LETTER

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Novel one-pot synthesis of quaternary ammonium halides: new route to ionic liquids†

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Treatment of an amide with an alkyl or substituted alkyl halide in the presence of a weak base in a one-pot reaction leads to crystalline quaternary ammonium halides with reasonable chemical yields; some of the compounds show low melting points and a liquid range of over 50–100 °C before decomposition.

Most of the studies of tetraalkylammonium halides (especially bromides) focus on their properties as gemini surfactants,[1] classical surfactants[2] or phase-transfer catalysts.[3] Recently, certain ammonium compounds have found use in advanced battery technology[4] due to their ionic liquid[5] behaviour and as size-probing guests in molecular encapsulation studies.[6] The structures and synthetic methods for quaternary ammonium salts have been known and studied for a long time.[7] On many occasions the disadvantage of the earlier methods is the separation of the product from the potential side-products and solvent at the end of the reaction. Additionally, the final purification of the product has been found to be difficult and costly, resulting in low yields. Herein we describe a simple and cost-effective synthesis of $R_2R'R''N^+X^-$, $R_2R'_2N^+X^-$ and $R_4N^+X^-$ types of ammonium halides. One of the advantages of the presented synthetic method is that only the desired quaternary ammonium compound is produced as with quaternizing reactions of amines mixtures of quaternary ammonium salts are frequently obtained, consisting of the desired salt together with less substituted ammonium salts. Furthermore, less symmetric quaternary ammonium cations (up to three different R groups) can be achieved using the presented route. Such structural modifications provide one way of altering the physical properties, such as the melting point, to improve the potential applicability of the compounds, for example, as ionic liquids.

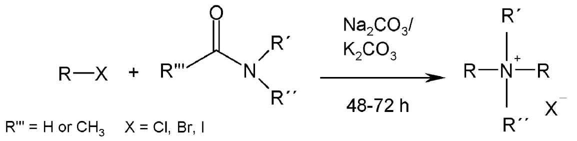
The synthesis is executed in a simple one-pot reaction (Scheme 1) with all reactants (an amide, alkyl or substituted alkyl halide and alkaline carbonate) being easily available; the reaction product, a quaternary ammonium halide, is conveniently separated by crystallization from the reaction filtrate using suitable solvent with yields: 24% (**1**), 31% (**2**), 24% (**3**), 32% (**4**), 52% (**5**), 43% (**6**), 46% (**7**), 23% (**8**), 31% (**9**) and 62% (**10**). Yields for compounds **2** and **5**, when prepared from dimethylacetamide, were 8% and 9%, respectively.

The molecular structures of **1**–**10** were verified by electrospray ionization time-of-flight mass spectrometry (ESI TOF MS) along with ^1H and ^{13}C NMR studies. In most cases the formation of the quaternary ammonium salt was easily detected by both ^1H and ^{13}C NMR since the electric quadrupolar moment of the quaternized nitrogen-14 is so small that the spin-spin couplings, $^3J(^1H,^{14}N)$ and $^1J(^{13}C,^{14}N)$, are well-resolved.[8]

As the synthesis route works well with formamides, the potential generality of the route was examined by preparing the $R_4N^+X^-$ type ammonium halide (tetraethylammonium bromide) and by synthesizing the compounds **2** and **5** using a tertiary amide (*N*,*N*-dimethylacetamide) instead of formamide. Surprisingly, the tertiary amide was reactive towards the alkyl halide, although the yields of the syntheses were below 10% under the reaction conditions used.

The reaction conditions were tested further by changing the reaction temperature, inorganic base and the molar ratio of the base. The best yields were obtained at 80–85 °C (best reaction time 48–72 h) with the alkyl and substituted alkyl halides having higher boiling points and for the smaller halides by using reflux temperatures. Furthermore, the threshold temperature for the start of the reaction was in most cases around 40 °C. The yields were clearly better if sodium or potassium carbonates (with molar ratio of 1 : 2–1 : 1 to halide) were used instead of cesium, lithium and calcium carbonates, which were also tested. The most prominent effect was observed in the synthesis of quaternary ammonium chlorides as the yields increased substantially when sodium carbonate was used instead of the other carbonates.

