



Synthesis and characterization of perfluorinated nitriles and the corresponding sodium 5-perfluoroalkyltetrazolate salts

Margaret-J. Crawford, Thomas M. Klapötke*, Hendrik Radies

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

ARTICLE INFO

Article history:

Received 29 July 2008

Received in revised form 3 September 2008

Accepted 16 September 2008

Available online 25 September 2008

Keywords:

5-Perfluoroalkyltetrazolate

Vibrational spectroscopy

Multinuclear NMR spectroscopy

Differential scanning calorimetry

Mass spectrometry

Crystal structure

ABSTRACT

The high-yield syntheses of trifluoroacetonitrile (**1a**), pentafluoropropionitrile (**1b**) and heptafluorobutyronitrile (**1c**) under mild reaction conditions using readily available starting materials (trifluoroacetamide, pentafluoropropionamide, heptafluorobutanamide) are described. Furthermore, the reactions of the perfluoroalkyl nitriles with sodium azide in acetonitrile forming sodium 5-trifluoromethyltetrazolate (**2a**), sodium 5-pentafluoroethyltetrazolate (**2b**) and sodium 5-heptafluoropropyltetrazolate (**2c**) were undertaken. The 5-perfluoroalkyltetrazolate salts were characterized using vibrational (Raman and infrared) and multinuclear (^{13}C , $^{14/15}\text{N}$, ^{19}F) NMR spectroscopy, differential scanning calorimetry, mass spectrometry and elemental analysis. Additionally, the single crystal X-ray structure of the monohydrate of **2a** was determined. Crystal data: **2a**·H₂O: monoclinic, $C2/m$, $a = 18.8588(6)$ Å, $b = 7.1857(2)$ Å, $c = 9.3731(3)$ Å, $\beta = 102.938(3)^\circ$, $V = 1237.94(7)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.911$ g cm⁻³.

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1. Introduction

Perfluoroalkyltetrazolates were first synthesized in the late 1950s by W.G. Finnegan via the [2 + 3] cycloaddition of sodium azide with the corresponding perfluorinated nitrile [1] and in the following decade, the syntheses and properties of a large variety of salts of new 5-perfluoroalkyltetrazolates were published [2–4]. Some of these materials have been characterized by spectroscopic, analytical and structural methods and have also found pharmaceutical applications as analgesic or anti-inflammatory agents [5,6].

5-Perfluoroalkyltetrazoles and their derivatives are not only of interest to the pharmaceutical industry, but also for defense applications as fluorine-rich components of magnesium-based decoy flares. In this context, a more thorough investigation of the properties of these materials was undertaken. However, the synthesis of tetrazoles bearing an electron-withdrawing substituent such as a NO₂ group is often complicated since hazardous or inaccessible starting materials or side products are involved [7–9]. In particular, the perfluorinated nitriles required for the synthesis of the 5-perfluoroalkyltetrazolates reported in this work are toxic, difficult to obtain commercially and very expensive.

One way to obtain literature known perfluorinated nitriles is the reaction of the corresponding perfluorinated amide with phosphorus pentoxide at a high temperature [10]. A second way to synthesize trifluoroacetonitrile in high yields was developed by Parker and is the reaction of a perfluorinated amide with a mixture of pyridine and trifluoroacetic anhydride at ambient temperature. In order to overcome the above mentioned difficulties, we extended the second method (dehydration of the corresponding perfluorinated acetamide) for the in situ synthesis of trifluoroacetonitrile to prepare other perfluorinated nitriles [11]. The nitriles generated by this method were then reacted in situ with sodium azide to yield the series of sodium 5-perfluoroalkyltetrazolates presented in this study. Here we present the details of the modified synthetic method for the high-yield synthesis under mild conditions of these materials from readily available, low-cost amides. In addition, the spectroscopic and analytic characterization of the corresponding series of sodium 5-perfluoroalkyltetrazolate salts is discussed.

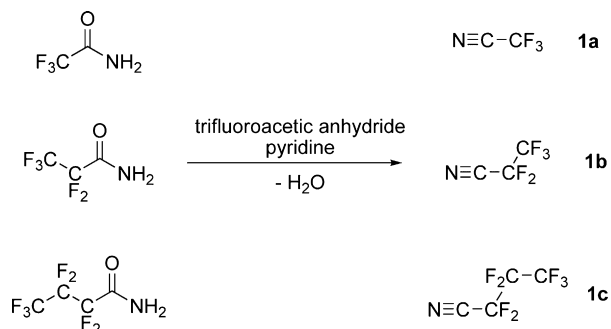
2. Results and discussion

2.1. Synthesis

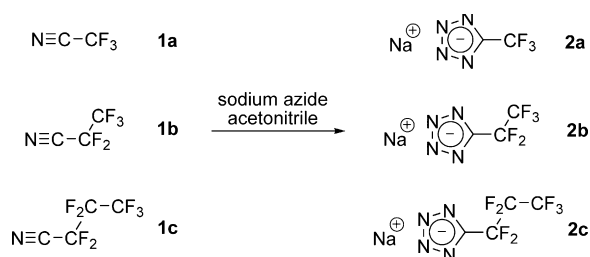
The nitriles were synthesized by the drop-wise addition of a mixture of pyridine and trifluoroacetic anhydride to the corresponding perfluorinated amides (trifluoroacetamide, pentafluor-

* Corresponding author. Tel.: +49 89 2180 77491 fax: +49 89 2180 77492.

