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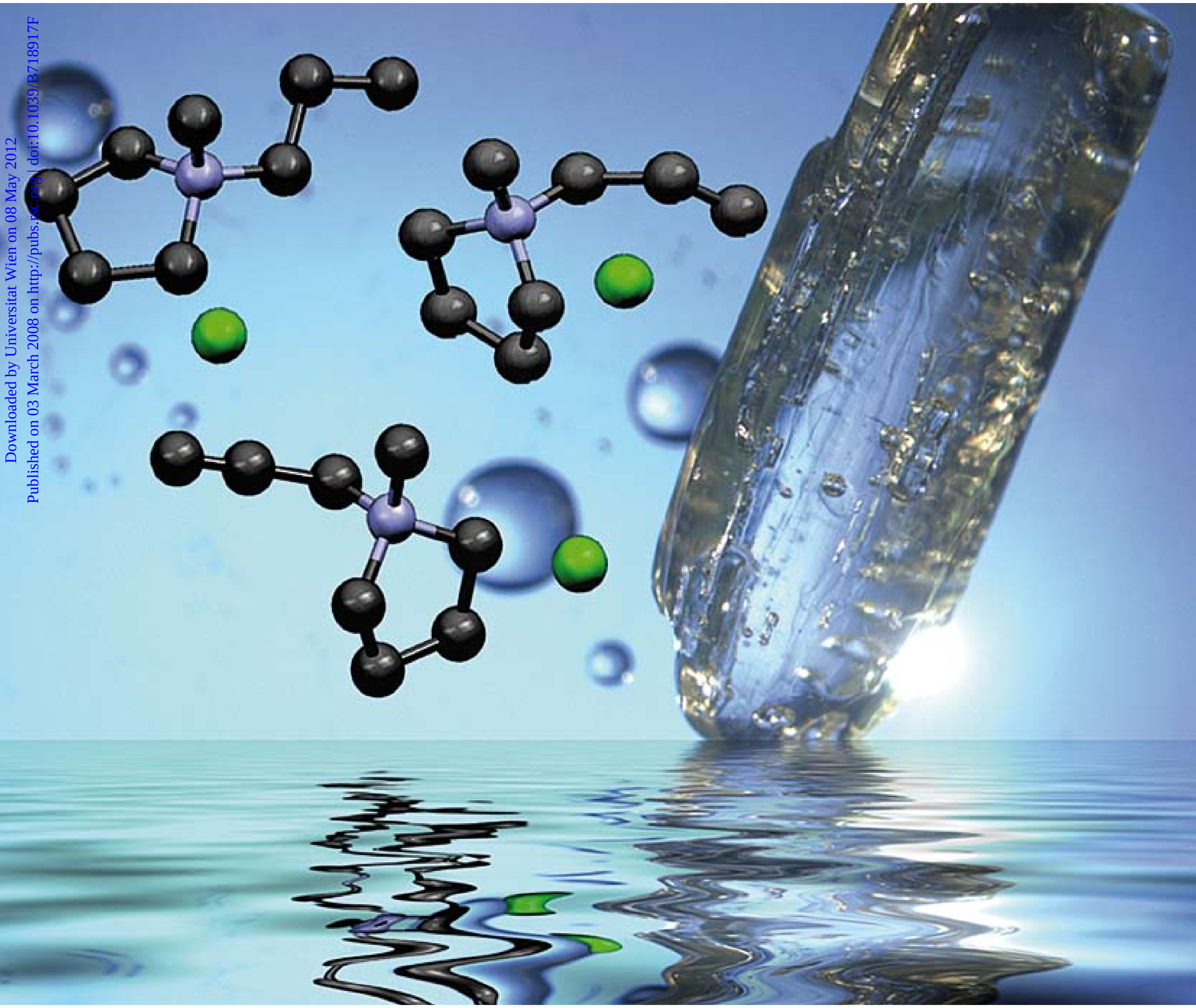

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Syntheses, crystal structures, and polymorphism of quaternary pyrrolidinium chlorides†

