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Alkene- and alkyne- substituted methylimidazolium bromides: structural effects and physical properties (PREPRINT)

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Abstract. Several bromide salts composed of methylimidazolium cations possessing unsaturated sidechains (allyl-, 3-butenyl-, propargyl-, 2-butynyl-, and 2-pentynyl-) have been synthesized and characterized by multinuclear NMR, vibrational spectroscopy, and DSC, X-ray and elemental analysis. X-ray structures of 1-(2-butynyl)-3-methylimidazolium bromide, 1-propargyl-3-methylimidazolium bromide as well as the X-ray structure of 1-allyl-3- methylimidazolium bromide which was previously identified as a room temperature ionic liquid, were all determined.

Keywords: ionic liquids; methylimidazolium; bromides; DSC; crystal structure

Introduction

In recent years ionic liquids have become a material class of intensive research and development. [1-7] They owe their popularity to the fact that, besides being exceptionally interesting materials for basic research programs, they show great potential for many different applications including electrochemistry, [8-10] separation science, [11-14] chemical synthesis, [2, 4, 5, 15-19] and catalysis. [4, 5, 17] Salts with a melting point at or below 100°C are broadly accepted to qualify as an ionic liquid. However, for many of the above mentioned applications, it is much more desirable to find and develop so called room-temperature ionic liquids which possess the distinctive characteristics of negligible volatility and consequently very low vapor toxicity, great thermal stability, and large liquidous range. The ongoing chase after new room

temperature ionic liquids with specific chemical and physical properties make it crucial to incorporate different functional groups. The N-allyl functionality was subject to multiple studies and has been found to effectively suppress crystallization. [20-26] A series of substituted allylimidazolium halides have been obtained as room temperature ionic liquids and some have already been found to be useful as solvents for specific applications. [27, 28] It should be mentioned, that methylimidazolium salts possessing alkene- (i.e. allyl) and alkyne- (i.e. 2-butyne) functionalities have been reported as early as 1971 by Jones et al. At that time they had not been termed ionic liquids, and no details on their structural and thermal properties were provided due to the extremely deliquescent properties of the salts which made any further purification of the compounds impossible. [20] This paucity of detailed data motivated Mizumo et al. to a careful investigation of allylimidazolium halides to clarify their physical properties. [23] An entire sequence of N-allyl substituted imidazolium halide salts was investigated and all were obtained as liquids at ambient temperature. However, after storing at low temperature they started to slowly crystallize. In the case of 1-allyl-3-methyl-imidazolium bromide a melting point of +53.1°C was established which clearly disqualifies it as a true room temperature ionic liquid. The same compound has been reported by others showing a melting point of -52.5°C without mentioning a solid state, and is today commercially available as a liquid (~97% purity). [24] These findings provoked us to look further into detailed physical properties of ionic liquids with unsaturated side chains. In the present work, the synthesis of a series of substituted

methylimidazolium bromide salts with allyl- **1**, 3-butene- **2**, propargyl- **3**, 2-butyne- **4**, and 2-pentyne- **5** side chains and their structural and physical properties have been investigated. Three of the salts, **1**, **3**, and **4**, have been additionally characterized by single X-ray crystallography identifying substantial cation-anion interactions via hydrogen bonding.

Experimental Section

All synthesis materials were purchased from Aldrich Chemical Company, Inc. and their purities were checked by ^{1}H and ^{13}C NMR prior to use. The alkyl bromides (allyl bromide, propargyl bromide, 2-butyne bromide, 3-butene bromide and 2-pentyne bromide), methanol (99.93% A.C.S. HPLC grade) and diethyl ether (anhydrous, 99+%, A.C.S. Reagent) were used as received. 1-methylimidazole was distilled and stored inside a sealed Schlenk vessel under nitrogen. Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. Infrared spectra were recorded on a Nicolet 710 SX FT-IR spectrometer from 4000-400 cm^{-1} using dry powders pressed as KBr pellets in an Econo press (Barnes Engineering Co.). Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries or 5mm glass NMR tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield^{TM} spectrometer at room temperature with each salt sample being dissolved in DMSO-d_6 in 5mm NMR tubes. The ^{1}H, ^{13}C,

spectra were referenced to external samples of neat TMS. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box. Elemental analyses were performed out on a PerkinElmer 2400 Series II CHNS/O elemental analysis instrument equipped with AD6 Autobalance.