The colourless single crystals of compound **1** were obtained from a MeOH–EtOAc solution and the structure was determined by the X-ray single-crystal method. In case of the **5** the structure was successfully solved from the microcrystalline powder by X-ray powder diffraction. Compound **1** crystallizes in the orthorhombic space group $Cmc2_1$ and **5** in the monoclinic space group $P2_1/c$. Both X-ray structures show ion-pair type of packing without any solvent molecules. The shortest bromide-cation distances are $N^+\cdots Br^- = 4.15$, $Br1\cdots C4 = 3.82(1)$, $Br1\cdots C5 = 3.89(1)$, $Br1\cdots C3^* = 3.87(1)$, $Br1\cdots C4^* = 3.90(1)$, $Br1\cdots C6^{**} = 3.86(1)$, $Br1\cdots C2^{3*} = 3.76(2)$ Å for **1** (Fig. 1)[9a] and $N^+\cdots Br^- = 4.11$, $Br1\cdots C3 = 3.70(2)$, $Br1\cdots C4^* =$



1: R = ethyl, R' = R'' = methyl, X = Br
2: R = propyl, R' = R'' = methyl, X = Br
3: R = butyl, R' = R'' = methyl, X = Br
4: R = pentyl, R' = R'' = methyl, X = Br
5: R = benzyl, R' = R'' = methyl, X = Br
6: R = benzyl, R' = R'' = ethyl, X = Br
7: R = R' = R'' = ethyl, X = Br
8: R = pentyl, R' = R'' = methyl, X = I
9: R = benzyl, R' = R'' = methyl, X = Cl
10: R = 4-methylbenzyl, R' = R'' = methyl, X = Cl

Scheme 1

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† Electronic supplementary information (ESI) available: final Rietveld refinement plot for **5**. See http://www.rsc.org/suppdata/nj/b4/b409062b/

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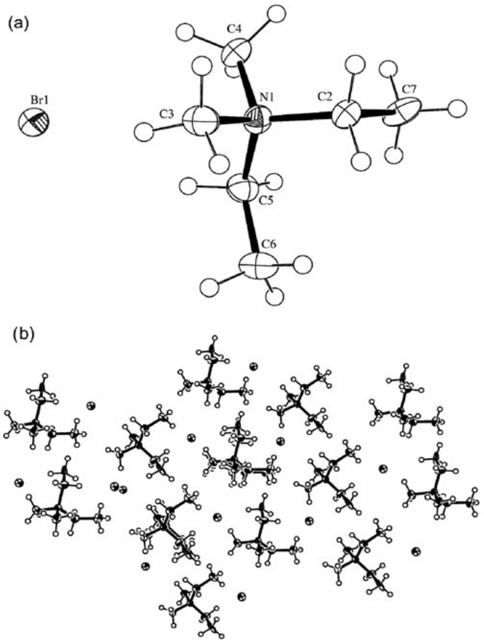

Fig. 1 (a) Ion-pair ordering and (b) packing mode of compound **1**. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Only one position of the disordered cation is shown.

3.70(3), Br1···C2* = 3.85(2), Br1···C9** = 3.90(3), Br1···C7^{3}* = 3.90(3), Br1···C1 = 3.94(2) Å for **5** (Fig. 2).[9b]

The ion-pairs of compound **1** are interconnected by the weak Br1^{-}···H hydrogen bonds, hydrogen bond angles being 152.2–160.0° and the bromide being tetra-coordinated by four H atoms (from two C3* and two C2^{3}* atoms)[9a] with distances of 2.82–2.99 Å. Similar tetra-coordination of bromide by H atoms (C2* and C4* from same cation, C3 and C9** from separate cations)[9b] is observed for **5**; bond angles being 150.0–158.1° and with distances of 2.77–3.01 Å. In addition, one of the phenyl ring shows π-π interactions with the adjacent phenyl ring, further stabilizing the packing [Fig. 2(b)].

