Methylated Derivatives of Hydrazinium Azide

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The synthesis and characterization of polymethylated hydrazinium azide species is reported. The crystal structure of methylhydrazinium azide and *N,N′*-dimethylhydrazinium azide was determined. The thermal, shock and friction sensitivity as well as the explosion products of some of the compounds were investigated.

Introduction

Hydrazinium azide, first reported by Curtius in 1891,[1] is a powerful explosive. The explosion of hydrazinium azide produces nitrogen, hydrogen and ammonia.[2]

$$[N_2H_5]^+[N_3]^- \xrightarrow[30\ \text{bar}]{\Delta} 2.18\ N_2 + 1.52\ H_2 + 0.65\ NH \tag{1}$$

This encouraged us to investigate hydrazinium azide for use as a nitrogen rich, highly energetic material.[3−8] We replaced the hydrogen atoms in hydrazinium azide step-by-step with methyl groups, characterized these compounds and tested the explosive characteristics of the most promising compounds.

Results and Discussion

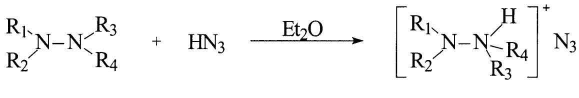
Of all possible methyl-substituted hydrazine azide compounds, *N,N*-dimethylhydrazinium azide **(1)** and *N,N,N*-trimethylhydrazinium azide **(2)** have been reported previously.[4,7] Here, we report the syntheses and characterization of methylhydrazinium azide **(3)**, *N,N′*-dimethylhydrazinium azide **(4)**, *N,N,N′*-trimethylhydrazinium azide **(5)**, *N,N,N′,N′*-tetramethylhydrazinium azide tetramethylhydrazinate **(6)**, *N,N,N,N′*-tetramethylhydrazinium azide **(7)** and pentamethylhydrazinium azide **(8)**.

Azides **3**,**4**,**5** and **6** (Table 1) were prepared by adding a solution of HN_3 in ether to the anhydrous hydrazine at 0 °C. Methylhydrazinium azide **(3)** was isolated as a colorless solid and purified by sublimation. *N,N′*-dimethylhydrazinium azide **(4)** and *N,N,N′*-trimethylhydrazinium azide **(5)** were isolated as ether insoluble liquids that were purified by low temperature sublimation.

Table 1. Numbering scheme for methylated hydrazinium derivatives

	R_1	R_2	R_3	R_4
3	CH_3	H	H	H
1	CH_3	CH_3	H	H
4	CH_3	H	CH_3	H
5	CH_3	CH_3	CH_3	H
6	CH_3	CH_3	CH_3	CH_3

The reaction of tetramethylhydrazine with HN_3 is different from the other reactions since a clear solution forms after the addition of HN_3. After distilling off ether and HN_3, it was possible to isolate a yellowish oil that was purified by low temperature sublimation.



(2)

Compounds **3−6** are all sensitive to oxidation. The oxidation is faster in compounds where more methyl groups are present. Methylhydrazinium azide **(3)** is hygroscopic but can be stored in air for several minutes before a color change occurs, while the liquid HN_3 salts turn brown immediately and form black residues in minutes. The HN_3 salts **3−6** are very volatile. TG analysis of **3** showed that the compound sublimes at ambient temperature and a drastic increase of sublimation rate occurs at temperatures higher than 50 °C.

Compounds **7** and **8** (Table 2) were made by halogen exchange of the respective iodide salts with silver azide. They were purified by recrystallization from methanol. Compounds **7** and **8** are hygroscopic but not sensitive to oxidation.

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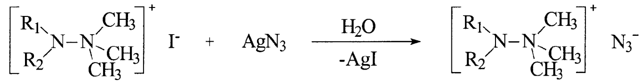
Table 2. Numbering scheme for methylated hydrazinium azide derivatives with methylated nitrogen atoms

	R_1	R_2
2	H	H
7	CH_3	H
8	CH_3	CH_3



(3)

The vibrational spectra (Table 3) show the characteristic absorptions of the azide anion around 2030 cm^{-1} [$\nu_{as}(N_3^-)$, IR] and around 1330 cm^{-1} [$\nu_s(N_3^-)$, Raman] for all the compounds. *N,N,N′,N′*-tetramethylhydrazinium azide tetramethylhydrazinate **(6)** also shows an absorption at 2131 cm^{-1} (IR) and 2129 cm^{-1} (Raman) that is assigned to the HN_3 moiety. We believe that this band is due to the dissociation of the tetramethylhydrazine−HN_3 adduct, explaining the fierce explosions observed with this compound.