Synthesis of 1-allyl-3-methylimidazolium bromide (1). 4.90 g (59.68 mmol) of 1-methylimidazole was added to a nitrogen-purged, pre-weighed 250 ml Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. 14.30 g (118.20 mmol) of allylbromide was added drop-wise to the continuously stirred solution. The mixture was stirred until TLC monitoring indicated a complete reaction of 1-methylimidazole. All the volatiles were removed in a dynamic vacuum at elevated temperature leaving behind a highly viscous liquid. Great care was taken drying the product and removing traces of solvent. This procedure required up to eight days of pumping in a dynamic vacuum at temperatures as high as 100°C and regular rolling of the flask. The purity of the product was frequently checked by ^{1}H NMR. Only upon storage in a refrigerator, by mechanical stimuli or after long periods of standing the liquid finally solidified. However, it could not simply be recrystallized from methanol solutions layered with diethylether. (yield 97%), mp. 59.5°C, DSC onset 252.5°C. IR

(KBr, cm^{-1}) ν = 3079(s, br), 2942(m, sh), 2856(m), 2058(w), 1646(4), 1573(vs), 1448(s), 1424(s), 1384(w), 1336(m), 1292(w), 1165(vs), 998(s), 947(s), 841(m), 764(s), 675(m), 626(s); Raman (500mW, 25°C, cm^{-1}) ν = 3077(44), 3011(76), 2978(73), 2945(100), 2883(29), 2824(17), 1645(53), 1562(9), 1413(49), 1384(12), 1331(19), 1292(25), 1222(3), 1164(1), 1094(7), 1021(46), 951(3), 918(3), 761(5), 673(8), 622(12), 569(5), 500(4), 396(7), 357(3), 269(3), 232(4), 112(56), 84(97); δ_H (400 MHz, neat liquid) 8.97 (1H s, br), 7.30 (1H, s, br), 7.27 (1H, s, br), 5.20 (1H, s, br, $CH_2C\mathit{H}CH_2$), 4.45 (2H, s, br, $C\mathit{H}_2CHCH_2$), 4.33 (2H, s, br, $CH_2CHC\mathit{H}_2$),3.30(3H, s, br, CH_3); δ_C (100 MHz, neat liquid) 136.8, 132.0, 124.0, 122.4, 120.7, 51.1, 37.3. Found: C, 41.35; H, 5.68; N, 13.58. Calc. for $C_7H_{11}N_2Br$: C, 41.40; H, 5.46; N, 13.79.

Synthesis of 1-(3-butenyl)-3-methylimidazolium bromide (2). 3.98 g (48.41 mmol) of 1-methylimidazole was added to a nitrogen-purged, pre-weighed 250 ml Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. 14.20 g (105.18 mmol) of 4-bromo-1-butene was added drop-wise to the continuously stirred solution. Following the procedure described above the reaction yielded 66% of a highly pure product. mp. 44.1 °C, DSC onset 291.6°C. IR (KBr, cm^{-1}) ν = 3082(s, br), 2848(s), 2071(w), 1641(s), 1574(vs), 1439(s), 1380(w), 1368(w), 1339(m), 1289(w), 1218(w), 1172(vs), 1132(m), 997(s), 930(s), 828(m, br), 752(s, br), 700(m), 661(m), 623(s); Raman (500mW, 25°C, cm^{-1}) ν = 3130(14), 3087(17), 3073(19), 2997(64), 2974(95), 2951(100), 2926(54), 2909(76), 2864(10), 2835(19), 1640(60), 1558(7), 1458(12), 1414(62), 1377(17), 1335(36), 1294(21), 1279(10), 1231(17), 1216(7),

1161(2), 1134(9), 1089(19), 1033(9), 1014(36), 1001(10), 933(4), 890(7), 849(9), 800(1), 700(19), 657(5), 630(3), 599(24), 463(5), 411(16), 319(4), 266(11), 226(7), 152(40), 110(81), 85(98); δ_H (400 MHz, DMSO-*d*$_6$) 9.24 (1H s), 7.82 (1H, dd, *J* 1.7), 7.74 (1H, dd, *J* 1.7), 5.81-5.70 (1H, m $CH_2CH_2CHCH_2$), 5.08-5.03 (2H, m, $CH_2CH_2CHCH_2$), 4.27 (2H, t, *J* 6.9 $CH_2CH_2CHCH_2$), 3.86 (3H, s, CH_3), 2.56 (2H, d, *J* 6.8 $CH_2CH_2CHCH_2$); δ_C (100 MHz, DMSO-*d*$_6$) 137.0, 134.1, 124.0, 122.8, 118.8, 48.3, 36.2, 34.0; Found: C, 44.32; H, 5.79; N, 12.19. Calc. for $C_8H_{13}N_2Br$: C, 44.26; H, 6.04; N, 12.90.

