.163(2), N(2)−N(1)−C(1) 107.16(9), N(2)−N(1)−C(2) 109.4(1), N(2)−N(1)−C(3) 107.14(9), C(1)−N(1)−C(3) 109.8(1), C(1)−N(1)−C(2) 110.2(1), C(3)−N(1)−C(2) 109.4(1), N(5)−N(4)−N(3) 179.9(1).

Tetraethylphosphonium azide lacks hydrogen bonds.[15] Therefore, there are only alternating layers of phosphonium and azide ions. In **2** there are also alternating layers of hydrazinium and azide ions. In contrast to tetraethylphosphonium azide the layer of the hydrazinium ions is ordered due to the hydrogen bonds.

Conclusion

The volatility of hydrazine azide can be reduced by attaching organic substituents to the hydrazine. The melting point of such substituted hydrazinium azides also rises. **1** and **2** have very symmetric crystal structures. In both compounds, hydrogen bridges are an important factor. Substance **2** is very hygroscopic, preventing its use for commercial purposes. Substance **1** does not show hygroscopicity, but has yet to be tested for its explosive properties

Experimental Section

General Remarks: ***CAUTION:*** Silver azide, hydrazoic acid, and compounds **1** and **2** are explosives. Safety equipment like leather gloves, face-shield, and ear plugs is recommended. The synthesis of **1** was carried out using standard schlenk-line techniques under dry nitrogen. Diethyl ether was purified by destillation over Na/benzophenone, methanol by destillation over Na. The destillates were stored under nitrogen. − *tert*-Butylhydrazine was prepared by the reaction of potassium hydroxide with *tert*-buylhydrazine dihydrochloride (Aldrich), *N,N,N*-Trimethylhydrazinium iodide was prepared by literature methods.[15] − NMR: Jeol EX 400 (^{1}H (400 MHz), ^{13}C (100 MHz): chemical shifts refer to $\delta_{TMS} = 0.00$; ^{14}N (28.6 MHz): external standard CH_3NO_2). − IR: Nicolet 520 FT-IR (as KBr pellets). − Raman: Perkin−Elmer FTIR-2000 spektrometer (Nd-Yag Laser: 1064 nm, Laser power: 100 mW, scattering angle: 90°). − CHN analysis: Elementar Vario EL analysator. − Melting points: Büchi B450.

***tert*-Butylhydrazinium Azide (1):** 45 mL of a 2 M solution of hydrazoic acid in ether were slowly added to 4.0 g (55 mmol) of anhydrous *tert*-butylhydrazine. A white precipitate was isolated and purified by sublimation at 10^{-3} Torr. Recrystallization from methanol yielded colorless prisms. Yield: 5.3 g (90%); m.p. 137°C. − IR (cm^{-1}): $\tilde{\nu}$ = 3428 w, 3319 m, 3194 w, 2981 w, 2828 vw, 2784 vw, 2696 vw, 2696 vw, 2506 w, 2037 s (ν_{as} N_3^-), 1605 m, 1490 w, 1469w, 1455 w, 1398 m, 1378 m, 1337 w, 1288 vw, 1254 vw, 1200 vw, 1121 m, 1031 w, 947 w, 924 w, 840 w, 728 w, 651 w and 639 vw (ν and δN_3^-), 619 vw, 518 w, 467 w, 356 w, 325 w. − Raman (cm^{-1}): $\tilde{\nu}$ = 3321 w, 3213 w, 2986 m, 2928 m, 2748 vw,2503 vw, 1509 vw, 1494 vw, 1460 w, 1340 s(ν_s N_3^-), 1289 w, 1223 w, 1120 w, 941.0 vw, 924 vw, 851 vw, 735 m, 652 vw, 517 m, 474 w, 365 w, 241 vw, 115 s. − ^{1}H NMR ([D6]DMSO): δ = 1.15 (s, 9 H, CH_3), 7.26 (s, 4 H, NH). − ^{13}C NMR ([D$_6$]DMSO): δ = 23.9 (CH_3), 57.4 (C quat.). − ^{14}N NMR ([D$_6$]DMSO): δ = −134 (*N*N*N*), −277 (N*N*N). − $C_4H_{13}N_5$ (131.18): calcd. C 36.62, H 9.99, N 53.39; found C 36.35, H 10.38, N 54.03.