Table 3. Characteristic analytical data for hydrazinium azide derivatives

	N*H* (^{1}H)	^{14}N NMR	$\nu_{as}(N_3^-)$	$\nu_s(N_3^-)$	m.p.
3	6.89	−134 −278 −323	2037	1340	68 °C
4	7.33	−134 −275	2034	1339	−8 °C
5	7.54	−134 −275	−	1336	10 °C
6	6.22	−130 −255	2131 (HN_3) 2018	1331	−20 °C
7	6.49	−131 −278 −301	2037	1332	174 °C
8	−	−132 −278 −291	2009	1321	180 °C

The ^{14}N NMR spectra for **3**,**4**,**5**,**7** and **8** (Table 3) show two signals around $\delta = -134$ and -277, the first corresponding to the terminal nitrogen atoms, and the second to the central nitrogen atom. Compound **6** has two signals at $\delta = -130$ and -258. The shift of $\delta = -258$ suggests that the azide ion is bound differently from that of the other compounds. A similar ^{14}N NMR shift is observed for phenylhydrazinium azide phenylhydrazinate at $\delta = -255$.[9] This compound consists of two phenylhydrazine units that are bridged by a proton via hydrogen bonds. The azide anion is connected through weaker hydrogen bonds to the two phenylhydrazine units. Azide **6** seems to be a similar compound because of the ^{14}N NMR shifts, the easy elimination of HN_3 and because hydrazinium azide salts, in general, are not soluble in ether. Tetramethylhydrazine is the weakest base of the hydrazines[10] used here, which explains this behavior. Hydrogen diazide shows a similar structure with two azide ions being bridged by a proton via hydrogen bonds.[11] This is not possible here because tetramethylhydrazine is more basic than an azide ion. In solution no third signal in the ^{14}N NMR around $\delta = -320$ for HN_3 was detected for **6**. We believe that the bands for HN_3 that were detected in the vibrational spectra display belong to only trace amounts of HN_3 due to their high intensity. Elemental analysis for **4**, **5** and **6** was not performed because of serious security hazards. Compounds **7** and **8** show a third, broad signal at $\delta = -301$ and -306, respectively, for the nitrogen atoms of the hydrazinium ions. The ^{1}H NMR spectra in [D$_6$]DMSO show signals for the NH protons at around $\delta = 7$. The signals for the CH protons and their ^{13}C NMR resonances are in similar ranges to that of the starting materials.

Crystal Structure of 3

Crystals of **3** are orthorhombic, space group *Pnma* with $Z = 8$ molecules in the unit cell. The bond lengths and angles of the methylhydrazinium ion as indicated in Figure 1 are in good agreement with methylhydrazinium trifluoroacetate.[12] Two pairs of hydrogen bonds connect the methylhydrazinium ion to four adjacent azide ions. The shorter pair connects the protonated central nitrogen atom N4 with two N3 atoms of an azide ion, the longer pair of hydrogen bonds connects the terminal hydrazine nitrogen atom with two N1 atoms of an azide atom. The azide atoms show a small difference in N−N bond lengths. The N1−N2 bond is 1.167(1) Å long, slightly shorter than the N2−N3 bond which is 1.184(1) Å. This is caused by stronger hydrogen bonding of N3 [N4−H4−N3 contact distance 2.8815(7) Å] than N1 [N5−H5−N1 contact distance 3.1018(9) Å].

Crystal Structure of 4

The crystals used for the structure determination of **4** were twinned, monoclinic, with space group *Cc* and $Z = 4$. The bond lengths and angles of the dimethylhydrazinium ion (Figure 2) are in good agreement with the bond lengths of other hydrazinium ions. The torsion angles of the hydrazinium ion are 175.2(3)° and 176.6(3)°, i.e. almost 180°. This conformation is stabilized with hydrogen bonds. The N−N bond lengths of both independent azide ions are different in length, as is the case with the azide ion in **3**. The longer N−N bond length in the azide ion corresponds to two shorter hydrogen bonds to adjacent hydrazinium ions; the shorter N−N bond length corresponds to a longer hydrogen bond to the next hydrazinium ion, as in **3**.

The hydrogen-bonded hydrazinium and azide ions form layers (Figure 3). The methyl groups of the hydrazinium ions are above and below these layers, so that two methyl groups are between each layer. The weak interactions between the layers explain the low melting point of the compound. The structure of compound **5**, which also has a melting point below room temperature, should be similar.