Synthesis of 1-propargyl-3-methylimidazolium bromide (3). 3.71 g (45.14 mmol) of 1-methylimidazole was added to a nitrogen-purged, pre-weighed 250 ml Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. 12.00 g (100.87 mmol) of propargylbromide was added drop-wise to the continuously stirred solution. Following the procedure described above, the reaction yielded 73% of a highly pure product. mp. 116.9°C, DSC onset 192.4°C. IR (KBr, cm^{-1}) ν = 3175(m), 3130(vw), 3100(vw), 3073(m), 3061(m), 3041(m), 3025(m), 3008(vw), 2952(w), 2934(w), 2906(w), 2848(vw), 2466(m), 2408(m), 2119(s), 1624(w), 1576(s), 1560(s), 1461(w), 1449(w), 1424(m), 1389(w), 1361(w), 1328(w), 1295(m), 1215(w), 1201(w), 1175(vs), 1110(w), 1097(w), 1020(m), 943(s), 866(s), 857(s), 784(m), 754(s), 719(m), 670(m), 622(s), 613(m); Raman (400mW, 25°C, cm^{-1}) ν = 3163(9), 3129(3), 3102(4), 3073(10), 3063(10), 3027(10), 3009(12), 2985(19), 2955(34), 2930(48), 2908(31), 2860(13), 2820(6), 2117(100), 1560(4), 1476(4), 1460(3), 1448(5), 1408(33),

1388(11), 1348(6), 1328(9), 1294(6), 1215(7), 1202(10), 1174(4), 1116(9), 1097(2), 1032(8), 1021(42), 943(6), 884(1), 869(4), 856(2), 784(1), 750(4), 737(12), 717(5), 671(11), 614(15), 453(11), 402(5), 330(10), 321(16), 283(11), 274(12), 230(8), 149(49), 111(16), 85(17); δ_H (400 MHz, DMSO-*d*$_6$) 9.46 (1H s), 7.88 (1H, s), 7.87 (1H, s), 5.35 (2H, d, *J* 2.5 C*H*$_2$CCH), 3.91 (3H, s, CH_3), 3.89 (1H, t, *J* 2.5 CH_2CCH); δ_C (100 MHz, DMSO-*d*$_6$) 136.4, 123.9, 122.0, 78.9, 76.0, 38.6, 36.1. Found: C, 41.52; H, 4.60; N, 13.46. Calc. for $C_7H_9N_2Br$: C, 41.82; H, 4.51; N, 13.93.

Synthesis of 1-(2-butynyl)-3-methylimidazolium bromide (4). 4.31 g (52.54 mmol) of 1-methylimidazole was added to a nitrogen-purged, pre-weighed 250 ml Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. 9.80 g (73.69 mmol) of 1-bromo-2-butyne was added drop-wise to the continuously stirred solution. Following the procedure described above the reaction yielded 93% of a highly pure product. mp. 130.8°C, DSC onset 253.5°C. IR (KBr, cm^{-1}) ν = 3172(vw), 3130(vw), 3096(m), 3004(m, br), 2930(m), 2317(w), 2300(w), 2234(m), 1617(m), 1570(s), 1441(w), 1419(w), 1384(w), 1343(m), 1219(w), 1172(s), 1142(s), 1091(w), 1021(vw), 967(w), 879(m), 787(vw), 758(m), 748(m), 646(s), 623(s); Raman (500mW, 25°C, cm^{-1}) ν = 3157(5), 3129(7), 3087(16), 2994(20), 2951(70), 2929(69), 2915(100), 2852(21), 2753(5), 2726(3), 2321(11), 2303(7), 2240(48), 1560(6), 1443(15), 1411(41), 1385(23), 1333(14), 1282(8), 1218(8), 1160(2), 1143(1), 1100(5), 1090(17), 1021(9), 1011(13), 965(2), 895(4), 866(1), 797(3), 749(2), 737(10), 716(1), 664(14), 650(3), 619(15), 448(16), 407(13), 361(20), 324(7), 283(2), 246(6), 182(9), 85(98); δ_H

(400 MHz, DMSO-d_6) 9.46 (1H s), 7.86 (1H, dd, *J* 1.7), 7.85 (1H, dd, *J* 1.7), 5.22 (2H, d *J* 2.4 CH_2CCCH$_3$), 3.91 (3H, s, CH$_3$), 1.863 (3H, t, *J* 2.4 CH$_2$CCCH$_3$); δ_C (100 MHz, DMSO-d_6) 136.8, 124.4, 122.5, 84.9, 72.0, 36.5, 3.8; Found: C, 43.48; H, 5.11; N, 12.95. Calc. for $C_8H_{11}N_2Br$: C, 44.67; H, 5.12; N, 13.03.