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The syntheses, properties, and X-ray crystal structures of 1-methyl-1-propylpyrrolidinium chloride **1**, 1-allyl-1-methylpyrrolidinium chloride **2**, and 1-methyl-1-propargylpyrrolidinium chloride **3** are described. Colorless plates of **1** ($C_8H_{18}ClN$) crystallize in the orthorhombic space group *Pnab* with $Z = 8$ and unit cell parameters $a = 10.0354(11)$ Å, $b = 13.254(2)$ Å, $c = 14.6231(16)$ Å. Colorless prisms of **2** ($C_8H_{16}ClN$) crystallize in the monoclinic space group $P2_1/c$ with $Z = 4$ and unit cell parameters $a = 6.4857(10)$ Å, $b = 12.005(3)$ Å, $c = 12.526(2)$ Å, and β=102.746(13)°. Colorless needles of **3** ($C_8H_{14}ClN$) crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$ and unit cell parameters $a = 8.4849(14)$ Å, $b = 8.1271(16)$ Å, $c = 13.501(2)$ Å, and β=100.408(13)°. The five-membered ring adopts a twisted conformation in **1** but an *N*-envelope in **2** and **3**. The salts form networks of weak C–H···Cl⁻ hydrogen bonds. Hot stage microscopy, differential scanning calorimetry and temperature-controlled X-ray powder diffractometry revealed that each of the three compounds exists in at least two different crystal forms.

Introduction

Quaternary pyrrolidinium chlorides are valuable precursors for the preparation of ionic liquids (ILs) by ion metathesis. The excellent conductivity, broad electrochemical window, thermal stability, and low volatility of ILs have made them promising media for electrochemical processes.[1] In this work, we prepared three 1-methylpyrrolidinium chlorides with short alkyl (C_3) side chains. So far, only a few crystallographic studies have been performed on C_3-substituted 1-methylpyrrolidinium salts.

Thus, 1-methyl-1-propylpyrrolidinium iodide has been reported to adopt the orthorhombic space group $P2_12_12_1$ with part of the ring disordered.[2] In contrast, 1-methyl-1-propylpyrrolidinium hexafluorophosphate crystallized in the monoclinic space group *C*2/*c* with the entire cation exhibiting positional disorder.[3] In addition, 1-methyl-1-propylpyrrolidinium tetrafluoroborate was found to transform into a plastic crystal phase prior to melting,[4] turning into a solid state ion conductor.[5] Polymorphism was also observed in 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide due to rotational disorder at elevated temperature.[6] Recently, crystal structures of 1-methyl-1-propylpyrrolidinium salts with complex anions containing alkaline earth metals or lanthanoids have been described.[7]

Theoretical calculations predict two preferred conformations of pyrrolidinium ions, a twisted ring and an envelope.[8] Herein, three new X-ray structures of quaternary pyrrolidinium chlorides without crystallographic disorder are presented, and their conformations, hydrogen bonding networks, and polymorphism are discussed.

Experimental

Synthesis

1-Methyl-1-propylpyrrolidinium chloride (**1**). 1-Methylpyrrolidine (44.5 g, 0.522 mol) and 1-chloropropane (45.1 g, 0.574 mol, 1.1 eq.) were dissolved in dry CH_3CN (170 mL). The mixture was heated to reflux for 48 h. The solution was cooled to room temperature, and the product crystallized in large colorless needles. The mother liquor was decanted and cooled to −20 °C after addition of Et_2O, giving an additional crop of product. The compound was recrystallized from acetone/CH_2Cl_2 and dried *in vacuo* to give 71.2 g (83%), mp ~245 °C (dec). ^{1}H NMR (D_2O): δ 0.98 (t, *J* 7.4 Hz, 3 H), 1.82 (m, 2 H), 2.21 (m, 4 H), 3.04 (s, 3 H), 3.30 (m, 2 H), 3.51 (m, 4 H) ppm. ^{13}C NMR (D_2O + DMSO-d_6): δ 11.6, 18.3, 22.7 (2C), 49.4, 65.6 (2C), 67.1 ppm. IR (neat): 3453, 3391, 3242, 2963, 2878, 1618, 1478, 1462, 1433, 1413, 1379, 1307, 1235, 1043, 1008, 976, 946, 908, 831, 759, 588, 520 cm^{-1}.