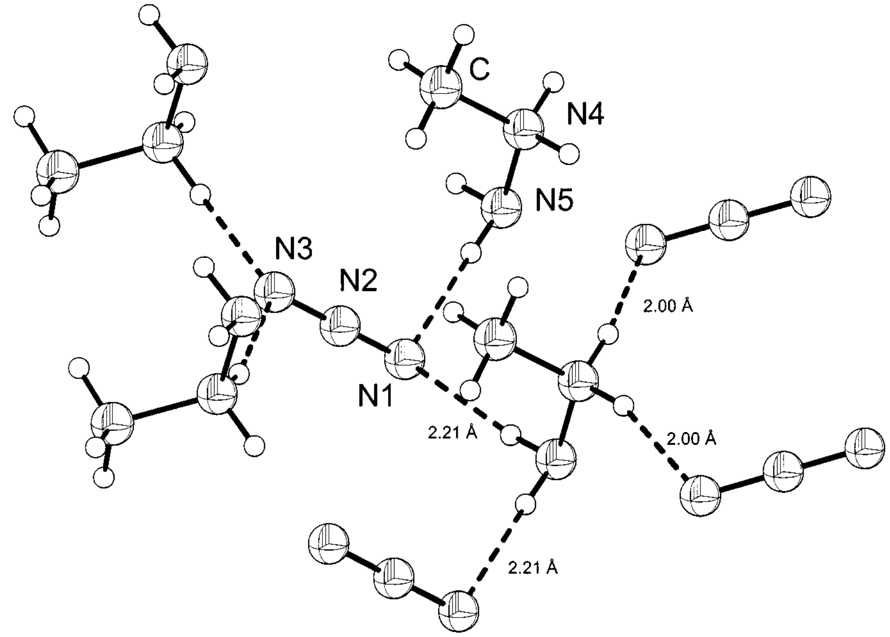


Figure 1. Molecular structure and hydrogen bonds of **3** as an ORTEP plot (thermal ellipsoids represent 25% probability); selected bond lengths [Å] and angles [°]: N1−N2 1.167(1), N2−N3 1.184(1), N4−N5 1.438(1), C−N4 1.484(1),N4−H4 0.91(1), N5−H5 0.89(1); N1−N2−N3 179.6(1), N5−N4−C 116.81(9), N5−N4−H4 105.6(7), C−N4−H4 110.4(7); contact distances [Å]: N4−N5−H5 105.1(8), N4−H4−N1 2.966(1), N4−H4−N3 2.8815(7), N5−H5−N1 3.1018(9)

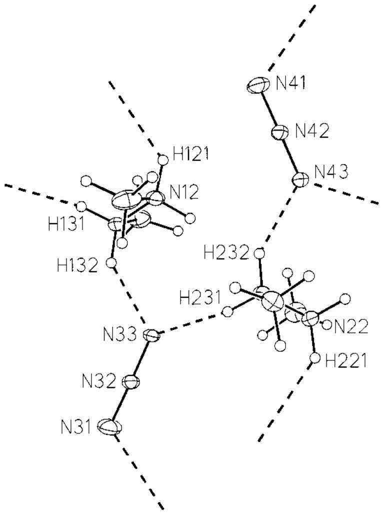


Figure 2. Molecular structure and atom numbering scheme of **4** (thermal ellipsoids represent 25% probability); selected bond lengths [Å] and angles [°]: C11−N12 1.471(5), C21−N22 1.488(4), N12−N13 1.446(3), N22−N23 1.441(3), N13−C14 1.476(4), N23−C24 1.471(4), N31−N32 1.166(4), N41−N42 1.173(4), N32−N33 1.182(4), N42−N43 1.186(4); C11−N12−N13 108.7(3), C21−N22−N23 107.3(2), N12−N13−C14 111.4(3), N22−N23−C24 109.5(2), N31−N32−N33 178.6(4), N41−N42−N43 178.4(3); contact distances [Å]: N12−N31 2.993(5), N22−N41 3.033(4), N12−N23 3.296(4), N13−N33 2.776(3), N23−N43 2.760(4), N13−N22 3.258(4), N13−N43 2.816(4), N23−N33 2.839(3); torsion angles: C11−N12−N13−C14 175.2(3), C21−N22−N23−C24 176.6(3)

