

Article

5-Azido-4-dimethylamino-1-methyl-1,2,4-triazolium Hexafluoridophosphate and Derivatives

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Academic Editor: Helmut Cölfen

Received: 14 January 2016; Accepted: 2 February 2016; Published: 5 February 2016

Abstract: 5-Azido-4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluoridophosphate was synthesized from the corresponding 5-bromo compound with NaN_3 . Reaction with bicyclo[2.2.1]hept-2-ene yielded a tricyclic aziridine, addition of an *N*-heterocyclic carbene resulted in a triazatrimethine cyanine, and reduction with triphenylphosphane gave the 5-amino derivative. The crystal structures of three nitrogen-rich salts were determined. Thermoanalysis of the cationic azide and triazene showed exothermal decomposition. The triazene exhibited negative solvatochromism in polar solvents involving the dipolarity π^* and hydrogen-bond donor acidity α of the solvent.

Keywords: azide; aziridine; cyanine; solvatochromism; thermoanalysis; triazene; triazole

1. Introduction

Azidoazoles, in particular azidotetrazoles [1–3] and azidotriazoles [4–6], are fine examples of “nitrogen-rich” materials. Reports on quaternary azidoazolium cations are more limited (benzimidazole, thiazole [7–9]). A 1,4-disubstituted 1,2,4-triazolium salt bearing an azide group at the less reactive 3-position was described [10]. Crystal structures of only one 1,3-disubstituted 2-azidoimidazolium salt [11] and one 1,3-disubstituted 2-azidoimidazolinium salt [12] are known. Organic azides were occasionally converted to triazenes, essentially by reaction with *N*-heterocyclic carbenes. Thus, a number of crystal structures of neutral aryl or alkyl triazenes have been reported [13–20]. The use of quaternary azidoazolium cations for this transformation resulted in cationic triazatrimethine cyanine dyes, but only one crystal structure of this type was reported, although with benzimidazole [21]. Until now azidotriazolium salts primarily received attention as energetic compounds but their reactions have been rarely examined. We tentatively explored some reactions of a new 1,4-disubstituted 5-azido-1,2,4-triazolium salt. Here we report the crystal structures of this reactive azide and two of its derivatives.

2. Results and Discussion

The title compound **1** was synthesized from the corresponding bromo compound and sodium azide (Figure 1) by analogy with a similar imidazolium salt [11]. The well-known versatility of azide chemistry [22] motivated us to attempt exemplary reactions of **1**. Thus, dipolar cycloaddition of azides with alkenes is known to produce 1,2,3-triazolines or aziridines [23]. In our hands, strained bicycloheptene (norbornene) [24,25] reacted with azidotriazolium salt **1** to give the tricyclic aziridine **2** in acceptable yield.