Synthesis of 1-(2-pentynyl)-3-methylimidazolium bromide (5). 4.02 g (48.89 mmol) of 1-methylimidazole was added to a nitrogen-purged, pre-weighed 250 ml Schlenk flask, dissolved in ca. 40 mL methanol and stirred vigorously with a Teflon® stir bar. 10.00 g (68.02 mmol) of 1-bromo-2-pentyne was added drop-wise to the continuously stirred solution. Following the procedure described above, the reaction yielded 95% of a highly pure product. mp. 66.1°C, DSC onset 215.8°C. IR (KBr, cm^{-1}) ν = 3134(w), 3089(w), 2984(m), 2938(m), 2923(m), 2902(w), 2881(w), 2852(vw), 2458(vw), 2405(m), 2308(m), 2242(s), 2075(m), 2056(m), 1626(s), 1570(vs), 1452(s), 1417(s), 1381(m), 1339(s), 1319(m), 1276(w), 1247(vw), 1211(vw), 1168(vs), 1142(s), 1109(m), 1095(m), 1083(m), 1063(m), 1022(m), 962(w), 869(m), 855(m), 833(m), 781(s), 758(vs), 745(s), 650(s), 625(s), 617(s); Raman (500mW, 25°C, cm^{-1}) ν = 3141(12), 3124(13), 3098(20), 2976(38), 2938(71), 2921(89), 2910(100), 2851(32), 2784(1), 2723(7), 2631(1), 2579(0+), 2457(0+), 2393(0+), 2303(13), 2281(11), 2232(59), 2199(4), 1558(4), 1447(19), 1429(24), 1417(39), 1377(18), 1333(16), 1276(11), 1229(3), 1213(11), 1160(1), 1137(0+), 1096(9), 1084(10), 1063(7), 1028(11), 1012(40), 960(7), 894(4), 864(1), 827(1), 780(3), 756(4), 730(3), 648(7), 614(11), 520(2), 505(2), 409(18), 329(1), 290(10), 277(11), 217(4), 184(5), 85(81); δ_H

(400 MHz, DMSO-d_6) 9.45 (1H s), 7.84 (1H, s), 7.84 (1H, s), 5.25 (2H, s $CH_2CCCH_2CH_3$), 3.91 (3H, s, CH_3), 2.21(2H, q *J* 7.6 $CH_2CCCH_2CH_3$) 0.99 (3H, t, *J* 7.6 $CH_2CCCH_2CH_3$); δ_C (100 MHz, DMSO-d_6) 136.6, 124.2, 122.3, 90.3, 71.9, 36.5, 13.7, 12.2; Found: C, 46.54; H, 5.65; N, 12.23. Calc. for $C_9H_{13}N_2Br$: C, 47.18; H, 5.72; N, 12.23.

All preparation can be carried out using toluene instead of methanol as a solvent. Products are formed almost instantaneously and crash out of the toluene solution. However, workup proved rather difficult because of the relative high boiling point of toluene and, in some cases, even after multiple washings, the solvent could never be removed completely.

X-ray Analyses.

The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART CCD (charge coupled device) detector with the χ-axis fixed at 54.74° and using MoK_α radiation (λ = 0.71073 Å) from a fine-focus tube. The diffractometer was equipped with KryoFlex apparatus for low temperature data collection using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop with a magnetic base, was used to mount the crystals using PFPE (perfluoropolyether) oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of ten-second per frame at a detector resolution of 512 x 512 pixels using the

SMART software. [29, 30] A total of 1271 frames were collected in three sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed on a PC running on Windows NT software by using the SAINT software [31, 32] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS [33] program. The structures were solved by the direct method using the SHELX-90 [34] program and refined by the least squares method on F^2, SHELXL-97 [35] incorporated in SHELXTL Suite 5.10 for Windows NT. [36, 37] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor. The hydrogen atoms were located either from difference electron density maps or generated at calculated positions.