The thermal studies were carried out by TG/DTA. Low melting points (below 100 °C) and/or broad liquid ranges were obtained for compounds **3**, **4** and **8** (Table 1). In the cases of compounds **1**, **2**, **5**, **6**, **9** and **10** melting points were not observed prior to the start of decomposition. More detailed thermodynamical studies will be reported elsewhere.[10]

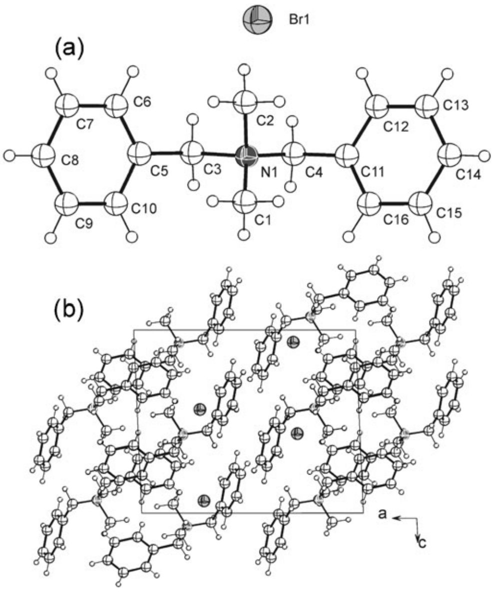

Fig. 2 (a) Ion-pair ordering and (b) packing mode of compound **5**.

Table 1 Melting points (peak onset) and decomposition temperatures (extrapolated onset) for compounds **1**–**10**

Compound	T_m/°C	Decomposition range/°C
1	50.1[a]	185–325
2	83.1[a]	230–310
3	69.9[a], 91.6[a], 158.3	225–315
4	74.1	220–305
5	—	195–250
6	—	175–225
7[11]	282–287	
8	84.2	230–325
9	—	180–250
10	—	205–250

[a] Solid–solid phase transition

The simple synthesis route presented here, from alkyl or substituted alkyl halides and *N*,*N*-formamides or secondary amides leading to high purity products in reasonable chemical yields, opens up a convenient access to a multitude of quaternary ammonium halides. Further studies are in progress, as various types of new quaternary ammonium iodides and chlorides are produced, which then are to be used as precursors for anion exchange tests (*e.g.*, triflate, tosylate, BF_4, PF_6, $CuBr_4$). By changing the anion, the properties of the compounds can be modified further to be more suitable for applications such as ionic liquids, molecular encapsulation guests, and phase-transfer catalysts. These studies are currently in progress and will be reported elsewhere.[12]

Experimental

Methods and materials

All reagents and other chemicals were purchased from commercial suppliers and used as received. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ or DMSO at 30 °C by using a Bruker Avance DRX 500 NMR spectrometer operating at 500 MHz for ^{1}H and 126 MHz for ^{13}C. Electrospray mass spectrometric measurements were obtained by using a Micromass LCT time-of-flight (TOF) mass spectrometer with electrospray ionization (ESI). All the compounds were measured by using positive mode with sample concentrations of 25 mg l^{-1} in methanol solution. The elemental analyses were carried out with a Vario EL III CHN elemental analyzer by using dried samples weighing 3–5 mg.

Syntheses

General procedure. All reactants were placed in the reaction flask. The reaction mixture was stirred at the chosen temperature for 48–72 h. After cooling down to RT the mixture was filtered to remove excess carbonate and alkaline metal halide, followed with the evaporation of filtrate to minimum volume. The final extraction of product was performed with one of the following methods.

Method A. A small amount of acetone, diethyl ether or toluene was added to the filtrate to give a white or light brown powder. The powder was washed with diethyl ether and dried *in vacuo* overnight.

Method B. Evaporation of filtrate gave the product as a pure gel. The gel was dried *in vacuo*.

Method C. Evaporation of filtrate gave the raw product (product, alkaline halide and carbonate residues) as a white or yellowish powder. The final product was extracted with dichloromethane, evaporated and dried *in vacuo* overnight.