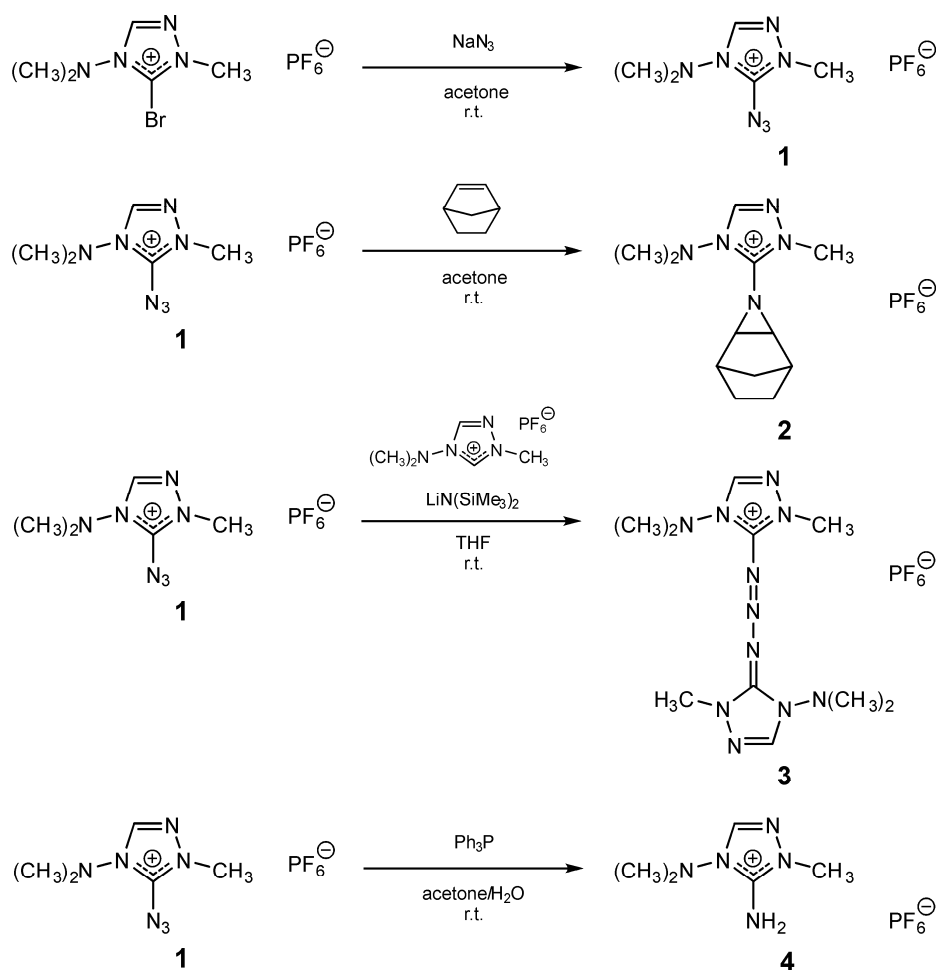


Figure 1. Reagents and conditions: (a) NaN_3 , acetone, rt; (b) bicyclo[2.2.1]hept-2-ene, acetone, rt; (c) 4-(dimethylamino)-1-methyl-1,2,4-triazolium PF_6 , $\text{LiN}(\text{SiMe}_3)_2$, THF, rt; (d) Ph_3P , acetone, H_2O , rt.

Recently, “click chemistry” (Cu-catalyzed cycloaddition of azide and alkyne) was successful with 2-azido-1-methylimidazole [26], but not with quaternary 2-azidoimidazolium salts, which can be explained by electron-deficiency of the cationic azide. Attempts to add phenylethyne to **1** were also not met with success, possibly due to the same reason.

Reaction of azide **1** with the carbene derived from the corresponding triazolium salt resulted in the formation of triazene **3** in modest yield. Staudinger reduction of the azide **1** with triphenylphosphane led to the 5-amino compound **4**. The progress of this transformation could be visually followed as the mixture turned yellow (formation of triazene), molecular nitrogen gas was evolved, and the colour disappeared again (formation of iminophosphorane). The product was obtained after final hydrolysis.

The hexafluoridophosphate was chosen as an advantageous anion because these salts crystallize readily and are non-hygroscopic. The role of fluorine in crystal structures of organic compounds has been reviewed [27]. It has been concluded that short C–H...F contacts between oppositely charged molecules are genuine interionic hydrogen bonds [28]. On the other hand, these interactions are weak enough to escape the undesirable formation of distracting aggregates, thus allowing to concentrate on the geometry of the cation. Crystal data and refinement details are summarized in Table 1. Selected bond lengths and angles are collected in Table 2. Hydrogen bond geometries are outlined in Table 3.

Table 1. Crystal data and structure refinement details for compounds 1–3.