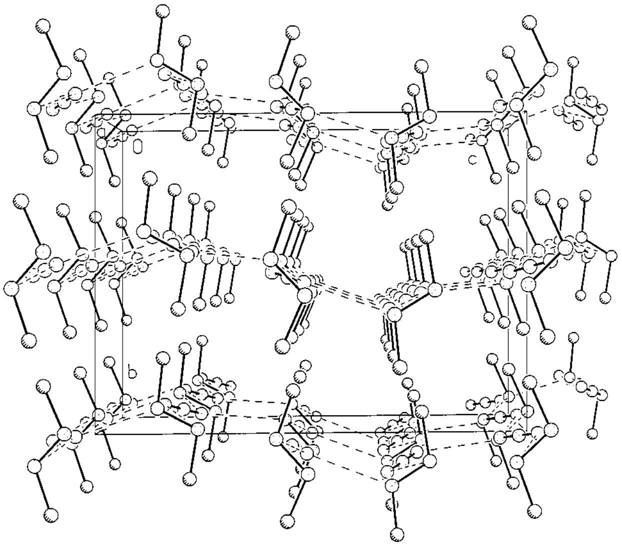


Figure 3. Layers in the crystal structure of **4**

Sensitivity Towards Shock, Friction and Electric Charge, and Thermal Sensitivity

All reported compounds show almost no sensitivity towards shock or friction. No detonation was observed after dropping a weight of 5 kg from 50 cm onto the compounds, nor was any detonation observed when grinding the compounds in a mortar. When exposing the compounds to an electric discharge of about 20 kV from a high frequency brush electrode, all compounds showed no sensitivity. The thermal sensitivity of the HN_3 salts differs from compounds with trimethylated nitrogen atoms. The HN_3 salts **1**, **3**, **4, 5** and **6** do not explode when heated with a heating rate of about 10 °C/min.; they sublime away from the heat source. An explosion can only be started by a strong heat source, for example a hot metal plate or a Bunsen burner. The more methyl groups that are attached to the hydrazinium ion, the fiercer the explosion gets. Methylhydrazinium azide **(3)** and the *N,N*-dimethylhydrazinium azide **(1)** show the same properties, while *N,N′*-dimethylhydrazinium azide **(4)** and compounds **5** and **6** give a much bigger explosion. *N,N′*-

dimethylhydrazinium azide **(4)** exploded in the microanalyser, damaging the glass tubing. In general one would expect less-fierce explosions with an increasing number of methyl groups. In our studies the compounds with more methyl groups are liquids and the bonding of HN_3 to the hydrazine unit is therefore weaker.

The trimethylated compounds **2**, **7** and **8** are less sensitive. While *N,N,N*-trimethylhydrazinium azide **(2)** gives a weak explosion on heating with a Bunsen flame, *N,N,N,N′*-tetramethylhydrazinium azide **(7)** only burns, and pentamethylhydrazinium azide **(8)** burns more sluggishly than **7**.

For methylhydrazinium azide **(3)**, *N,N*−dimethylhydrazinium azide **(1)**, *N,N′*-dimethylhydrazinium azide **(4)**, *N,N,N*-trimethylhydrazinium azide **(2)** and *N,N,N,N′*-tetramethylhydrazinium azide **(7)** the gaseous products were determined after their explosions. The appropriate azide (100 mg) was loaded into a 150 mL evacuated steel vessel. The explosion was started with a red hot metal wire and the gaseous products were analyzed by mass spectrometry and IR spectroscopy.

Explosion Products

After the explosion of methylhydrazinium azide **(3)**, H_2, N_2 and methane were detected. The IR spectrum also showed trace amounts of HN_3. *N,N*-Dimethylhydrazinium azide **(1)** produced dinitrogen as the main product. Small amounts of dihydrogen, methane and methylated amines were also detected.

N,N′-dimethylhydrazinium azide **(4)** produced dinitrogen, dihydrogen and methane as well as trace amounts of methylated amines. *N,N,N*-Trimethylhydrazinium azide **(2)** exploded to dinitrogen, dihydrogen, trimethylamine and trace amounts of methane. *N,N,N,N′*-Tetramethylhydrazinium azide gave dinitrogen, trimethylamine, trace amounts of dihydrogen, and other methylated amines. For all compounds no carbon soot was found after the explosion.

Conclusion

We substituted the hydrogen atoms of hydrazinium azide with methyl groups and the products formed during the explosion of methylhydrazinium azide **(3)**, *N,N′*-dimethylhydrazinium azide **(1)**, *N,N′*-dimethylhydrazinium azide and *N,N,N*-trimethylhydrazinium azide **(2)** include hydrogen.

N,N′-Dimethylhydrazine, *N,N,N′*-trimethylhydrazine and *N,N,N′,N′*-tetramethylhydrazine give salts with HN_3 that are liquid at room temperature and give rise to fiercer explosions than solid compounds.