1-Allyl-1-methylpyrrolidinium chloride (**2**). 1-Methylpyrrolidine (30.0 g, 0.358 mol) and allyl chloride (29.6 g, 0.387 mol, 1.1 eq.) were dissolved in dry CH_3CN (100 mL), and the reaction mixture was refluxed for 24 h and then cooled to 0 °C, causing the crude product to precipitate. After addition of Et_2O, additional product was obtained. The crystalline mass was

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filtered and recrystallized from a mixture of acetone/CH_2Cl_2 to yield 48.3 g (85%), mp 168 °C. ^1H NMR ($CDCl_3$): δ 2.40 (s, 4 H), 3.41 (s, 3 H), 3.90 (m, 2 H), 3.98 (m, 2 H), 4.51 (d, *J* 7.3 Hz, 2 H), 5.85 (m, 2 H), 6.15 (m, 1 H) ppm. ^{13}C NMR ($CDCl_3$): δ 20.9 (2C), 47.8, 62.7 (2C), 64.6, 124.7, 128.3 ppm. IR (neat): 3003, 2964, 2897, 1478, 1466, 1432, 1377, 1308, 1063, 1021, 982, 958, 922, 900, 885, 749 cm^{-1}.

1-Methyl-1-propargylpyrrolidinium chloride (**3**). 1-Methylpyrrolidine (1.91 g; 22.5 mmol) and propargyl chloride (1.84 g, 24.7 mmol, 1.1 eq.) were dissolved in dry CH_3CN (10 mL) and stirred at room temperature for 12 h, then the reaction mixture was refluxed for 3 h. The solvent was removed under reduced pressure. The remaining brownish, viscous liquid crystallized slowly at room temperature to afford 3.59 g (100%), mp ~90–96 °C. ^1H NMR (DMSO-d_6): δ 2.10 (m, 4 H), 3.18 (s, 3 H), 3.60 (m, 4 H), 4.12 (t, *J* 2.4 Hz, 1 H), 4.66 (d, *J* 2.4 Hz, 2 H) ppm. ^{13}C NMR (DMSO-d_6): δ 21.4 (2C), 48.5, 52.1, 62.8 (2C), 73.4, 81.9 ppm. IR (neat): 3133, 2996, 2938, 2868, 2118, 1473, 1467, 1379, 1354, 1304, 1088, 1008, 990, 903, 888, 780, 740 cm^{-1}.

Spectroscopy

NMR spectra were recorded with a Bruker AC 300 spectrometer and referenced to internal TMS. IR spectra were obtained with a Nicolet 5700 FT instrument with a diamond ATR device calibrated with a polystyrol foil.

Crystal structure determination

X-Ray intensity data were collected on a Stoe IPDS-2 imaging plate diffractometer equipped with a graphite monochromator (Mo Kα radiation, λ = 0.71073 Å) by the rotation method. Data reduction was performed with the Stoe X-AREA package.[9] The structures were solved by direct methods using the SIR2002 program suite.[10] Full-matrix least-squares refinement was carried out using SHELXL97 software. All H atoms were geometrically fixed and allowed to ride on the corresponding carrier atoms with C–H = 0.98–0.99 Å, and $U_{iso}(H) = 1.5\ U_{eq}(C)$ of the attached C atom for methyl H atoms and 1.2 $U_{eq}(C)$ for other H atoms. Maximum parameter shift to s.u. ratio for all atoms in the final refinement cycle was <0.001.

CCDC 617232, 617233, and 644230 contain the supplementary crystallographic data for this paper.† These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

X-Ray powder diffractometry (XRPD)

The powder X-ray diffraction patterns were obtained with a Siemens D-5000 diffractometer using a Cu Kα radiation (λ=1.540598 Å) source. The patterns were recorded at 40 kV and 35 mA. The chamber was purged with dry nitrogen (about 300 mL min^{-1}), and subambient temperatures were achieved with liquid nitrogen as coolant.