Compound	1	2	3
CCDC No.	1444906	1444907	1444908
Empirical formula	C ₅ H ₁₀ N ₇ ·F ₆ P	C ₁₂ H ₂₀ N ₅ ·F ₆ P	C ₁₀ H ₂₀ N ₁₁ ·F ₆ P
Formula weight	313.17	379.30	439.34
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pnma</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	7.6592(2)	16.8383(3)	9.6566(6)
<i>b</i> /Å	11.3231(4)	8.6698(2)	18.3957(8)
<i>c</i> /Å	13.9886(4)	11.6179(2)	11.6647(7)
β/°	101.275(3)		113.308(7)
Volume/Å ³	1189.76(6)	1696.04(6)	1903.0(2)
<i>Z</i>	4	4	4
<i>D</i> _x /g·cm ^{−3}	1.75	1.49	1.53
μ/mm ^{−1}	0.31	2.08	0.22
<i>F</i> (000)	632	784	904
Radiation	MoKα	CuKα	MoKα
Crystal size/mm ³	0.40 × 0.40 × 0.40	0.40 × 0.28 × 0.24	0.39 × 0.12 × 0.09
θ _{max} /°	25.4	67.4	25.4
Index ranges	−9 ≤ <i>h</i> ≤ 9 −13 ≤ <i>k</i> ≤ 12 −14 ≤ <i>l</i> ≤ 16	−19 ≤ <i>h</i> ≤ 20 −10 ≤ <i>k</i> ≤ 10 −13 ≤ <i>l</i> ≤ 13	−11 ≤ <i>h</i> ≤ 11 −21 ≤ <i>k</i> ≤ 21 −12 ≤ <i>l</i> ≤ 14
Reflections collected	7844	9779	10926
Independent reflections (<i>R</i> _{int})	2185 (0.023)	1630 (0.033)	3452 (0.032)
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	1777	1523	2845
Restraints/parameters	0/176	0/195	57/307
Goodness-of-fit on <i>F</i> ²	1.09	1.07	1.01
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.027, 0.067	0.058, 0.158	0.049, 0.122
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.034, 0.068	0.061, 0.161	0.060, 0.130
Largest diff. peak and hole/e·Å ^{−3}	0.19, −0.30	0.30, −0.26	0.44, −0.32

Table 2. Selected bond lengths, angles, and torsions for compounds 1 and 3 (Å, °).

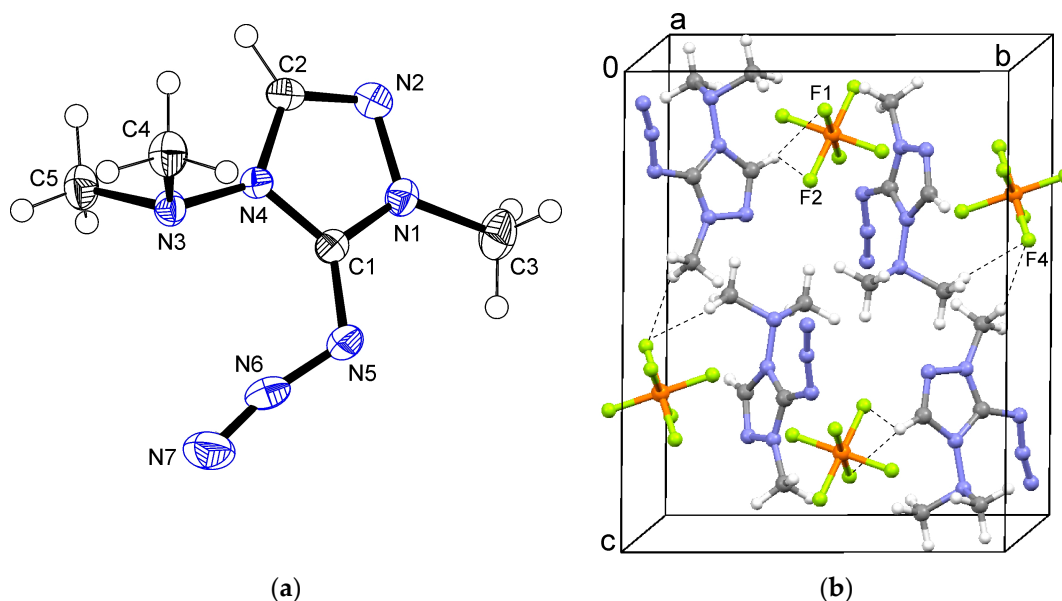
	1	3
C1–N5	1.367(2)	1.357(3)
N5–N6	1.255(2)	1.303(3)
N6–N7	1.118(29)	1.302(3)
N7–C6		1.352(4)
C1–N5–N6	116.6(1)	112.7(2)
N5–N6–N7	168.8(2)	109.8(2)
N6–N7–C6		114.0(2)
C1–N5–N6–N7	171.9(8)	176.8(2)
N5–N6–N7–C6		178.4(2)

Table 3. C–H...F interactions in compounds 1–3 (Å, °).