Hydrazinium azides with a trimethylated nitrogen atom are not sensitive to oxidation and are not volatile, but are very hygroscopic. Due to the increased number of methyl groups the compounds explode only sluggishly.

Experimental Section

General Remarks: *CAUTION: Silver azide, hydrazoic acid and all the reported compounds are explosives. Safety equipment like leather gloves, face-shields and ear-plugs are recommended.* All syntheses were carried out using standard Schlenk techniques under dry nitrogen or argon. Ether was purified by distillation over Na/benzophenone, and methanol by distillation over Na. The distilled solvents were stored under nitrogen. Methylhydrazine and *N,N*-dimethylhydrazine were used as provided by Aldrich, *N,N′*-dimethylhydrazine was prepared by reacting *N,N′*-dimethylhydrazinium chloride from Fluka with sodium hydroxide and was dried over BaO and CaH_2. *N,N,N′*-trimethylhydrazine,[13] *N,N,N′,N′*-tetramethylhydrazine,[14] *N,N,N,N′*-tetramethylhydrazinium iodide[15] and pentamethylhydrazinium iodide[13] were prepared according to known procedures. − NMR: Jeol EX 400, ^1H (400.0 MHz), ^{13}C (100.0 MHz): chemical shifts refer to $\delta_{TMS} = 0.00$; ^{14}N (28.6 MHz): shifts refer to CH_3NO_2. − IR: Nicolet 520 FT-IR (solid compounds as KBr pellets, liquid compounds as film between KBr plates). − Raman: Perkin−Elmer FTIR-2000 spectrometer (Nd-Yag Laser: 1064 nm, Laser power: 100 mW). − CHN analysis: Elementar Vario EL analyzer. − Melting points: Büchi B450. − DSC: Setaram DSC 141. − TG: Setaram DTA-TG 92. − MS: Balzers QMS 420.

Methylhydrazinium Azide (3): A 2 M solution of HN_3 in ether (25 mL) was slowly added to anhydrous methylhydrazine (0.55 g, 12.0 mmol). During the addition a colorless precipitate was formed. After the addition the reaction mixture was stirred for an hour. The precipitate was separated, washed with ether and pentane. Methylhydrazinium azide was sublimed to give colorless crystals. − Yield: 0.91 g (86%). − m.p.: 68 °C. − IR: $\tilde{\nu}$ = 3355 m, 3290 m, 3202 s, 3121 s, 3033 m, 2974s, 2864 m, 2776 m, 2505 m, 2037 s(ν_{as}, N_3), 1605 m, 1591 m, 1486 m, 1454 w, 1402 w, 1339 m, 1333 m, 1112 s, 1009 s, 934 s, 890 m, 802 w, 649 m, 642 m, 515 m, 427 m cm^{-1}. − Raman: $\tilde{\nu}$ = 3167 w, 3018 m, 2953 s, 2795 w, 1459 w, 1340 vs(ν_s N_3), 1290 w, 1013 w, 877 w, 253 w, 181 m, 122 m cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 2.50 (s, 3 H, CH_3), 6.89 (s, 4 H, NH). − ^{13}C NMR ([D_6]DMSO): δ = 37.6 (CH_3). − ^{14}N NMR ([D_6]DMSO): δ = −134 (*N*N*N*), −278 (N*N*N), −323 (Me*N*H_2*N*H_2). − DSC: 69.3 °C (m.p.), 151.5 °C. − CH_7N_5 (89.10): calcd. C 13.48, H 7.92, N 78.60; found C 13.23, H 7.83, N 78.55.

***N,N′*-Dimethylhydrazinium Azide (4):** A 2 M solution of hydrazoic acid in ether (25 mL) was slowly added to anhydrous *N,N′*-dimethylhydrazine (1.25 g, 20.8 mmol). Two liquid phases formed. The lower phase was separated, washed with ether and pentane and purified by sublimation at −20 °C. − Yield: 1.3 g (61%). − M.p.: −8 °C. − IR: $\tilde{\nu}$ = 3333 m, 3223 m, 2966 m, 2747 m, 2477 m, 2018 s(ν_{as} N_3), 1607 mm, 1463 w, 1408 w, 1332 w, 1248 w, 1190 w, 1108 w, 946 w, 823 w, 640 w, 627 vw, 494 w, 476 w, 397 w cm^{-1}. − Raman: $\tilde{\nu}$ = 3213 w, 2964 m, 2803 w, 1465 w, 1339 (ν_s N_3), 834 w, 464 w, 103 s cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 2.53 (s, 6 H, CH_3), 7.33 (s, 3 H, NH). − ^{13}C NMR ([D_6]DMSO): δ = 33.8 (CH_3). − ^{14}N NMR ([D_6]DMSO): δ = −134 (*N*N*N*), −275 (N*N*N). − DSC: 137.4 °C (decomp.). − $C_2H_9N_5$ (103.13): calcd. C 23.29, H 8.80, N 67.91; found C 21.66, H 8.84, N 61.09.