Differential scanning calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC 7 system. The temperature calibration was performed with benzophenone and caffeine, and energy calibration with indium. For low-temperature DSC experiments a Perkin Elmer Diamond DSC equipped with a CCA-7 controlled cooling device was used. The instrument was calibrated with *n*-decane, water and In. Samples of approximately 2 to 5 mg were weighed (Mettler UM3 ultramicrobalance) into Al pans (25 µl) and kept in a dry nitrogen purge before the heating program was started. In order to minimize the exposure time of the highly hygroscopic samples to the atmosphere, experiments were also performed without weighing.

Hot stage microscopy (HSM)

Experiments were performed with a Reichert Thermovar polarization microscope equipped with a Kofler hot stage and a Linkam LTS350 stage equipped with a TP92 controller and a LNP1 liquid nitrogen pump for low temperature control. Photomicrographs were recorded with an Olympus ColorView IIIu camera attached to an Olympus BX-50 microscope.

Results

Three new quaternary chlorides derived from 1-methylpyrrolidine with C_3 side chains (propyl **1**, allyl **2**, and propargyl **3**) have been prepared and crystallized. Crystal data and refinement details are summarized in Table 1. The pyrrolidinium ring in **1** is twisted, whereas in **2** and **3** it adopts an envelope conformation: in both cases N(1) deviates by 0.63 Å from the plane through C(2), C(3), C(4) and C(5). The methyl group occupies a pseudo-axial position in **1**, but pseudo-equatorial in **2** and **3**. The torsion angles N(1)–C(6)–C(7)–C(8) in the propyl and allyl groups are 177.2 and 124.0°, respectively. The C=C–C angle in **2** is 121.5°, and the C≡C–C angle in **3** is 177.9°. Each cation forms a network of weak C–H···Cl^- hydrogen bonds[11] to surrounding chloride ions. Seven contacts to four anions with H···Cl^- distances shorter than the sum of the van der Waals radii (2.95 Å)[12] are observed in the propyl derivative (Fig. 1), whereas in the allyl compound there are nine such contacts (Fig. 2). The propargyl compound forms seven hydrogen bonds to five anions. In this case, the additional chloride accepts a short hydrogen bond from the acetylenic C–H group (Fig. 3). Details of these interactions are collected in Table 2.

It was observed with hot stage microscopy (HSM), differential scanning calorimetry (DSC) and temperature-controlled X-ray powder diffractometry (XRPD) that the three compounds can exist in at least one additional crystal form. Due to their very high hygroscopicity (all compounds deliquesce within a few minutes in the laboratory atmosphere) the handling of the substances is rather challenging, and the reproducibility of the thermal experiments is poor. Although the samples were stored in argon-filled tubes placed in an evacuated desiccator over silica and despite efforts to keep sample preparation times very short, the presence of a few percent of water could not be avoided. For most experiments larger single crystals were used to minimize the uptake of moisture during preparation. These experiments were performed after the single crystal structures had been