E-mail address: tmk@cup.uni-muenchen.de (T.M. Klapötke).



Scheme 1. Synthesis of perfluorinated nitriles **1a–c**.



Scheme 2. Synthesis of sodium 5-perfluoroalkyltetrazolates **2a–c**.

opropionamide, heptafluorobutanamide) in pyridine solution at room temperature. Addition of the pyridine–trifluoroacetic anhydride mixture results immediately in the evolution of gas (perfluorinated nitrile) and the reaction rate can therefore be controlled by the rate of pyridine–trifluoroacetic anhydride addition. The gas evolved was directly condensed into a cold trap cooled by liquid nitrogen (Scheme 1).

The nitriles collected were then reacted with a suspension of sodium azide in dry acetonitrile yielding the corresponding sodium tetrazolate salts. These reactions were carried out at room temperature. Compared to acetonitrile the reactivities of the perfluorinated nitriles are higher, due to the electron-withdrawing effect of the perfluorinated groups. Moreover, only the desired products and no byproducts are observed. The water free compounds obtained are very hygroscopic in consequence the analytical data were collected as hydrates (Scheme 2).

Table 1

Crystal data and structure refinement for sodium 5-trifluoromethyltetrazolate monohydrate.

Compound name	Sodium 5-trifluoromethyltetrazolate monohydrate
Chemical formula	C ₂ H ₂ F ₃ N ₄ NaO
Formula weight (g mol ⁻¹)	178.07
CSD deposit no.	419701
Crystal size (mm)	0.18 × 0.12 × 0.08
Crystal system	Monoclinic
Space group	C2/m
<i>a</i> (Å)	18.8588(6)
<i>b</i> (Å)	7.1857(2)
<i>c</i> (Å)	9.3731(3)
α (°)	90
β (°)	102.938(3)
γ (°)	90
<i>V</i> (Å ³)	1237.94(7)
<i>Z</i>	8
<i>D</i> _{calc} (g cm ⁻³)	1.911
μ (mm ⁻¹)	0.262
<i>F</i> (0 0 0), <i>e</i>	704
θ range (°)	3.92–26.50
Index ranges	–23 ≤ <i>h</i> ≤ 23 –9 ≤ <i>k</i> ≤ 9 –11 ≤ <i>l</i> ≤ 11
Reflections collected	6556
Reflections unique	1376 (<i>R</i> _{int} = 0.0403)
Final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0342, <i>wR</i> ₂ = 0.0903
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0438, <i>wR</i> ₂ = 0.0962
Goodness of fit (<i>F</i> ²)	1.079
Data/restraints/parameters	1376/1/132
Large diff. peaks and hole	0.364 and –0.461

2.2. Crystal structure

The molecular structure of **2a** was determined using single crystal X-ray diffraction. Crystals suitable for X-ray diffraction were obtained by the slow evaporation of a solution of **2a** in a methanol at room temperature. The compound crystallized as a monohydrate in the space group *C2/m* with 8 formula units in the unit cell and a calculated density of 1.911 g cm⁻³ at 200 K. The asymmetric unit contains two crystallographically independent ion pairs. The crystal and structure refinement data are given in Table 1.

Fig. 1 shows an ORTEP plot of the distorted octahedral coordination sphere of Na1 consisting of two water molecules