Compound	Interaction	H...F	C...F	C–H...F	Symmetry Operation F
1	C2–H...F1	2.329	3.263(2)	167.7	x, y, z
	C2–H...F2	2.399	3.133(2)	133.9	x, y, z
	C5–H _C ...F4	2.468	3.416(2)	162.8	$1 + x, y, z$
	C3–H _A ...F4	2.530	3.425(2)	151.8	$1/2 + x, 3/2 - y, -1/2 + z$
2	C2–H...F3	2.383	3.281	157.4	$-1/2 + x, 1/2 - y, 3/2 - z$
	C4–H _A ...F2	2.298	3.227(7)	158.0	$1/2 - x, -1/2 + y, -1/2 + z$
	C10–H...F1	2.396	3.206(6)	137.5	x, y, z
	C6–H...F1	2.458	3.397(5)	156.5	$1/2 - x, 1/2 + y, -1/2 + z$
3	C7–H...F4	2.283	3.15(1)	152.0	$1 - x, -y, 1 - z$
	C2–H...F1	2.298	3.16(1)	151.0	$3/2 - x, 1/2 + y, 3/2 - z$
	C5–H _C ...F3	2.432	3.211(5)	136.2	$3/2 - x, 1/2 + y, 3/2 - z$
	C9–H _B ...F5	2.523	3.485(5)	167.1	$x, y, 1 + z$

2.1. Crystal Structures

The $C_5H_{10}N_7^+$ cation contains 58.3 wt.% nitrogen and, thus, can be considered to be “nitrogen-rich”. The azide group in **1** deviates considerably from linearity with an N5–N6–N7 angle of $168.8(2)^\circ$, it is rotated out of the ring plane by 26.4° (Figure 2a), likely due to a repelling interaction between a lone electron pair on the N atom and the ring π system. The heteroaromatic C2–H donates bifurcated hydrogen bonds to F1 and F2, whereas H atoms of two methyl groups form contacts to F4 (Figure 2b).

**Figure 2.** (a) ORTEP plot of the cation in **1**; and (b) packing in the crystal structure of **1**.

In the crystal structure of aziridine **2**, the asymmetric unit contained half a formula unit. The triazole rings were located in the crystallographic mirror plane, whereas the C4 methyl groups are situated out of this plane. The C3 methyl group was found to be disordered over two orientations related by mirror symmetry. Part of the cation showed a 1:1 positional disorder by a crystallographic mirror plane. In the tricyclic group including N5, only C7 lay exactly in the mirror plane. All other atoms of this group were refined in general positions with occupancies of 0.5 (Figure 3a, only one disorder component shown).