Table 1 Crystal data and refinement details of compounds **1**–**3**

Compound	**1**	**2**	**3**
Empirical formula	$C_8H_{18}N.Cl$	$C_8H_{16}N.Cl$	$C_8H_{14}N.Cl$
Formula weight	163.68	161.67	159.65
Crystal form, color	Plate, colorless	Prism, colorless	Fragment, colorless
Crystal size/mm	0.40 × 0.37 × 0.36	0.20 × 0.13 × 0.10	0.40 × 0.32 × 0.30
Melting point/°C	245	168	90–96
Temperature/K	173(2)	173(2)	173 (2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pnab*	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a/Å	10.0354(11)	6.4857(10)	8.4849 (14)
b/Å	13.254(2)	12.005(3)	8.1271 (16)
c/Å	14.6231(16)	12.526(2)	13.501 (2)
β/°		102.746(13)	100.408 (13)
Volume/Å^3	1945.0(4)	951.3(3)	915.7 (3)
Z	8	4	4
D_x/g cm^{-3}	1.118	1.129	1.158
F_{000}	720	352	344
μ/mm^{-1}	0.329	0.336	0.35
θ range for data collection	2.07–26.91	2.38–26.55	2.64–24.61
Reflections measured	13824	7080	5415
Independent reflections	2088 (R_{int} = 0.047)	1900 (R_{int} = 0.062)	1457 (R_{int}=0.022)
Observed reflections [$I > 2\sigma(I)$]	1666	1402	1333
Range of *h*, *k*, *l*	$-11 < h < 12$	$-8 < h < 7$	$-9 < h < 9$
	$-16 < k < 16$	$-15 < k < 15$	$-9 < h < 9$
	$-18 < l < 17$	$-15 < l < 15$	$-15 < l < 15$
Data, restraints, parameters	2088, 0, 93	1900, 0, 93	1457, 0, 92
Goodness of fit on F^2	1.047	1.035	1.067
Final *R* indices [$I > 2\sigma(I)$]	R_1=0.0406, wR_2 = 0.0813	R_1=0.0406, wR_2 = 0.0878	R_1=0.0254, wR_2 = 0.0699
R indices (all data)	R_1=0.0587, wR_2 = 0.0876	R_1=0.0662, wR_2 = 0.0970	R_1=0.0308, wR_2 = 0.0713
$\Delta\rho_{max}$, $\Delta\rho_{min}$/e Å^{-3}	0.18, −0.19	0.20, −0.21	0.17, −0.15

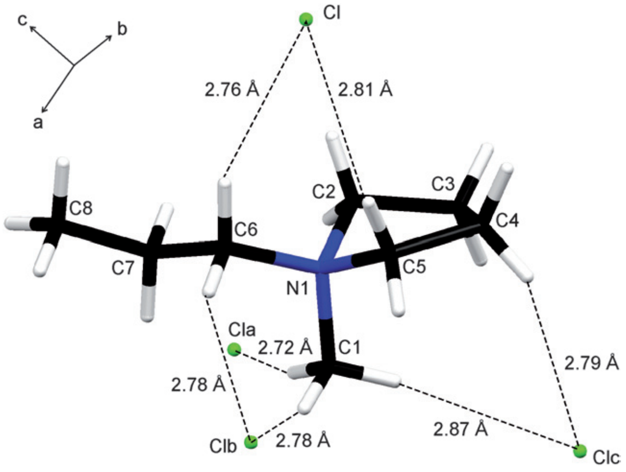

Fig. 1 Weak C–H···Cl$^-$ hydrogen bonds and atom-labelling scheme in **1**.

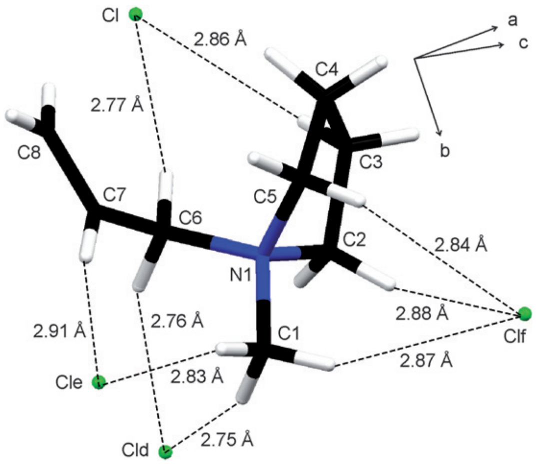

Fig. 2 Weak C–H···Cl$^-$ hydrogen bonds and atom-labelling scheme in **2**.

determined. Therefore, the low temperature phases are named "form A" and the subsequently identified forms "form B", respectively.

HSM shows that 1-methyl-1-propylpyrrolidinium chloride (**1**) liquifies partially at about 60 °C and on further heating the residual prismatic crystals disappear slowly in the liquid but at the boundary a crystalline (birefringent) layer is formed which grows when the temperature is kept constant (Fig. S1, ESI).† This indicates that the highly hydrophilic substance recrystallizes due to the loss of water from the solution which is formed with small amounts of water introduced during preparation. On cooling, the sample recrystallizes slowly (form B) and below 15 °C a phase transition (to form A) can be observed which is reversible. The retransformation on heating (to form B) occurs at 25 °C.