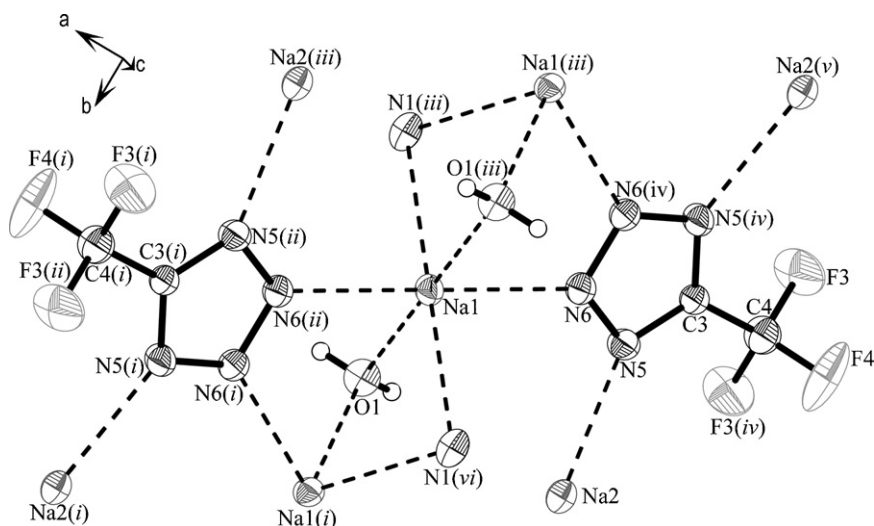


Fig. 1. ORTEP plot of **2a**·H₂O in the solid state showing the coordination sphere of the Na1 atom, with *i* = 1.5 – *x*, 0.5 + *y*, 2 – *z*; *ii* = 1.5 – *x*, –0.5 – *y*, 2 – *z*; *iii* = 1.5 – *x*, –0.5 + *y*, 2 – *z*; *iv* = *x*, –1 – *y*, *z*; *v* = *x*, –1 + *y*, *z*; *vi* = 1 – *x*, *y*, 2 – *z*.

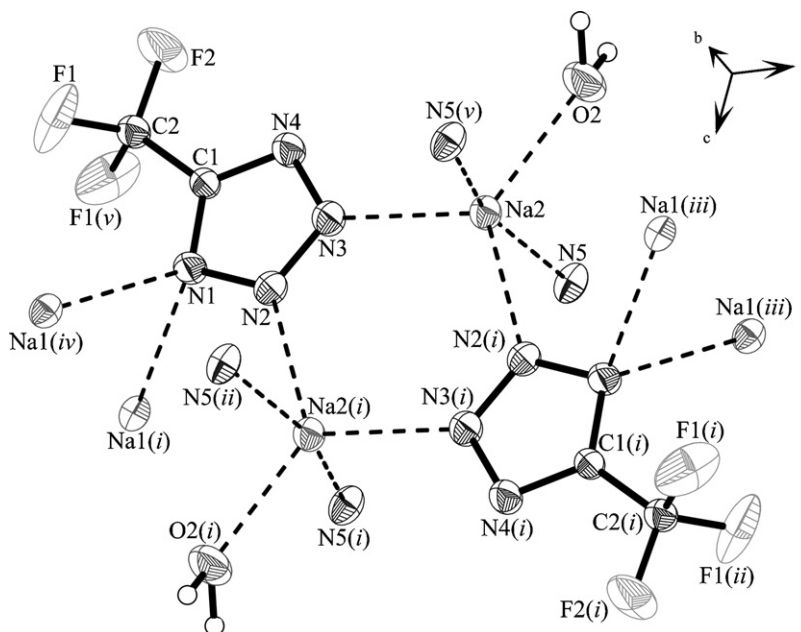


Fig. 2. ORTEP plot of **2a**·H₂O in the solid state showing the coordination sphere of the Na2 atom, with $i = 1 - x, y, 2 - z$; $ii = 1 - x, -y, 2 - z$; $iii = 1.5 - x, 0.5 + y, 2 - z$; $iv = -0.5 + x, 0.5 + y, z$; $v = x, -y, z$.

and four tetrazolate nitrogen atoms. The angles surrounding Na1 are between $80.44(6)^\circ$ (O1–Na1–N6(ii)) and $99.56(6)^\circ$ (O1–Na1–N6). The sodium atoms form chains along the *b*-axis with the sodium atoms connected via the O1 atoms, through the N1 atoms and via a Na1–N6–N6–Na1 bridge.

The solid state structure of **2a** shows two tetrazolate anions with different coordination environments. One tetrazolate shows the coordination of all ring N atoms to different sodium cations and is shown in Fig. 1. Whereas, the N5 tetrazolate ring atoms show coordination to Na2, the N6 atoms to Na1. The Na–N distances

range from $2.456(1)$ Å to $2.666(2)$ Å, whereas the Na1–O1 distance is shorter ($2.403(1)$ Å). Selected bond lengths and contact distances for **2a** are listed in Table 2.

Fig. 2 shows the coordination sphere of Na2 as an ORTEP plot. The coordination sphere around Na2 can be described being distorted trigonal bipyramid and comprises one water molecule and four N atoms of four tetrazolates. The equatorial coordination sites are occupied by one water molecule and the N2 and N3 atoms of two tetrazolate anions. The N5 atoms of two further tetrazolates occupy the axial coordination sites of Na2. The angles in the