***N,N,N′*-Trimethylhydrazinium Azide (5):** A 2 M solution of hydrazoic acid in ether (15 mL) was slowly added to anhydrous *N,N,N′*-trimethylhydrazine (0.50 g, 6.8 mmol). After the addition of 3 mL of the solution the reaction mixture became turbid. After all of the HN_3 had been added to the reaction mixture, two liquid phases formed. The bottom phase was separated and stored at −30 °C. After several days colorless crystals sublimed onto the walls of the reaction vessel. − Yield: 0.36 g (46%). − M.p.: 10 °C. − Raman: $\tilde{\nu}$ = 3152 w, 3026 w, 2964 m, 1580 w, 1456 w, 1336 s(ν_s N_3), 1247 vw, 1181 vw, 1139 vw, 999 vw, 889 vw, 818 m, 474 m, 220 s, 155 s, 99 s cm^{-1}. − ^1H NMR ([D_6]DMSO): δ = 2.50 (s, 3 H, CH_3), 2.63 (s, 6 H, $(CH_3)_2$), 7.54 (s, 2 H, NH). − ^{13}C NMR ([D$_6$]DMSO): δ = 34.3 ($NHCH_3$), 46.6 [$N(CH_3)_2$]. − ^{14}N NMR ([D$_6$]DMSO): δ= −134 (*N*N*N*), −275 (N*N*N).

***N,N,N′,N′*-Tetramethylhydrazinium Azide Tetramethylhydrazinate(6):** A 2 M solution of hydrazoic acid in ether (10 mL) was slowly added to anhydrous tetramethylhydrazine (0.77 g, 8.8 mmol). After the addition of 3 mL of the HN_3 solution the reaction mixture became turbid. After all of the HN_3 solution had been added, a clear solution was obtained. HN_3 and ether were distilled off and a syrupy yellow liquid remained. At −78 °C a colorless solid was isolated by fractional sublimation at 10^{-3} Torr. − Yield: 0.57 g (55%) − M.p.: − 22 °C − IR: $\tilde{\nu}$ = 3319 m, 2969 s, 2669 m, 2594 m, 2497 m, 2451 m, 2131 s (HN_3), 2018 s(ν_{as} N_3), 1645 w, 1469 m, 1443 w, 1412 w, 1326 w, 1244 w, 1215 m, 1182 m, 1146 w, 1134 m, 1097 m, 1059 m, 1026 m, 989 w, 962 w, 880 w, 729 w, 639 w, 623 vw, 548 m, 500 m, 439 vw. cm^{-1} − Raman: $\tilde{\nu}$ = 3006 m, 2967 s, 2800 m, 2129 w (ν_{as} N_3, HN_3), 1475 m, 1445 m, 1331 (ν_s N_3), 989 vw, 963 w, 882 w, 732 m, 550 w, 502 w, 97 s cm^{-1}. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.28 (s, 12 H, C*H*$_3$), 7.33 (s, 3 H, N*H*). − ^{13}C NMR ([D$_6$]DMSO): δ = 38.5 (*C*H$_3$). − ^{14}N NMR ([D$_6$]DMSO): δ= −135 (*N*N*N*), −258 (N*N*N).