This result was confirmed by DSC showing mostly an endothermic double peak between 50 and 65 °C (liquefaction) on heating. The transformation to form A on cooling (between 5 and 15 °C) is exothermic and the endothermic retransformation to B occurs at 25 °C with about the same enthalpy. The reversibility of this process indicates an enantiotropic relationship between the low temperature form A and the "high"

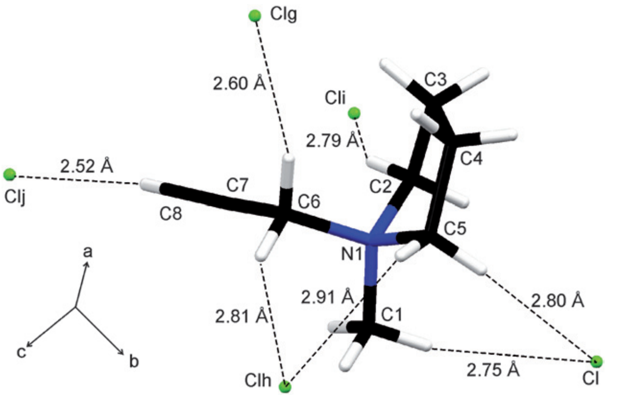

Fig. 3 Weak C–H···Cl⁻ hydrogen bonds and atom-labelling scheme in **3**.

Table 2 Weak C–H···Cl⁻ hydrogen bonds in **1–3**

	D–H···*A*	H···*A* (Å)	*D*···*A* (Å)	*D*–H···*A* (°)
1	C(5)–H···Cl	2.81	3.626	140
	C(6)–H···Cl	2.76	3.679	154
	C(1)–H···Cl^a	2.72	3.665	162
	C(1)–H···Cl^b	2.78	3.663	150
	C(6)–H···Cl^b	2.78	3.677	151
	C(1)–H···Cl^c	2.87	3.818	163
	C(4)–H···Cl^c	2.79	3.649	146
2	C(3)–H···Cl	2.86	3.703	144
	C(6)–H···Cl	2.77	3.738	168
	C(1)–H···Cl^d	2.75	3.650	152
	C(6)–H···Cl^d	2.76	3.659	152
	C(1)–H···Cl^e	2.83	3.796	170
	C(7)–H···Cl^e	2.91	3.846	167
	C(1)–H···Cl^f	2.87	3.753	150
	C(5)–H···Cl^f	2.84	3.697	145
	C(2)–H···Cl^f	2.88	3.710	143
3	C(5)–H···Cl	2.80	3.722	155
	C(1)–H···Cl	2.75	3.663	156
	C(6)–H···Cl^g	2.60	3.566	165
	C(6)–H···Cl^h	2.81	3.697	150
	C(5)–H···Cl^h	2.91	3.728	140
	C(2)–H···Cl^i	2.79	3.648	146
	C(8)–H···Cl^j	2.52	3.418	159

[a] Symmetry code: $x, -1/2 + y, 1/2 - z$. [b] $1/2 + x, 1/2 - y, 1/2 - z$. [c] $1 - x, 1/2 - y, -1/2 + z$. [d] $1 - x, 1/2 + y, 3/2 - z$. [e] $x, 1/2 - y, -1/2 + z$. [f] $2 - x, 1/2 + y, 3/2 - z$. [g] $x, -1 + y, z$. [h] $1/2 - x, -1/2 + y, 1/2 - z$. [i] $3/2 - x, -1/2 + y, 1/2 - z$. [j] $1/2 + x, 1/2 - y, 1/2 + z$.

temperature form B. The structural difference was confirmed in temperature-controlled XRPD experiments. Representative diffractograms are shown in Fig. 4a. Barring the peak intensities, the experimental pattern of the low temperature form (form A) matches rather well the calculated pattern, albeit there are also additional peaks indicating the presence of a smaller fraction of an additional phase which was not examined in more detail. From the diffractograms it is obvious that forms A and B exhibit different crystal structures. The pattern of the original sample recorded at about 22 °C showed also the reflections of form B, but the sample consists mainly of form A. The presence of both phases is not surprising in view of the observed transition behaviour. Form B melts at a rather high temperature (~245 °C) under decomposition.