Results and Discussion

Among a series of methylimidazolium halides with unsaturated side chains 1-allyl-, and 1-propargyl-3-methyl-imidazolium halides (X = Cl, Br, I), and 1-(2-butyne)-3-methyl imidazolium bromide have been mentioned earlier. [20, 21, 23-28, 38, 39] However, detailed physical properties on these compounds are either completely missing or in the case of **1** reported properties are not consistent. [23, 24] Hence, we have prepared a sequence of substituted methylimidazolium bromides, including the previously reported

and novel salts, i.e. 1-(3-butenyl)- and 1-(2-pentynyl)-3-methyl imidazolium bromide, and investigated their physical and structural properties for the first time in detail.

Synthesis and physical properties

The synthesis of the alkene and alkyne substituted methylimidazolium bromides followed the procedure by Jones et al. [20] In a typical experiment the alkyl halide was used in excess and the reaction was run at elevated temperature up to 65°C in solvents such as toluene or methanol. Initially, all the substituted methylimidazolium bromides were obtained as highly viscous, slightly yellowish to amber liquids. Only after prolonged storage in a refrigerator, by mechanical stimuli or after long periods of standing the liquids started to slowly crystallize or completely solidified. **1**, **3**, and **4** crystallized within weeks upon storage at -18°C. However, solids generated by this process could not simply be recrystallized from saturated polar solvent solutions layered with diethylether. After recrystallization the material was obtained again in the liquid state. This is owed to the tendency of forming supercooled liquids rather than crystallizing upon cooling, a behavior very typical to many ionic liquids. All salts are highly deliquescent and should be handled in the dry nitrogen atmosphere of a glove box. They are soluble in a wide array of polar solvents, e.g. methanol, ethanol, isopropanol, acetonitrile, dimethylsulfoxide, and are insoluble in ethyl acetate, methylene chloride, diethyl ether, and toluene.

Thermal investigations

The melting transition and thermal decomposition (decomposition onset) was determined by DSC analysis (Table 1). Due to the tendency to form supercooled liquids, these compounds can easily be misjudged as true room temperature ionic liquids. Only by investing the time and patience required to allow materials to crystallize and ensuring purity, we were able to discover their accurate physical properties. Melting points range from 44°C for **2** up to 131°C for **4**, clearly beyond room temperature. The propargyl- (**3)** and 3-butyne- (**4**) salts possess melting points of 117°C and 131°C respectively, and therefore do not technically qualify as ionic liquids, according to the commonly used definition (i.e. a salt with a mp. ≤ 100°C). Generally, the salts containing alkyne functionalities show higher melting points and lower decomposition onsets than their corresponding alkene counterparts most likely due to the "rigidity" of the carbon-carbon triple bond. Samples heated to +150°C on a DSC and then cooled back to -100°C using LN_2 did not, upon reheating, display the prior established melting point (with the exception of 1-(2-butynyl)-3-methylimidazolium bromide). Instead, all samples showed glass transition at low temperatures during a second and third cycle (Table 1). Simply allowing the samples to cool from +150°C back to ambient temperature by themselves was still too fast to induce crystallization; they remained in a supercooled phase.

X-ray Crystallography.

Crystals suitable for single crystal X-ray structure determination were obtained for three of the salts, **1**, **3**, and **4** by storing samples of the liquids at -18°C for several weeks (Table 2). The different substituents have little effect on the bond lengths and angles within the imidazolium cations. The alkene- and alkyne- groups show no abnormalities within the CC single, double, or triple bonds. The overall packing is dominated by attractive Coulomb forces accompanied by substantial hydrogen bonding from imidazolium ring hydrogens and hydrogen atoms from substituent groups to the bromide anion.

1-allyl-3-methylimidazolium bromide crystallized in a monoclinic space group. Figure 1 shows the asymmetric unit and the packing arrangement along the *c* axis. The allyl- chain is oriented perpendicular to the plane of the imidazolium ring and the pendant group arranges like a "C" shaped handle curved towards the imidazolium ring. It is a relatively simple, packed structure with alternating layers of cations and anions. Along the *a* axis, the cations align in offset, zig-zag chains. Two strong intramolecular contacts are present within the cation, i.e. N(2)···H(10) 2.57(3) Å, between the imidazolium ring nitrogen atom N(1) and the terminal allyl proton H(11), which is considerably shorter than Σ_{vdW} (2.75 Å, sum Van der Waals radii [41]), and C(1)···C(7) 3.364(3) Å between the imidazolium ring carbon C(3) and the terminal allyl carbon C(7), which is still less than Σ_{vdW} (3.40 Å). These two contacts cause the pendant group to bend towards the ring forming a "C" handle. The bromide anion shows five strong hydrogen bonds with different cations through the ring, allyl group, and the

methyl group hydrogens forming a three dimensional network. They range from 2.76(2) Å, Br(1)···H(3), to 3.00(4) Å, Br(1)···H(5) being the longest contact just short of the Σ_{vdW} (3.05 Å).