Diethyldimethylammonium bromide (1). *Method A*. Reagents: ethyl bromide (6.51 ml, 87.86 mmol), potassium carbonate (18.21 g, 131.80 mmol) and dimethylformamide (50 ml). Reaction temperature 35 °C and reaction time 66 h. Yield (white powder): 1.92 g (24%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 1.29 (6H, t, J = 7.29 Hz, N–CH$_2$CH_3), 3.20 (6H, s, N–CH_3), 3.56 (4H, quartet, J = 7.30 Hz, N–CH_2CH$_3$). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 8.26 (2C, N–CH$_2$$CH_3$), 49.81 (2C, N–$CH_3$), 58.78 (2C, N–$CH_2CH_3$). ESI-TOF-MS: m/z calcd for $C_6H_{16}NBr$ [M – Br]$^+$: 102.13; found: 102.08. Anal. calcd for $C_6H_{16}NBr$: C, 39.57; H, 8.86; N, 7.69; found: C, 41.00; H, 8.81; N, 6.27 (very hygroscopic and sticky even after drying; results match when water and crystallization solvent, toluene, are added).

Dimethyldipropylammonium bromide (2). *Method A*. Reagents: propyl bromide (8.64 ml, 95.17 mmol), potassium carbonate (9.86 g, 71.38 mmol) and dimethylformamide (30 ml). Reaction temperature 65 °C and reaction time 72 h. Yield (white powder): 3.11 g (31%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 1.03 (6H, t, J = 7.32 Hz, N–CH$_2$CH$_2$CH_3), 1.78 (4H, m, N–CH$_2$CH_2CH$_3$), 3.39 (6H, s, N–CH_3), 3.51 (4H, m, N–CH_2CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 10.64 (2C, N–CH$_2$CH$_2$$CH_3$), 16.29 (2C, N–CH$_2$$CH_2CH_3$), 51.22 (2C, N–$CH_3$), 65.48 (2C, N–$CH_2CH_2CH_3$). ESI-TOF-MS: m/z calcd for $C_8H_{20}NBr$ [M – Br]$^+$: 130.16; found: 130.12. Anal. calcd for $C_8H_{20}NBr$: C, 45.72; H, 9.59; N, 6.66; found: C, 45.06; H, 9.72; N, 6.69.

Dibutyldimethylammonium bromide (3). *Method A*. Reagents: butyl bromide (9.02 ml, 83.96 mmol), potassium carbonate (8.70 g, 62.97 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 72 h. Yield (white powder): 2.42 g (24%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 0.95 (6H, t, J = 7.36 Hz, N–CH$_2$CH$_2$CH$_2$CH_3), 1.41 (4H, sextet, J = 7.42 Hz, N–CH$_2$CH$_2$CH_2CH$_3$), 1.67 (4H, m, N–CH$_2$CH_2CH$_2$CH$_3$), 3.35 (6H, s, N–CH_3), 3.53 (4H, m, N–CH_2CH$_2$CH$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 13.59 (2C, N–CH$_2$CH$_2$CH$_2$$CH_3$), 19.51 (2C, N–CH$_2CH_2$$CH_2CH_3$), 24.57 (2C, N–CH$_2$$CH_2CH_2CH_3$), 51.10 (2C, N–$CH_3$), 63.74 (2C, N–$CH_2CH_2CH_2CH_3$). ESI-TOF-MS: m/z calcd for $C_{10}H_{24}NBr$ [M – Br]$^+$: 158.19; found: 158.15. Anal. calcd for $C_{10}H_{24}NBr$: C, 50.42; H, 10.16; N, 5.88; found: C, 50.72; H, 10.43; N, 5.95.

Dimethyldipentylammonium bromide (4). *Method B*. Reagents: pentyl bromide (9.32 ml, 75.12 mmol), potassium carbonate (10.38 g, 75.12 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 69 h. Yield (brown gel): 3.19 g (32%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 0.88 (6H, t, J = 6.88 Hz, N–CH$_2$CH$_2$(CH$_2$)$_2$CH_3), 1.35 (8H, m, N–CH$_2$CH$_2$(CH_2)$_2$CH$_3$), 1.68 (4H, m, N–CH$_2$CH_2(CH$_2$)$_2$CH$_3$), 3.37 (6H, s, N–CH_3), 3.51 (4H, m, N–CH_2CH$_2$(CH$_2$)$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 13.92 (2C, N–CH$_2$CH$_2$(CH$_2$)$_2$$CH_3$)), 22.40 and 22.61 (4C, N–CH$_2$CH$_2$(CH$_2$)$_2$CH$_3$), 28.40 (2C, N–CH$_2$$CH_2$(CH$_2$)$_2CH_3$), 51.36 (2C, N–$CH_3$), 64.09 (2C, N–$CH_2CH_2$(CH$_2$)$_2CH_3$). ESI-TOF-MS: m/z calcd for $C_{12}H_{28}NBr$ [M – Br]$^+$: 186.22; found: 186.19. Anal. calcd for $C_{12}H_{28}NBr$: C, 54.13; H, 10.60; N, 5.26; found: C, 53.85; H, 10.56; N, 5.21.