1-Allyl-1-methylpyrrolidinium chloride (**2**) also shows a high temperature phase (form B), the formation of which can be observed with HSM (Fig. S2, ESI).† The deliquescence process on heating starts earlier than in compound **1** and proceeds slowly until form B crystallizes rapidly (92–93 °C) in the partially or largely liquefied substance. On heating beyond 100 °C form B slowly liquefies but in the boundary areas, where water can escape, crystals remain until the melting point at 168 °C is reached. If the preparation is heated to about 120 °C and subsequently cooled, form B recrystallizes again and around 5 °C a spontaneous retransformation to form A can be observed.

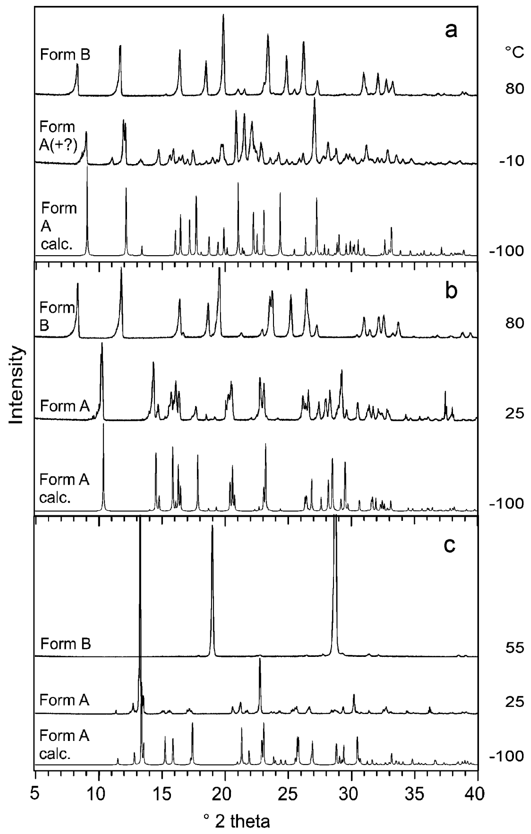

Fig. 4 Experimental and calculated X-ray powder diffraction patterns of the two forms of **1**, **2** and **3**, respectively. The numbers on the right hand indicate the recording temperatures.

In DSC experiments, a rather sharp endothermic peak between 70 and 90 °C indicates the transformation of form A to B and one or more exothermic events may occur in the retransformation process to form A on cooling below 10 °C. If the water content of the sample is low, the melting peak of form B (168 °C) is rather sharp but at higher amounts of water the event becomes broad and is shifted to lower temperatures by a few degrees. The melting process consumes about twice the energy as the transformation process from form A to form B. The transformation was confirmed by temperature-controlled X-ray powder diffraction. The experimental patterns of the two forms are shown in Fig. 4b along with the calculated pattern of form A. The pattern of form B was measured at 80 °C and the retransformation to form A can be clearly confirmed after cooling to temperatures below ambient. It should be mentioned that both HSM and DSC showed sometimes additional phase transformations which could not be clearly assigned and suggest the existence of one or even two additional polymorphs of compound **2**.

1-Methyl-1-propargylpyrrolidinium chloride (**3**) shows the highest hygroscopicity. Therefore, all preparations contained significant amounts of water that hampered the thermoanalytical investigations. However, HSM, DSC and temperature-controlled XRPD confirm consistently a phase transition at about 45–50 °C to a high temperature form B which liquefies and melts between 90 and 96 °C. Further heating results in discoloration and decomposition of the liquid at about 220 °C. The XRPD pattern of form B (Fig. 4c) shows mainly two lines due to a very strong preferred orientation of the crystals in the preparation. Cooling form B to room temperature gave no indication of a retransformation to form A in the XRPD chamber under dry N_2 purge.

In summary, the three quaternary pyrrolidinium chlorides exhibit polymorphism and their crystal structures feature weak $CH\cdots Cl^-$ contacts.

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