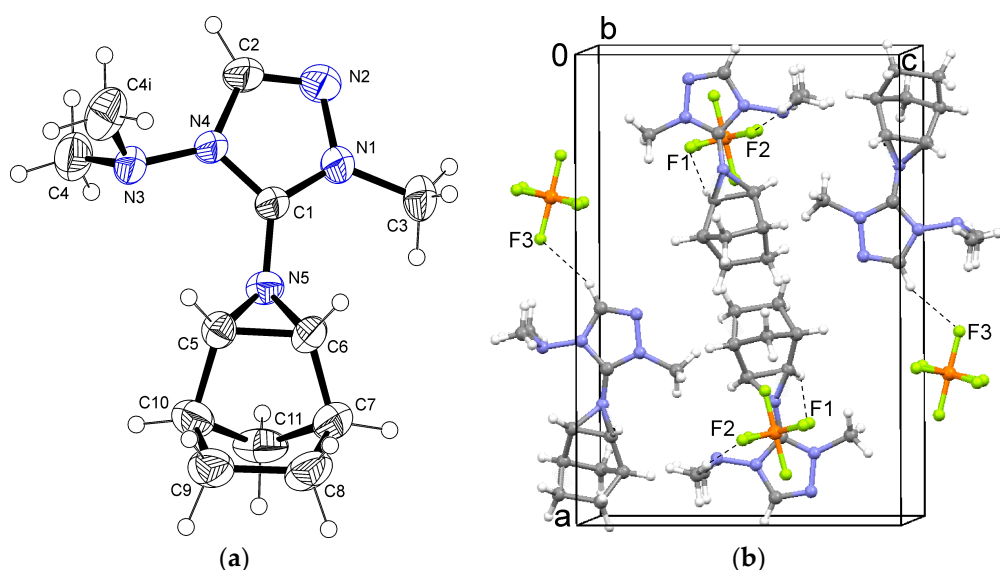


Figure 3. (a) ORTEP plot of the cation in **2**; (b) Packing and C–H...F interactions in the crystal structure of **2**. Symmetry operation $i: x, 1/2 - y, z$.

A positional disorder of the PF₆ anion with ratio 7:3 (ratio refined as free variable) was observed. Again, the heteroaromatic C2–H donates a hydrogen bond to F3, and aliphatic hydrogen atoms form contacts to F1 and F2 (Figure 3b).

The triazole-substituted triazine system in **3** is almost planar. The dihedral angle between the triazole rings is only 9.3°. The N5–N6 bond is twisted out of the plane of the adjacent triazole ring by 17.2°, and the N7–N6 bond out of the plane of the second triazole ring by 14.6° (Figure 4a). Several C–H...F interactions involve the heteroaromatic C2–H and C7–H, as well as the C5 and C9 methyl groups. Additionally, a C5–H...N5 interaction is observed (Figure 4b).

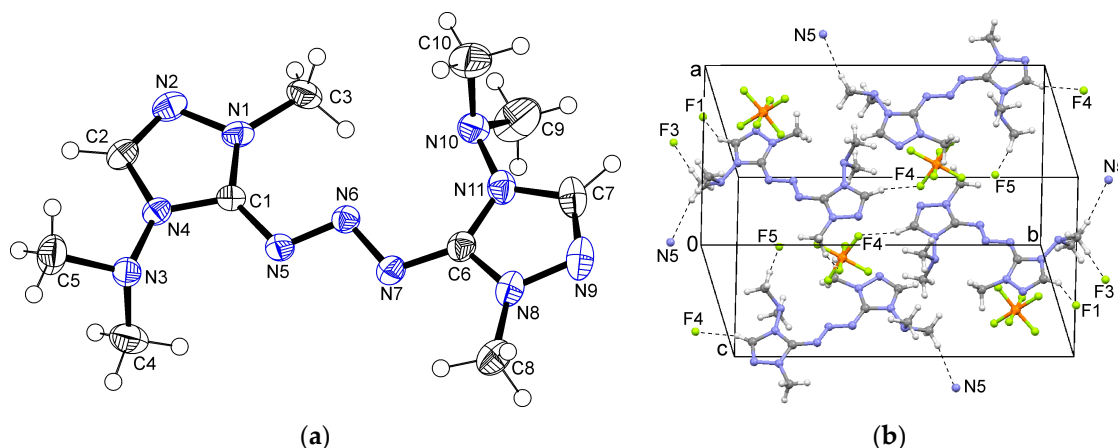


Figure 4. (a) ORTEP plot of the cation in **3**. (b) Packing in the crystal structure of **3**.