Dibenzyldimethylammonium bromide (5). *Method A*. Reagents: benzyl bromide (6.21 ml, 52.25 mmol), potassium carbonate (7.22 g, 52.25 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 48 h. Yield (white powder): 4.12 g (52%). ^{1}H NMR (DMSO, 500 MHz, ppm): 2.89 (6H, s, N–CH_3), 4.70 (4H, s, Ph–CH_2), 7.50–7.57 (6H, m, Ar–H), 7.61–7.63 (4H, m, Ar–H). ^{13}C NMR (DMSO, 126 MHz, ppm): 48.01 (2C, N–CH$_3$), 66.86 (2C, Ph–CH$_2$), 127.97 (2C, Ar–C(1)), 128.84 (4C, Ar–C), 130.21 (2C, Ar–C(4)), 133.08 (4C, Ar–C). ESI-TOF-MS: m/z calcd for $C_{16}H_{20}NBr$ [M – Br]$^+$: 226.2; found: 226.2. Anal. calcd for $C_{16}H_{20}NBr$: C, 62.75; H, 6.58; N, 4.57; found: C, 61.65; H, 6.55; N, 4.39 (yygroscopic, results match when 0.25 water is added).

Dibenzyldiethylammonium bromide (6). *Method A*. Reagents: benzyl bromide (5.68 ml, 47.86 mmol), potassium carbonate (9.92 g, 71.79 mmol) and diethylformamide (60 ml). Reaction temperature 50 °C and reaction time 64 h. Yield (white powder): 3.52 g (44%). ^{1}H NMR (DMSO, 500 MHz, ppm): 1.35 (6H, t, J = 7.16 Hz, N–CH$_2$CH_3), 3.24 (4H, quartet, J = 7.16 Hz, N–CH_2CH$_3$), 4.59 (4H, s, Ph–CH_2), 7.49–7.56 (6H, m, Ar–H), 7.61-7.62 (4H, m, Ar–H). ^{13}C NMR (DMSO, 126 MHz, ppm): 8.39 (2C, N–CH$_2$$CH_3$), 52.54 (2C, N–$CH_2CH_3$), 61.73 (2C, Ph–$CH_2$), 127.95 (2C, Ar–$C$(1)), 128.94 (4C, Ar–$C$), 130.16 (2C, Ar–$C$(4)), 132.85 (4C, Ar–$C$). ESI-TOF-MS: m/z calcd for $C_{18}H_{24}NBr$ [M – Br]$^+$: 254.2; found: 254.2. Anal. calcd for $C_{18}H_{24}NBr$: C, 64.67; H, 7.24; N, 4.19; found: C, 64.34; H, 7.28; N, 4.09.

Tetraethylammonium bromide (7). Commercially available material. *Method A*. Reagents: ethyl bromide (3.55 ml, 47.58 mmol), potassium carbonate (6.58g, 71.37 mmol) and diethylformamide (30 ml). Yield (white powder): 1.3 g (26%). The formation of compound **7** was confirmed by ^{1}H and ^{13}C NMR and by ESI TOF MS.