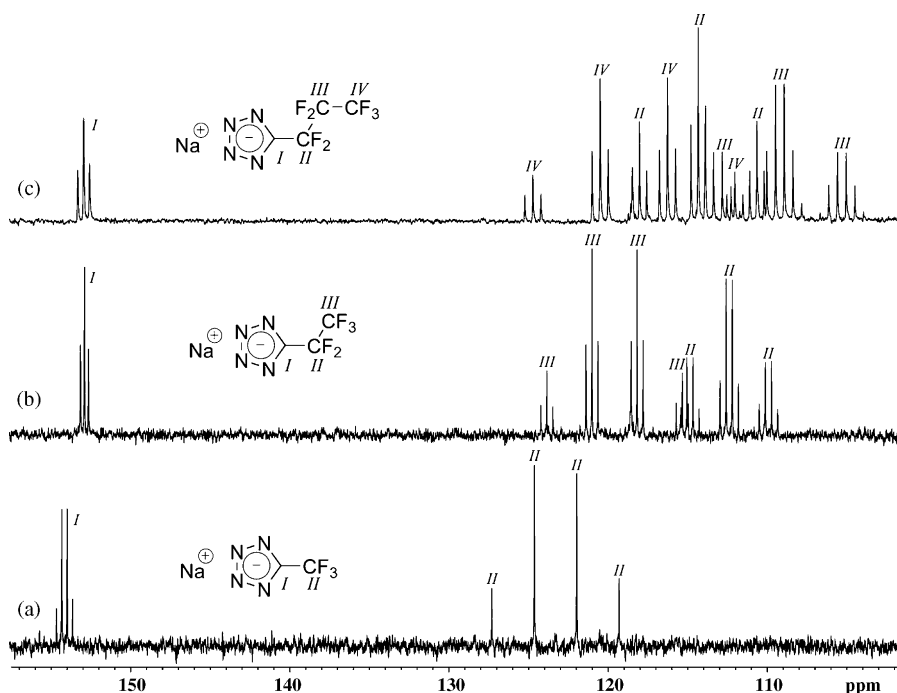


Fig. 3. ¹³C NMR spectra in *d*₆ DMSO of the perfluorinated tetrazolates (**2a–c**).

Table 2
Selected bond lengths of substance **2a**.

Distances (Å)		Distances (Å)	
Na1–O1	2.403(1)	C2–F2	1.306(3)
Na1–N1	2.666(2)	C2–F1	1.317(2)
Na1–N6	2.456(1)	C3–N5	1.327(2)
Na1–Na1	3.593(1)	C3–C4	1.488(3)
Na2–O2	2.373(2)	C4–F4	1.316(4)
Na2–N2	2.500(2)	C4–F3	1.326(2)
Na2–N3	2.429(2)	N1–N2	1.342(3)
Na2–N5	2.512(2)	N2–N3	1.309(3)
Na2–Na2	4.091(2)	N3–N4	1.343(3)
C1–N4	1.322(3)	N5–N6	1.343(2)
C1–N1	1.332(3)	N6–N6	1.315(3)
C1–C2	1.490(3)		

equatorial plane are $122.08(8)^\circ$ (O2–Na2–N3), $126.62(8)^\circ$ (O2–Na2–N2(i)) and $111.29(8)^\circ$ (N3–Na2–N2(i)). The N5–Na–N5' angle is not 180° as expected for a perfect trigonal bipyramid but slightly distorted to $162.87(8)^\circ$.

Each tetrazolate anion, shown in Fig. 2, shows coordination through N1 to two sodium atoms (Na1). In addition, the tetrazolate acts as a bridge between two sodium atoms (Na2) with the N2 and N3 tetrazolate ring nitrogen atoms. The O2 atom of the H₂O molecule, however, shows only coordination to one sodium atom (Na2) in contrast to the O1 atom of the H₂O molecule in Fig. 1 which bridges two Na cations.

2.3. NMR spectroscopy

The sodium 5-perfluoroalkyltetrazolates (**2a–c**) were characterized using ¹³C{¹H}, ¹⁹F and ¹⁵N NMR spectroscopy.

Fig. 3 shows a comparison of the ¹³C{¹H} NMR spectra of the sodium 5-perfluoroalkyltetrazolates in *d*₆ DMSO. The signal corresponding to the tetrazolate ring carbon atom shifts with increasing fluorine content of the organic group from 154.0 ppm to higher field (152.8 ppm). For sodium 5-trifluoromethyltetrazolate, a quartet with a ²J_{CF} coupling constant of 33.8 Hz is

Table 3
Computed isotropic magnetic shieldings (GIAO method [11,12], MPW1PW91/aug-cc-pVDZ) and relative ¹⁴N/¹⁵N NMR chemical shifts (ppm) referenced to MeNO₂.

		Abs. anisotropic shielding	Rel. shift, δ (ppm)	Exptl. ¹⁴ N/ ¹⁵ N, δ (ppm)
MeNO ₂		–116.7	0	0/0
F ₃ C–CN ₄ [–]	N (N1, N4 _{Ring})	–65.0	–52	–60/–60.0
	N (N2, N3 _{Ring})	–139.0	+22	+14/+13.6
F ₅ C ₂ –CN ₄ [–]	N (N1, N4 _{Ring})	–66.0	–51	–57/–57.9
	N (N2, N3 _{Ring})	–139.0	+22	+14/+14.0
F ₇ C ₃ –CN ₄ [–]	N (N1, N4 _{Ring})	–65.5	–51	–57/–57.3
	N (N2, N3 _{Ring})	–139.1	+22	+15/+14.3