2.2. UV Spectroscopy

Compound **3** exhibited negative solvatochromism in polar solvents the extent of which could be described by a linear combination of specific and non-specific solute–solvent interactions. The electronic absorption spectrum showed a single band in the UV region (Figure 5a). This band was shifted bathochromically by 13 nm on changing the solvent from water to dichloromethane (see Experimental Section). The electronic transition leads to less charge separation in the excited state than in the more dipolar ground state, so that increased solvent polarity leads to higher

transition energy. Transition energies E_T were calculated from the wavelengths of the absorption maxima according to the equation $E_T/\text{kJ}\cdot\text{mol}^{-1} = hcN/\lambda = 119625/(\lambda/\text{nm})$. A linear solvation energy relationship was established by least-squares fitting of the data to the simplified solvatochromic equation $E_T = E_{T0} + s\pi^* + a\alpha$ involving only the parameters π^* [29] and α [30] which represent the dipolarity/polarizability and hydrogen-bond donor acidity of the solvent. The hydrogen-bond acceptor parameter β [31] did not significantly contribute to the relationship. The coefficients s and a reflect the sensitivity of the solute to these solvent properties. The π^* and α values were taken from the compilation of Marcus [32]. From the spectral data, the following equation was derived by multiple linear regression (Figure 5b) which describes the solvatochromic behavior of the triazene 3.

$$E_T/\text{kJ}\cdot\text{mol}^{-1} = 323.10 + 14.20\pi^* + 8.72\alpha \quad (n = 7, r^2 = 0.985)$$

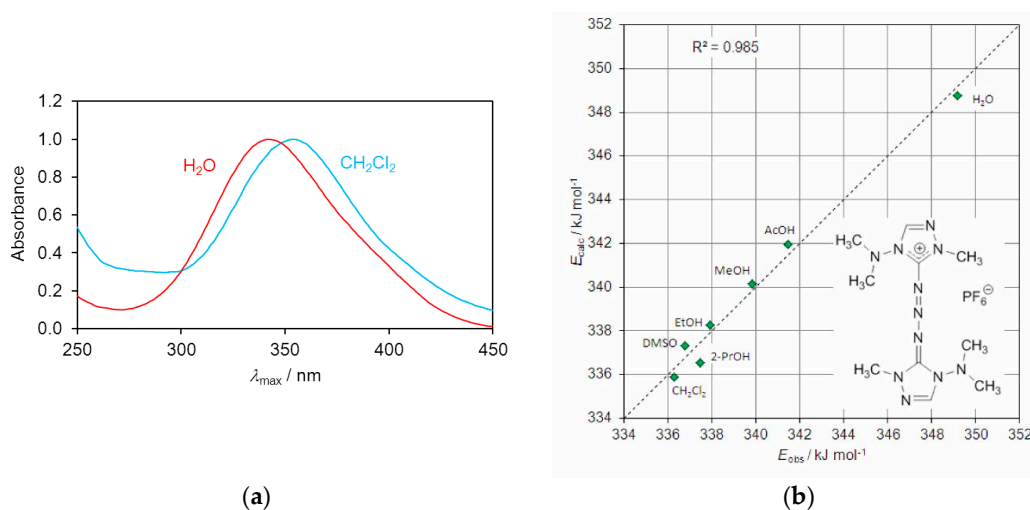


Figure 5. (a) Normalized UV spectra of triazene 3 in H₂O and CH₂Cl₂; (b) Correlation of observed vs. calculated UV transition energies of triazene 3 in seven polar solvents.

2.3. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Thermoanalysis of 1 showed a phase transition at 62 °C. Both compounds 1 and 3 exhibited exothermal decomposition at higher temperatures (decomposition maxima at 163 and 210 °C) with considerable mass loss (Figure 6). The melting point of compound 2 was unremarkable.

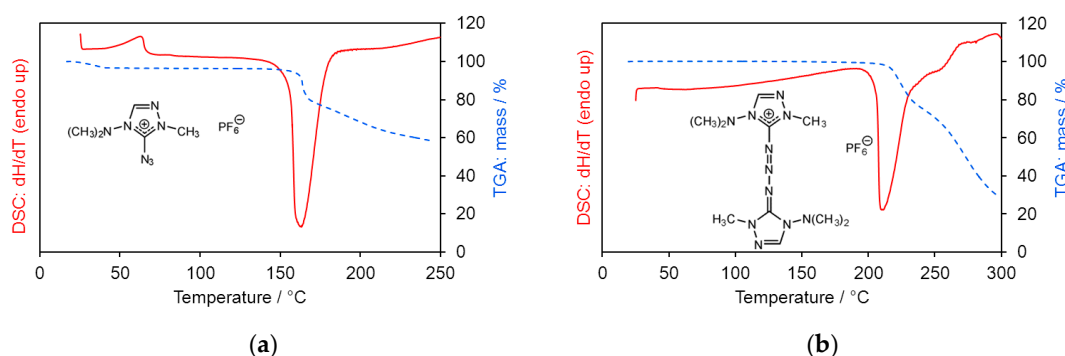


Figure 6. DSC and TGA (a) of 1 and (b) of 3. Heating rate 10 °C·min^{−1}.