Dimethyldipentylammonium iodide (8). *Method C*. Reagents: pentyl iodide (8.34 ml, 63.84 mmol), potassium carbonate (8.82 g, 63.84 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 48 h. Yield (white powder): 2.00 g (20%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 0.90 (6H, t, J = 6.96 Hz, N–CH$_2$CH$_2$(CH$_2$)$_2$CH_3), 1.38 (8H, m, N–CH$_2$CH$_2$(CH_2)$_2$CH$_3$), 1.72 (4H, m, N–CH$_2$CH_2(CH$_2$)$_2$CH$_3$), 3.36 (6H, s, N–CH_3), 3.53 (4H, m, N–CH_2CH$_2$(CH$_2$)$_2$CH$_3$). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 13.74 (2C, N–CH$_2$CH$_2$(CH$_2$)$_2$$CH_3$), 22.19, 22.45 and 28.11 (6C, N–CH$_2$(CH$_2$)$_3$CH$_3$), 51.46 (2C, N–CH$_3$), 64.26 (2C, N–CH$_2$CH$_2$(CH$_2$)$_2$CH$_3$). ESI-TOF-MS: m/z calcd for $C_{12}H_{28}NI$ [M – I]$^+$: 186.22; found: 186.21. Anal. calcd for $C_{12}H_{28}NI$: C, 46.01; H, 9.01; N, 4.47; found: C, 46.01; H, 9.18; N, 4.34.

Dibenzyldimethylammonium chloride (9). *Method A*. Reagents: benzyl chloride (8.79 ml, 76.40 mmol), sodium carbonate (8.10 g, 76.40 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 72 h. Yield (white powder): 3.12 g (31%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 3.12 (6H, s, N–CH_3), 5.16 (4H, s, Ph–CH_2), 7.33 (4H, t, Ar–H(3,5)), 7.39 (2H, t, Ar–H(4)), 7.66 (4H, d, Ar–H(2,6)). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 48.00 (2C, N–CH$_3$), 67.52 (2C, Ph–CH$_2$), 127.63 (2C, Ar–C(1)), 128.98 (4C, Ar–C(3,5)), 130.44 (2C, Ar–C(4)), 133.37 (4C, Ar–C(2,6)). ESI-TOF-MS: m/z calcd for $C_{16}H_{20}NCl$ [M – Cl]$^+$: 226.16; found: 226.15. Anal. calcd for $C_{16}H_{20}NCl$: C, 73.41; H, 7.70; N, 5.35; found: C, 72.71; H, 7.84; N, 5.12.

Dimethyldi(4-methylbenzyl)ammonium chloride (10). *Method A*. Reagents: 4-methylbenzyl chloride (9.15 ml, 69.00 mmol), sodium carbonate (7.31 g, 69.00 mmol) and dimethylformamide (30 ml). Reaction temperature 80 °C and reaction time 72 h. Yield (white powder): 6.18 g (62%). ^{1}H NMR (CDCl$_3$, 500 MHz, ppm): 2.33 (6H, s, CH_3), 3.09 (6H, s, CH_3), 5.06 (4H, s, Ph–CH_2), 7.16 (4H, d, Ar–H), 7.51 (4H, d, Ar–H). ^{13}C NMR (CDCl$_3$, 126 MHz, ppm): 21.23 (2C, CH$_3$), 47.96 (2C, CH$_3$), 67.49 (2C, Ph–CH$_2$), 124.53 (2C, Ar–C), 129.72 (4C, Ar–C), 133.26 (4C, Ar–*C*), 140.73 (2C, Ar–*C*). ESI-TOF-MS: *m*/*z* calcd for $C_{18}H_{24}NCl$ $[M - Cl]^+$: 254.19; found: 254.19. Anal. calcd for $C_{18}H_{24}NCl$: C, 74.59; H, 8.35; N, 4.84; found: C, 74.05; H, 8.32; N, 4.66.

X-Ray crystallography

Single-crystal data for compound **1** were recorded with a Nonius Kappa CCD diffractometer and processed with Denzo-SMN (v. 0.95.373).[13] The structure was solved by direct methods (SHELXS-97[14]) and refined on F^2 by full-matrix least-squares techniques (SHELXL-97[15]). The hydrogen atoms were calculated in their idealized positions with isotropic temperature factors (1.2 or 1.5 times the carbon temperature factor) and refined as riding atoms. In the final structure, the cation is disordered over two equal positions generated by symmetry.