observed which corresponds to the coupling of the ring carbon atom with the neighboring CF₃ group. For tetrazolate salts **2b** and **2c**, a triplet (25.4 Hz and 25.2 Hz) is observed instead which corresponds to the coupling of the ring carbon atom with the fluorine atoms of the neighboring CF₂ group. The CF₃ group resonances appear as quartets at 123.8 ppm (**2a**), 119.5 ppm (**2b**) and 118.3 ppm (**2c**) with coupling constants of 267.5 Hz, 285.4 Hz and 287.3 Hz, respectively. Additionally, the pentafluoroethyl- and heptafluoropropyltetrazolates show a small coupling of the carbon atom of the CF₃ group to the neighboring CF₂ group. The NMR spectrum of **2b** shows, as expected, a triplet of quartets at 112.3 ppm for the CF₂ group. The coupling constants are 248.2 Hz for the ¹J_{CF} and 39.0 Hz for the ²J_{CF}. Sodium 5-heptafluoropropyltetrazolate shows a triplet of triplets at 114.2 ppm with a coupling constant of 250.7 Hz and 30.9 Hz corresponding to the CF₂ group directly bonded to the tetrazole ring. In contrast, the second CF₂ group shows a triplet of sextets at 109.1 ppm (264.6 Hz and 37.2 Hz) indicating similar ²J_{CF} coupling constants to the adjacent CF₂ and CF₃ groups.

The ¹⁹F NMR spectra show the signal corresponding to the CF₃ group of sodium 5-trifluoromethyltetrazolate at –59.7 ppm, whereas sodium 5-pentafluoroethyltetrazolate shows signals at

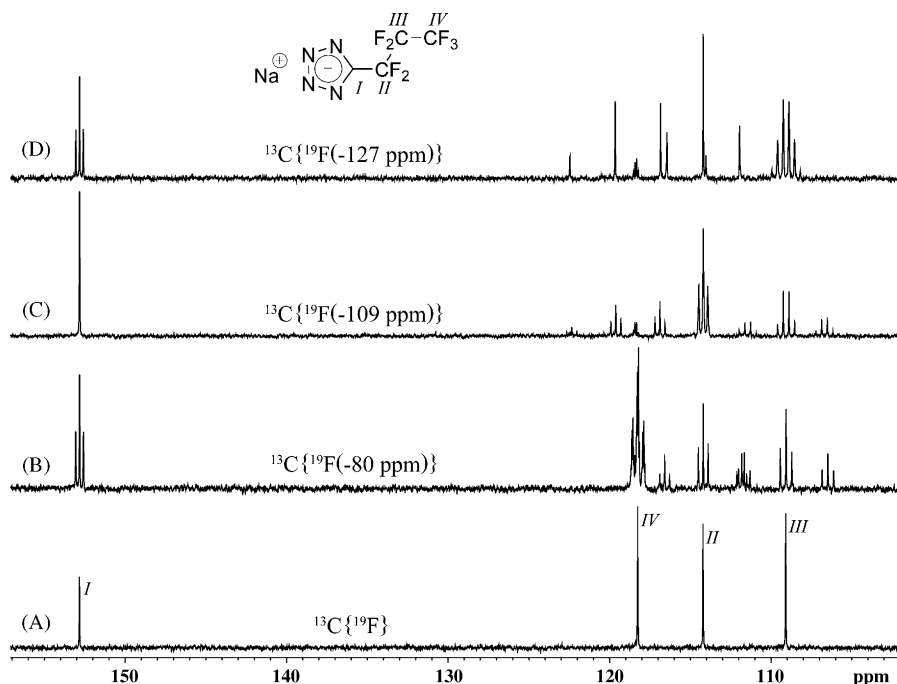


Fig. 4. ¹³C{¹⁹F} NMR spectra of **2a** in *d*₆ DMSO with selective ¹⁹F decoupling.

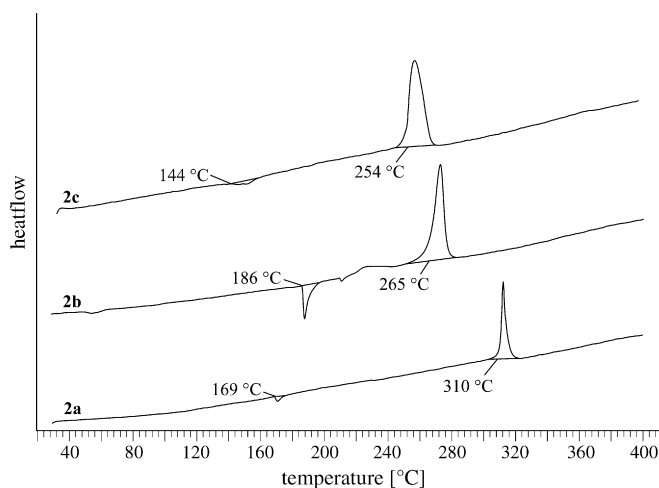


Fig. 5. DSC-thermograms of **2a–c** (endo up).

Table 4
Properties of sodium perfluoroalkyltetrazolate salts.