3. Experimental Section

4-(Dimethylamino)-1-methyl-1,2,4-triazolium hexafluoridophosphate and 5-bromo-4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluoridophosphate were prepared as described previously [33].

All other chemicals were purchased from Sigma-Aldrich (European affiliate, Steinheim, Germany). NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer (Billerica, MA, USA). IR spectra were obtained with a Nicolet 5700 FT spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA) in ATR mode. UV spectra were recorded with a Perkin-Elmer Lambda XLS+ spectrometer (Waltham, MA, USA); mean values of five replicates were taken. DSC and TGA were recorded with Perkin-Elmer DSC 7 and TGA 7 instruments (Waltham, MA, USA) at a heating rate of 10 °C·min^{−1}. High-resolution mass spectra were measured with a Finnigan MAT 95 mass spectrometer. In general, spectra were recorded from the crude but pure compounds, not from single-crystalline material. Single crystal diffraction intensity data were recorded by ω scans with an Oxford Diffraction Gemini-R Ultra (Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK) diffractometer at 173(2) K. Absorption corrections were applied in all cases (multi-scan). The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 . CCDC 1444906–1444908 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

3.1. 5-Azido-4-(dimethylamino)-1-methyl-1,2,4-triazolium Hexafluoridophosphate (1)

Cautionary note: although we did not encounter any difficulties, azides should generally be treated with respect because they are potentially explosive. To a solution of 5-bromo-4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluoridophosphate (1.00 g, 2.84 mmol) in acetone (20 mL), NaN₃ (185 mg, 2.84 mmol) was added. The mixture was stirred for 20 h at room temperature. The precipitate was filtered off, washed with acetone (5 mL), and the solvent was evaporated at reduced pressure. The residue was washed with Et₂O (5 mL) and dried to yield a colorless powder (0.66 g, 74%). Single crystals were obtained by slow evaporation of a solution in acetone. M.p. 155 °C (decomposition). ¹H NMR (DMSO-*d*₆, 300 MHz, δ): 2.97 (s, 6H), 3.73 (s, 3H), 9.65 (s, 1H) ppm. ¹³C NMR (DMSO-*d*₆, 75 MHz, δ): 36.2, 46.9 (2C), 139.7 (CH), 144.0 ppm. ¹H NMR (acetone-*d*₆, 300 MHz, δ): 3.17 (s, 6H), 3.83 (s, 3H), 9.39 (s, 1H) ppm. ¹³C NMR (acetone-*d*₆, 75 MHz, δ): 37.0, 47.7 (2C), 140.1 (CH), 145.4 ppm. IR (neat) $\tilde{\nu}$: 3166, 2166, 1600, 823, 555 cm^{−1}.

3.2. 5-(3-Azatricyclo[3.2.1.0^{2,4}]oct-3-yl)-4-(dimethylamino)-1-methyl-1,2,4-triazolium Hexafluorido-Phosphate (2)

A solution of azide **1** (0.35 g, 1.1 mmol) and bicyclo[2.2.1]hept-2-ene (0.12 g, 1.3 mmol) in acetone (10 mL) was stirred for 17 h at room temperature. The volatiles were removed, and the residue was washed with Et₂O (3 × 5 mL) and dried to yield **2** (0.28 g, 66%). Single crystals were obtained by diffusion of Et₂O into a solution in acetone. M.p. 164 °C. ¹H NMR (acetone-*d*₆, 300 MHz, δ): 1.03 (d, J = 10.3 Hz, 1H), 1.36 (m, 2H), 1.52 (d, J = 10.5 Hz, 1H), 1.62 (d, J = 9.0 Hz, 2H), 2.76 (s, 2H), 3.03 (s, 6H), 3.60 (s, 2H), 3.91 (s, 3H), 9.07 (s, 1H) ppm. ¹³C NMR (acetone-*d*₆, 75 MHz, δ): 26.3 (2C), 29.3, 37.4, 37.6 (2C), 46.1 (2C), 47.8 (2C), 138.4 (CH), 152.4 ppm. IR (neat) $\tilde{\nu}$: 3150, 2972, 1600, 825, 554 cm^{−1}.