Crystallographic data for **1**: colorless crystals of size 0.05 × 0.20 × 0.20 mm^3, M = 182.11, orthorhombic, space group $Cmc2_1$ (No. 36), a = 6.2816(4), b = 11.7524(9), c = 11.464(1) Å, U = 846.4(1) $Å^3$, $T = 173.0 \pm 0.1$ K, Z = 4, D_{calc} = 1.429 g cm^{-3}, $\mu(MoK_\alpha)$ = 4.773 mm^{-1}, absorption correction was made but not used in the final refinement, 1296 reflections, 617 independent reflections (R_{int} = 0.0336), R_1 = 0.026 and wR_2 = 0.063 for 580 reflections with $I > 2\sigma(I)$, R_1 = 0.029 and wR_2 = 0.064 for all data.‡

Powder diffraction

The high-resolution X-ray powder diffraction data for compound **5** were obtained at room temperature with a Huber G670 imaging plate Guinier camera. The sealed-tube X-ray generator system was operated at 45 kV and 25 mA and pure line-focused $CuK\alpha_1$ radiation (λ = 1.5406 Å) was produced by a primary beam curved germanium monochromator (d = 3.266 Å). The hand-ground samples were prepared on a vaseline-coated Mylar foil of 3.5 μm thickness and were measured in the Guinier-type transmission geometry with an angle of incidence of 45° to the sample normal. Diffracted data with the angular range of 4–100° (2θ) was recorded at the curved imaging plate with a recording time of 60 min. The step resolution of the data was 0.005° (2θ). The instrumental resolution of the equipment was determined using highly crystalline silicon standard (SRM 640b, National Institute of Standards & Technology). For silicon, the sharpest full-width-half-maximum (FWHM) value of 0.09° (2θ) was obtained from the diffraction peak at 28.44° (2θ). The equipment was aligned and calibrated using a mixture of LaB_6 (SRM 660, National Institute of Standards & Technology) and silicon standards so that an absolute error of less than 0.02° (2θ) on peak positions was achieved. The range of 5.8–38° (2θ) was used for the structure determination and that of 5.8–50° (2θ) for the Rietveld refinement. The peak search and the background subtraction were made using DASH (v. 2.01).[16] The indexing was carried out with CRYSFIRE (v. 9.34g) [17] and the congruent monoclinic cell was achieved by means of the subprograms TREOR,[18] KOHL,[19] DICVOL [20] and ITO.[21] CHEKCELL (v. 23.4.2002) [22] was used for the space group analysis. The structure was solved by direct space and simulating annealing methods implemented in DASH (v. 2.01). The structural model was refined by Rietveld full-matrix full-powder data fitting using FULLPROF (2000 v. 2.10).[23]

Crystallographic data for **5**: colorless microcrystalline powder, M = 306.23, monoclinic, space group $P2_1/c$ (No. 14), a = 13.0855(3), b = 10.4132(3), c = 10.8449(3) Å, β = 92.456(1)°, U = 1476.4(1) $Å^3$, $T = 293.0 \pm 0.5$ K, Z = 4, D_{calc} = 1.377 g cm^{-3}, $\gamma(CuK\alpha_1)$ = 1.5406 Å, 345 reflections, R_p = 0.0721, R_{wp} = 0.0973, R_B = 0.0487, R_F = 0.039, 80 variables, in which isotropic temperature factors of non-hydrogen atoms and profile asymmetry parameters were separately refined and then fixed in the final refinement. §

TG/DTA studies

The thermal decomposition paths of compounds **1**–**6** and **8**–**10** were obtained with a Perkin–Elmer Diamond TG/DTA. Measurements were carried out using platinum pans under synthetic air atmosphere (flow rate of 110 ml min^{-1}) in the temperature range of 20–400 °C (heating rate of 10 °C min^{-1}). The temperature calibration of the TG/DTA equipment was carried out using melting points of five reference materials (In, Sn, Zn, Al, Au). The weight balance was calibrated by measuring the standard weight as a function of temperature. The sample weights used in the measurements were about 10 mg.

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‡ CCDC reference number 210522. See http://www.rsc.org/suppdata/nj/b4/b409062b/ for crystallographic data in .cif or other electronic format.

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