	2a	2b	2c
Friction (N)	>360	>360	>360
Impact (J)	>100	>100	>100
Decomposition point (°C)	310	265	254
Dehydration point (°C)	169	186	144

–83.9 ppm (quartet) for the CF₃ group and at –110.4 ppm (triplet) for the CF₂ group. Sodium 5-heptafluoropropyltetrazolate shows signals at –80.6 ppm, –109.1 ppm and –127.2 ppm in the ¹⁹F NMR spectrum corresponding to the CF₃ group, the ring neighbored CF₂ group and the central CF₂ group.

The assignment of the ¹⁹F NMR and ¹³C NMR signals and ¹³C, ¹⁹F coupling constants for **2a–c** is based on a series of selectively ¹⁹F decoupled ¹³C{¹⁹F} NMR spectra, which are shown in Fig. 4.

On irradiation of the frequency of the CF₃ group the signal at 188.3 ppm collapses to a triplet with a coupling constant of 31.4 Hz (spectrum B). Irradiation at –109 ppm (CF₂ group bonded to the tetrazole ring) eliminates the C–F coupling of the ring carbon atom (spectrum C). Correspondingly irradiation at –127 ppm (central CF₂ group) causes the ¹³C NMR signal of the CF₃ group to appear as a quartet only. The ¹³C NMR experiments with selective ¹⁹F irradiation confirm the assignment of the ¹³C NMR signals.

All sodium 5-perfluoroalkyltetrazolates show two signals in the ^{14/15}N NMR spectra. The signal for the nitrogen atom N1 is observed at –60 ppm (**2a**), –57.9 ppm (**2b**) and –57.3 ppm (**2c**), and for N2 chemical shifts at 13.6 ppm (**2a**), 14.0 ppm (**2b**) and 14.3 ppm (**2c**). Assignments were made by comparison to ¹⁵N spectra of sodium 5-nitrotetrazolate.

In order to compute the ^{14/15}N NMR chemical shifts for all three anions, the isotropic magnetic shieldings were computed using the GIAO (Gauge-Independent Atomic Orbital) method implemented in G03 [12,13]. The NMR shielding tensors were calculated at the MPW1PW91/aug-cc-pVDZ level of theory using the GIAO method [13]. Table 3 summarizes the computed isotropic magnetic shieldings and relative ^{14/15}N NMR chemical shifts (ppm) referenced to MeNO₂.

2.4. Properties

The DSC data (Fig. 5) provide a comparison between the sodium salts of trifluoromethyl- (**2a**), pentafluoroethyl- (**2b**) and heptafluoropropyltetrazolate (**2c**).

From the DSC measurements it is evident that the decomposition points decrease from 310 °C for **2a** to 254 °C for **2c** as the fluorine content increases. For **2a** a dehydration temperature of 169 °C was observed. Dehydration of **2b** occurs at 186 °C and for **2c** at 144 °C. In all cases the sodium salts were hygroscopic.

Additionally, the sensitivity data of the sodium salts (**2a–c**) were collected and listed in Table 4.

The sodium 5-perfluoroalkyltetrazolate salts (**2a–c**) show no sensitivity toward friction and impact.

3. Conclusion

Trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile were obtained at controllable rates from the corresponding perfluorinated amides via dehydration with a pyridine/trifluoroacetic anhydride mixture.

Sodium 5-trifluoromethyltetrazolate (**2a**), sodium 5-pentafluoroethyltetrazolate (**2b**) and sodium 5-heptafluoropropyltetrazolate (**2c**) were prepared from sodium azide and the corresponding nitriles in dry acetonitrile and were characterized using vibrational (Raman, infrared) and NMR spectroscopy (¹³C, ^{14/15}N and ¹⁹F), DSC measurements, mass spectrometry and elemental analysis. Additionally, the single crystal X-ray structure of the monohydrate of **2a** was determined. Crystal data: **2a**·H₂O: monoclinic, *C*2/*m*, *a* = 18.8588(6) Å, *b* = 7.1857(2) Å, *c* = 9.3731(3) Å, β = 102.938(3)°, *V* = 1237.94(7) Å³, *Z* = 8, σ = 1.911 g cm^{–3}.

4. Experimental

Trifluoroacetamide was supplied by ABCR GmbH & Co.KG. Pentafluoropropionamide and heptafluorobutyramide were obtained from Apollo Scientific. Acetonitrile (analytical grade) was supplied by Acros Organics and was dried over P₄O₁₀ and freshly distilled before use. The remaining reagents were also supplied by Acros Organics and were used as supplied.

The crystallographic data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected using CRYCALIS CCD software [14] and reduced with CRYCALIS RED [15]. The structure was solved by direct methods (SHELXS-97) [16] and refined using SHELXL-97 [17]. Finally, the structure was checked using PLATON [18]. A multi-scan empirical absorption correction using spherical harmonics was applied using SCALE3 ABSPACK [19]. All non-

hydrogen atoms were refined anisotropically. The H1a and H1b atoms were found from Fourier difference maps and freely refined. The H2a atom was found Fourier difference maps and refined with the O2–H2a distance restrained to 0.9(5) Å. All Ortep plots show thermal ellipsoids with 50% probability for the non-hydrogen atoms.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666, e-mail: crysdata@fizkarlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD number: 419701

The DSC data were obtained using a Linseis DSC PT10 in closed aluminium containers with a hole (1 µm) on the top for gas release in a nitrogen atmosphere (nitrogen flow 5 mL/min). The used heating rate was 5 °C/min. Additionally, the melting points were also independently determined using Büchi B-540.