***N,N,N*-Trimethylhydrazinium Azide (2):** Silver azide was prepared by adding a solution of 7.94 g (53.3 mmol) of silver nitrate in 50 mL of water to a solution of 3.46 g (53.3 mmol) of sodium azide in 50 mL of water. Silver azide was filtered off and washed with water. The wet product was introduced to a solution of 4.12 g (20.3 mmol) *N,N,N*-trimethylhydrazinium iodide. Yellow silver iodide precipitated immediately. The reaction mixture was stirred over night, silver iodide was filtered off, and the water removed under vacuum. The crude product was washed with CH_2Cl_2 and recrystallized from methanol yielding 1.96 g (81%) of colorless needles. m.p. 174°C. − IR (cm^{-1}): $\tilde{\nu}$ = 3409 vw, 3358 m, 3316 vw, 3287 m, 3213 m, 3113 m, 2946 w, 2849 w, 2055 s, (ν_{as} N_3^-), 1632 s, 1485 s, 1467 m, 1450 w, 1397 m, 1292 m, 1159 m, 1068 w, 954 s, 922 m, 749 m, 504 m, 459 m. − Raman (cm^{-1}): $\tilde{\nu}$ = 3268 vw, 3140 w, 3034 m, 2952 m, 2876 vw, 1465 m, 1399 vw, 1327 s (ν_s N_3^-), 1246 m, 944 w, 913 w, 749 m, 465 w, 390 vw, 106 s. − ^{1}H NMR ([D$_6$]DMSO): δ = 3.25 (s, 9 H, CH_3), 6.21 (s, 2 H, NH). − ^{13}C NMR ([D$_6$]DMSO): δ = 57.1 (CH_3). − ^{14}N NMR ([D$_6$]DMSO): δ = −133 (*N*N*N*), −278 (N*N*N), −306 (H_2N*N*$(CH_3)_3$). − $C_3H_{11}N_5$ (117.15): calcd. C 30.76, H 9.46, N 59.78; found C 29.64, H 8.85, N 57.81.

Crystal Structure Determinations: Crystals of each compound were mounted on a glass fibre with a small amount of perflourether oil. Data was collected at 193 K on a Siemens P4 diffractometer, equipped with a Siemens CCD area detector with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXL 93 and 97).

Table 1. Crystallographic data and data related to data aquisition and refinement for compounds **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_4H_{13}N_5$	$C_3H_{11}N_5$
Molecular mass	131.19	117.17
Cryst. size [mm]	0.20×0.30×0.30	0.20×0.20×0.30
Cryst. system	Orthorhombic	Orthorhombic
Space group	*Pbcm*	*Pbca*
a [Å]	6.9234(1)	10.9689(1)
b [Å]	12.1203(3)	10.5082(3)
c [Å]	9.5133(3)	11.0937(2)
V, [Å^3]	798.30(3)	1278.70(4)
Z	4	8
ρ(calcd.), [mg/m^3]	1.092	1.217
μ [mm^{-1}]	0.076	0.087
F(000)	288	512
Index range	$-8 \le h \le 8$	$-13 \le h \le 14$
	$-15 \le k \le 15$	$-13 \le k \le 9$
	$-9 \le l \le 12$	$-14 \le l \le 13$
2 θ [°]	57.70	58.58
Temp. [K]	183(2)	193
Refl. collected	4320	6762
Refl. unique	903	1339
Refl. observed (4σ)	737	1066
R (int.)	0.0212	0.0345
No. Variables	77	78
Weighting scheme[a] x/y	/	0.0534/0.2582
GOOF	1.042	1.100
Final *R*(4σ)	0.0346	0.0408
Final *wR*2	0.0927	0.1014
Larg. res. Peak [e/Å^3]	0.180	0.156

[a] $w^{-1} = \sigma^2 F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2\,F_c^2)/3$.

Further information on the crystal-structure determinations has been entered in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 106145/106146 and may be obtained from CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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