3.3. 4-(Dimethylamino)-1-methyl-5-(1-(4-(dimethylamino)-1-methyl-1,2,4-triazolin-5-ylidene)triazene-3-yl)-1,2,4-triazolium Hexafluoridophosphate (3)

A LiN(SiMe₃)₂ solution (1M in THF, 0.40 mL) was added to a solution of 4-(dimethylamino)-1-methyl-1,2,4-triazolium hexafluoridophosphate (0.10 g, 0.37 mmol) in THF (5 mL) and stirred at room temperature for 30 min. Then azide **1** (0.12 g, 0.38 mmol) was added, and the mixture was stirred at room temperature for 30 h. The precipitate was filtered off and dried to yield a yellow powder (25 mg, 15%). Single crystals were obtained by slow evaporation of a solution in acetone. M.p. 203 °C (decomposition). ¹H NMR (acetone-*d*₆, 300 MHz, δ): 3.10 (s, 6H), 4.04 (s, 3H), 9.04 (s, 1H) ppm. ¹³C NMR (acetone-*d*₆, 75 MHz, δ): 39.6, 47.0 (2C), 140.7, 153.6 ppm. IR (neat) $\tilde{\nu}$: 3159, 1537, 1446, 1276, 1250, 1183, 1156, 832, 724, 554 cm^{−1}. HRMS (ES): m/z = 294.1893 (calcd. 294.1898 for C₁₀H₂₀N₁₁, [M]⁺). UV (solvent): λ_{\max} 342.6 (H₂O), 350.3 (AcOH), 352.0 (MeOH), 354.0 (EtOH), 354.5 (2-PrOH), 355.2 (DMSO), 355.8 (CH₂Cl₂) nm.

3.4. 4-(Dimethylamino)-1-methyl-5-amino-1,2,4-triazolium Hexafluoridophosphate (4)

A solution of azide **1** (0.10 g, 0.32 mmol) and triphenylphosphane (84 mg, 0.32 mmol) in acetone (3 mL) was stirred for 5 h at room temperature. The volatiles were removed, and the residue was partitioned between H₂O (2 mL) and CH₂Cl₂ (2 × 1 mL). The aqueous phase was dried to yield **4** (50 mg, 29%). ¹H NMR (acetone-d₆, 300 MHz, δ): 2.97 (s, 6H), 3.82 (s, 3H), 8.94 (s, 1H) ppm. ¹³C NMR (acetone-d₆, 75 MHz, δ): 36.0, 47.1 (2C), 136.3, 149.5 ppm. IR (neat) $\tilde{\nu}$: 3476, 3162, 1686, 1261, 824, 556 cm^{−1}. MS (ES): m/z = 142.111 (calcd. 142.109 for C₅H₁₂N₅, [M]⁺).

4. Conclusions

Nitrogen-rich azidoazolum salts are not only of interest as structural motifs in the area of energetic materials but also represent valuable intermediates in synthetic chemistry. The versatility of azide chemistry definitely contributes to the increasing popularity of this functional group in the field of heterocyclic chemistry.

Acknowledgments: The authors are grateful to E. Gstrein and Ulrich J. Griesser for the measurement of DSC and TGA.

Author Contributions: Gerhard Laus and Herwig Schottenberger conceived and designed this study. Gerhard Laus carried out experimental work (synthesis, crystallization and characterization) and wrote the manuscript. Volker Kahlenberg determined the crystal structures.

Conflicts of Interest: The authors declare no conflict of interest.

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