The ¹³C, ^{14/15}N and ¹⁹F NMR spectra were measured with a Jeol Eclipse 400 spectrometer operating at 100.6 MHz for ¹³C, 40.5 MHz for ¹⁵N and 376.5 MHz for ¹⁹F. Chemical shifts (in ppm) are given with respect to TMS (¹³C), MeNO₂ (^{14/15}N) and CFCl₃ (¹⁹F) as external standards.

IR spectra were obtained using a PerkinElmer Spectrum BX FT-IR System and Raman spectra were measured using a PerkinElmer Spectrum 2000 FT-Raman spectrometer fitted with a Nd-YAG-laser (λ = 1064 nm) as solids at room temperature (resolution = 4 cm⁻¹).

The friction and impact sensitivity data were obtained using a BAM drophammer and friction tester, in accordance with the BAM methods [20,21]. A description of the sensitivity test apparatus can be found in reference [22].

4.1. General preparation of perfluorinated nitriles (1a–c)

A mixture of 6.95 mL (10.5 g, 0.05 mol) trifluoroacetic anhydride and 8.5 mL (8.3 g, 0.10 mol) pyridine was added drop-wise to a solution of perfluorinated amide (0.05 mol) in 26 mL pyridine. The gas obtained was condensed into a cooling trap at –196 °C under a low stream of dried nitrogen gas [11]. The yield of perfluorinated nitrile obtained was not determined because it was reacted with sodium azide in situ to form the corresponding sodium 5-perfluoroalkyltetrazolate salts as described below in yields of 95–99%.

4.2. General preparation of the sodium 5-perfluoroalkyltetrazolates (2a–c)

Sodium azide (3.25 g, 0.05 mol) was suspended in 50 mL of dry acetonitrile in a 1 L round bottomed flask equipped with a Young valve and a magnetic stirrer bar. The perfluorinated nitrile prepared according to the described method above was then condensed into the reaction vessel at –196 °C. The flask containing the reaction mixture was then evacuated and then the Young valve closed. The reaction vessel was subsequently warmed slowly to room temperature and the reaction mixture stirred for 48 h. The suspension was then filtered and the solvent removed under reduced pressure, yielding the sodium 5-perfluoroalkyltetrazolate as a white solid (yield: 90–97%).

4.3. Sodium 5-trifluoromethyltetrazolate 2a

m.p.: –, dehydr. p.: 169 °C, decomp. p.: 310 °C. ¹³C NMR (100.6 MHz, *d*₆ DMSO): δ 123.8 (q, ¹J_{CF} 267.5, –CF₃), 154.0 (q, ²J_{CF} 33.8, C_{Ring}). ¹⁴N NMR (40.5 MHz, *d*₆ DMSO): δ 14 (N₂Ring), –60 (N₁Ring). ¹⁵N NMR (40.5 MHz, *d*₆ DMSO): δ 13.6 (N₂Ring), –60.0

(N₁Ring). ¹⁹F NMR (376.5 MHz, *d*₆ DMSO): δ –59.7 (3F, s, –CF₃); FAB–(C₂F₃N₄[–]), *m/z*: 137.1 [M][–] (100). IR (KBr): ν 3418 (s), 1642 (m), 1508 (s), 1417 (w), 1234 (vs), 1171 (vs), 1141 (vs), 1042 (s), 973 (w), 775 (w), 750 (m), 582 (w) cm⁻¹. Raman: (200 mW): ν 1516 (70), 1245 (13), 1177 (55), 1159 (31), 1054 (81), 996 (26), 754 (90), 422 (28), 394 (67), 171 (100) cm⁻¹. Anal. calcd. for NaC₂F₃N₄·0.33H₂O: C, 14.47; H, 0.40; N, 34.33. Found: C, 14.77; H, 0.48; N, 34.34. Sensitivity data: friction > 360 N; impact > 100 J.