***N,N,N,N′*-Tetramethylhydrazinium Azide (7):** Silver azide was prepared by adding a solution of silver nitrate (1.60 g, 9.4 mmol) in 20 mL of water to a solution of sodium azide (0.80 g, 12.3 mmol) in 20 mL of water. Silver azide was filtered off and washed with water. The wet product was then added to a solution of *N,N,N,N′*-tetramethylhydrazinium iodide (1.00 g, 4.6 mmol) in water. Yellow silver iodide immediately precipitated. The reaction mixture was stirred overnight and the water removed under vacuum. The product was recrystallized from methanol. − Yield: 0.35 g (58%) − M.p.: 174 °C (decomposition). − IR: $\tilde{\nu}$ = 3429 s, 3194 s, 3055 s, 2989 s, 2037 s(ν_{as}, N_3), 1730 w, 1635 m, 1541 w, 1485 m, 1456 m, 1385 m, 1278 w, 1268 w, 1186 w, 1121 w, 1049 w, 977 w, 939 w, 838 w, 712 w, 649 w, 642 w, 522 w, 451 w cm^{-1}. − Raman: $\tilde{\nu}$ = 3031 m, 2940 m, 2789 w, 1465 w, 1441 w, 1398 w, 1332 s(ν_s N_3), 1247 vw, 947 vw, 847 w, 715 w, 102 s cm^{-1}. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.57 (d, *J* = 3.0 Hz, 3 H, NHC*H*$_3$), 3.21 [s, 9 H, N(C*H*$_3$)$_3$], 6.61 (q, *J* = 6.2 Hz, 1 H, N*H*CH$_3$). − ^{13}C NMR ([D$_6$]DMSO): δ = 30.5 (NCH_3), 53.4 [$N(CH_3)_3$]. − ^{14}N NMR ([D$_6$]DMSO): δ= −131 (*N*N*N*), −278 (N*N*N), −301 [CH$_3$*N*H*N*(CH$_3$)$_3$]. − $C_4H_{13}N_5$ (131.18): calcd. C 36.62, H 9.99, N 53.38; found C 35.3, H 9.67, N 50.06.

Pentamethylhydrazinium Azide (8): Silver azide was prepared as above. The wet product was then reacted with a solution of pentamethylhydrazinium iodide (0.89 g, 3.8 mmol) in water. Yellow silver iodide immediately precipitated. The reaction mixture was stirred overnight and the water removed under vacuum. The product was washed with CH_2Cl_2 and dried under oil pump vacuum to give **8** as a colorless solid (0.34 g). − Yield: 0.34 g (61%) − M.p. 180 °C (decomposition). − IR: $\tilde{\nu}$ = 3304 s, 3321 s, 3025 s, 2945 m, 2819 m, 2615 w, 2528 w, 2009 s (ν_{as} N_3), 1654 w, 1473 s, 1263 w, 1254 w, 1223 m, 1196 m, 1169 w, 1121 m, 1092 m, 1070 w, 1021 s, 954 s, 929 m, 807 s, 672 m, 632 m, 528 m, 490 m, 408 m cm^{-1}. − Raman: $\tilde{\nu}$ = 3040 m, 3023 m, 2982 m, 2811 w, 1448 w, 1322 s (ν_s N_3), 1248 w, 1124 vw, 949 w, 930 w, 809 w, 675 m, 529 w, 492 w, 467 w, 403 vw, 104 s cm^{-1}. − ^{1}H NMR ([D$_6$]DMSO): δ = 2.64 [s, 6 H, N(C*H*$_3$)$_2$], 3.22 [s, 9 H, N(C*H*$_3$)$_3$]. − ^{13}C NMR ([D$_6$]DMSO): δ = 40.0 [N(*C*H$_3$)$_2$], 50.9 [N(*C*H$_3$)$_3$]. − ^{14}N NMR ([D$_6$]DMSO): δ = −132 (*N*N*N*), −278 (N*N*N), −291 [H$_2$*NN*(CH$_3$)$_3$]. − $C_5H_{15}N_5$ (145.20).

Explosion Results

1: MS (EI): *m*/*z* (%) = 1 (3), 2 (3) [H_2], 13 (0.6), 14 (12), 15 (8), 16 (6), 17 (2), 18 (5), 26 (0.8), 27 (2), 28 (100) [N_2], 29 (2), 30 (3), 35 (0.4), 42 (3), 56 (0.4), 57 (0.6), 71 (0.8), 72 (1). − IR: $\tilde{\nu}$ = 3175−3020 w (CH_4), 3017 m (CH_4), 3002−2750 w (CH_4), 1586 w, 1469 w, 1304 m, 1137 w, 1010 m, 890 w, 783 w cm^{-1}.

2: MS (EI): *m*/*z* (%) = 1(9), 2 (85) [H_2], 12 (1), 13 (3), 14 (17), 15 (46), 16 (27) [CH_4], 17 (2) [NH_3], 18 (4), 25 (0.5), 26 (3), 27 (7), 28 (100) [N_2], 29 (5), 30 (15), 39 (1), 40 (3), 41 (3), 42 (18), 43 (4), 44 (2), 50 (1), 52 (0.6), 56 (0.7), 57 (4), 58 (26), 59 (11) [$N(CH_3)_3$], 60 (0.4), 71 (2), 72 (3), 89 (0.3). − IR: $\tilde{\nu}$ = 3154−3050 m (CH_4), 2965 s [$N(CH_3)_3$], 2823 s [$N(CH_3)_3$], 2775 s [$N(CH_3)_3$], 2185 w (HN_3), 2117 m (HN_3), 2090 m (HN_3), 1583 w, 1459 s [$N(CH_3)_3$], 1283 s [$N(CH_3)_3$], 1185 m [$N(CH_3)_3$], 1042 m [$N(CH_3)_3$], 970 m, 827 m, 585 w cm^{-1}.

3: MS (EI): *m*/*z* (%) = 1 (2), 2 (100) [H_2], 12 (0.3), 13 (0.8), 14 (8), 15 (8), 16 (10) [CH_4], 17 (0.3) [NH_3], 18 (0.3), 27 (0.3), 28 (47) [N_2], 29 (0.6), 30 (0.2), 32 (3), 40 (0.44), 41 (0.2). − IR: $\tilde{\nu}$ = 3344 w, 3316 w, 3175−3020 m (CH_4), 3016 s (CH_4), 3002−2750 m (CH_4), 2192 m (HN_3), 2153 m (HN_3), 2118 s (HN_3), 1342 m, 1304, 1269 m, 1165 m, 1132 m, 1033 m, 816 m cm^{-1}.

4: MS (EI): *m*/*z* (%) = 1 (7), 2 (13) [H_2], 13 (3), 14 (16), 15 (50), 16 (31) [CH_4], 17 (2) [NH_3], 18 (4), 27 (3), 28 (100) [N_2], 29 (3), 43 (6), 44 (1), 58 (2). − IR: $\tilde{\nu}$ = 3175−3020 w (CH_4), 3017 m (CH_4), 3002−2750 w (CH_4), 1384 s, 1282 m, 1195 s, 1159 s, 970 m, 899 w cm^{-1}.

7: MS (EI): *m*/*z* (%) = 1 (7), 2 (6) [H_2], 12 (1), 13 (2), 14 (15), 15 (37), 16 (4), 17 (0.5), 18 (4), 26 (2), 27 (7), 28 (100) [N_2], 29 (5), 30 (22), 31 (0.5), 32 (11), 38 (0.5), 39 (1), 40 (4), 41 (5), 42 (28), 43 (6), 44 (6), 45 (0.9), 47 (0.5), 48 (0.4), 50 (0.6), 51 (0.4), 52 (0.5), 56 (1), 57 (7), 58 (47), 59 (20) [$N(CH_3)_3$], 60 (0.7). − IR: $\tilde{\nu}$ = 2964 m, 2823 m, 2117 w, 1384 m, 1279 m, 1195 s, 1124 s, 969 s, 900 m, 597 w cm^{-1}.

Table 4. Crystallographic data and data related to data acquisition and refinement for compounds **3** and **4**

Compound	3	4
Chem. formula	CH_7N_5	$C_2H_9N_5$
Formula weight	89.09	103.12
Crystal size [mm]	0.20 × 0.32 × 0.55	0.20 × 0.80 × 0.80
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	*Cc*
a [Å]	9.962(1)	7.982(2)
b [Å]	5.1316(5)	10.175(2)
c [Å]	9.2280(9)	13.745(3)
β [°]	90.00	90.0
V [Å^3]	471.77(9)	1016.4(4)
Z	8	4
ρ(calcd.) [mg/m^3]	1.2545(2)	1.227
μ [mm^{-1}]	0.097	0.091
F(000)	192	448
Temp, [K]	200(2)	173(2)
Refl. collected	4328	4012
Refl. unique	612	2881
Refl. observed (4σ)	545	2653
R (int.)	0.0624	0.0406
No. variables	52	144
GOOF	1.153	1.096
Final *R* (4σ)	0.0310	0.0564
Final *wR*2	0.0844	0.1400
Larg. res. peak [e/Å^3]	0.188	0.42
Twin matrix	−	−1 0 0 0 1 0 0 0 1
Twin scaling factor	−	0.487(3)

X-ray Crystallographic Study: Single crystals of **3** and **4** were submerged in dried perfluoropolyether oil under anaerobic conditions. Suitable crystals were mounted on a glass fiber, transferred to the diffractometer and cooled in the cold gas stream derived from liquid nitrogen. The measurement for **3** was performed on a Stoe IPDS diffractometer equipped with an image-plate area detector and for that of **4** on a Siemens P4 diffractometer, both with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). All calculations were performed using SIR-97[16] and SHELXL-97. Crystallographic data are reported in Table 4.[17]

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149154 (**3**) and CCDC-149571 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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