4.4. Sodium 5-pentafluoroethyltetrazolate 2b

m.p.: –, dehydr. p.: 186 °C, decomp. p.: 265 °C. ¹³C NMR (100.6 MHz, *d*₆ DMSO): δ 112.3 (tq, ¹J_{CF} = 248.2 Hz, ²J_{CF} = 39.0 Hz, –CF₂–CF₃), 119.5 (qt, ¹J_{CF} = 285.4 Hz, ²J_{CF} = 37.9 Hz, –CF₃), 152.8 (t, ²J_{CF} = 25.4 Hz, C_{Ring}). ¹⁴N NMR (40.5 MHz, *d*₆ DMSO): δ 14 (N₂Ring), –57 (N₁Ring). ¹⁵N NMR (40.5 MHz, *d*₆ DMSO): δ 14.0 (N₂Ring), –57.9 (N₁Ring). ¹⁹F NMR (376.5 MHz, *d*₆ DMSO): δ –83.9 (3F, t, ³J_{FF} = 3.0 Hz, –CF₃), –110.4 (2F, q, ³J_{FF} = 3.0 Hz, –CF₂–CF₃); FAB–(C₃F₅N₄[–]), *m/z*: 187.1 [M][–] (100). IR (KBr): ν 3423 (s), 1639 (w), 1486 (w), 1416 (w), 1342 (s), 1342 (s), 1210 (vs), 1159 (vs), 1086 (m), 1067 (m), 1040 (w), 975 (vs), 750 (m), 636 (w), 544 (w), 499 (w) cm⁻¹. Raman: (200 mW): ν 2943 (14), 1490 (75), 1344 (24), 1222 (24), 1169 (19), 1150 (27), 1092 (14), 1070 (42), 1040 (8), 986 (21), 919 (7), 770 (16), 752 (100), 640 (19), 601 (18), 546 (21), 399 (31), 379 (33), 358 (42), 343 (52), 266 (33), 189 (24), 153 (20) cm⁻¹. Anal. calcd. for NaC₃F₅N₄·0.5H₂O: C, 16.45; H, 0.46; N, 25.58. Found: C, 16.85; H, 0.84; N, 25.76. Sensitivity data: friction > 360 N; impact > 100 J.

4.5. Sodium 5-heptafluoropropyltetrazolate 2c

m.p.: –, dehydr. p.: 144 °C, decomp. p.: 254 °C. ¹³C NMR (100.6 MHz, *d*₆ DMSO): δ 109.1 (tsextet, ¹J_{CF} = 264.6 Hz, ²J_{CF} = 37.2 Hz, –CF₂–CF₃), 114.2 (tt, ¹J_{CF} = 250.7 Hz, ²J_{CF} = 30.9 Hz, –CF₂–CF₂–CF₃), 118.3 (qt, ¹J_{CF} = 287.3 Hz, ²J_{CF} = 34.5 Hz, –CF₃), 152.8 (t, ²J_{CF} = 25.2 Hz, C_{Ring}). ¹⁴N NMR (40.5 MHz, *d*₆ DMSO): δ 15 (N₂Ring), –57 (N₁Ring). ¹⁵N NMR (40.5 MHz, *d*₆ DMSO): δ 14.3 (N₂Ring), –57.3 (N₁Ring). ¹⁹F NMR (376.5 MHz, *d*₆ DMSO): δ –80.6 (3F, ²J_{FF} = 9.2 Hz, ³J_{FF} = 0.9 Hz, –CF₃), –109.1 (2F, m, CF₂–CF₂–CF₃), –127.2 (2F, m, –CF₂–CF₃); FAB–(C₄F₇N₄[–]), *m/z*: 237.0 [M][–] (100). IR (KBr): ν 3421 (m), 1642 (w), 1485 (w), 1418 (w), 1382 (w), 1345 (m), 1286 (m), 1232 (vs), 1194 (s), 1185 (s), 1158 (m), 1121 (s), 1051 (w), 1030 (w), 935 (m), 891 (vs), 765 (w), 741 (s), 675 (w), 600 (w), 563 (w), 535 (w) cm⁻¹. Raman: (200 mW): ν 1485 (74), 1348 (16), 1284 (28), 1211 (31), 1154 (47), 1089 (14), 1053 (42), 894 (29), 766 (20), 743 (100), 677 (34), 604 (23), 537 (15), 399 (34), 379 (34), 348 (46), 310 (71), 287 (39), 205 (18), 178 (21), 92 (12) cm⁻¹. Anal. calcd. for NaC₄F₇N₄·0.5H₂O: C, 17.86; H, 0.37; N, 20.82. Found: C, 17.71; H, 0.70; N, 21.20. Sensitivity data: friction > 360 N; impact > 100 J.

Acknowledgments

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the Fonds der Chemischen Industrie (FCI), the European Research Office (ERO) of the U.S. Army Research Laboratory (ARL) and ARDEC (Armament Research, Development and Engineering Center) under contract nos. N 62558-05-C-0027, R&D 1284-CH-01, R&D 1285-CH-01, 9939-AN-01 & W911NF-07-1-0569 and the Bundeswehr Research Institute for Materials, Explosives, Fuels and Lubricants (WIWEB) under contract nos. E/E210/4D004/X5143 & E/E210/7D002/4F088 is gratefully acknowledged. The authors acknowledge collaborations Dr. M. Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. M. Sućeska (Brodarski Institute, Croatia) in

the development of new computational codes to predict the detonation parameters of high-nitrogen explosives. We are indebted to and thank Dr. Betsy M. Rice (ARL, Aberdeen, Proving Ground, MD) for many helpful and inspired discussions and support of our work.

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