1-propargyl-3-methylimidazolium bromide crystallized in an orthorhombic space group. There are two cation-anion pairs in the asymmetric unit. Figure 2 shows the asymmetric unit and the packing arrangement along the *a* axis. Both asymmetric cations have essentially the same shape and show only small differences in bond length and angles. For both cations the pendant propargyl groups are again perpendicular to the plane of the imidazloium ring but the straight chain is twisted away from the ring (N(1)-C(4)-C(5) 111.3(1)º, C(3)-N(1)-C(4)-C(5) dihedral twist = 64.7(2)º; and N(3)-C(11)-C(12) = 111.3(1)º, C(10)-N(3)-C(11)-C(12) dihedral twist = 69.3(2)º respectively). There are significant hydrogen bonds, and intermolecular cation-cation contacts present in the crystal structure. The bromide anion is connected to different cations by a total of seven strong hydrogen bonds forming a three dimensional network. Similar to the case of the allyl substituted salt, the hydrogen atoms of the ring, propargyl group, and the methyl group are participating in the bonding, which range from 2.66(2) Å, Br(2)···H(10), to 3.01(2) Å, Br(1)···H(5). The bromide anion connects with two different cations via a ring proton from one of the cations and either a terminal or central hydrogen of the propargyl group from the other cation (Figure 2).The two asymmetric cations show different connectivity patterns via C(6)···H(9f) 2.73(2) Å, C(6)···C(1) = 3.346 (3) Å, C(13)···H(11o) 2.74(2) Å and C(13)···C(8q) 3.349(2) Å

respectively. Only one short contact connects the two different cations with each other, C(6)···C(8q) = 3.278 (3) Å. The cations and anions pack by forming alternating layers. However, the two asymmetric cations show very different motives in their packing assembly. One layer consists of one of the cations which pile on top of each other along the *a* axis forming a "V" shape structure with the pendant propargyl groups and the "V" shapes stack along the *b* axis (Figure 2). In the other cation layer the propargyl groups orient almost parallel to each other which results in a much less structured arrangement.

1-(2-butynyl)-3-methylimidazolium bromide crystallized in an orthorhombic space group. Figure 3 shows the asymmetric unit and the packing arrangement along the *a* axis. The 2-butynyl group is perpendicular to the plane of the imidazolium ring consistent with the previous examples. Like the propargyl- group, the linear butynyl-pendant chain is twisted in the same way, away from the ring by 111.0(2)º (N(1)-C(4)-C(5)). The dihedral twist, however, is considerable smaller with only 7.3(2)º. The bromide anion shows again extensive hydrogen bonding ranging from a very strong Br(1)···H(1) bond with 2.69(2) Å to an extremely week Br(1)···H(11) bond of 3.05(2) Å, which matches the Σ_{vdW} (3.05 Å) (Figure 3). Other contacts include an intermolecular cation link between C(1)···C(7a), 3.384(3) Å, and a strong intramolecular connection between C(5)···H(1) 2.59(2) Å, which is significantly shorter than Σ_{vdW} (2.90 Å). Via this intramolecular contact H(1)-C(1)-N(1)-C(4)-C(5) form a

five membered ring structure which prefers a planar configuration explaining the small dihedral twist.

Conclusion

In this work, the focus has been on the structural and physical properties of a series of new and previously prepared alkene- and alkyne- substituted methylimidazolium bromide salts. The true nature of these ionic liquids can be easily overlooked because of their tendency to form supercooled liquids rather than to crystallize. The results from this investigation should raise some caution in future work to identify room temperature ionic liquid. All salts, obtained as liquids at first, possess melting points significantly above room temperature and two of the salts **1** and **4**, do not even technically qualify as ionic liquids. The three crystal structures showed that hydrogen bonding is extremely dominant in the solid state of these bromide salts which explains the relatively high melting points.

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Table 1. Thermal data for the different bromide salts.

	Imidazolium Cation	$T_{g(peak)}$ (±1 °C)	$T_{m(peak)}$ (±1 °C)	$T_{dec(onset)}$ (±1 °C)
1	1-allyl-3-methyl-	-51	60	253
2	1-(3-butene)-3-methyl-	-57	44	292
3	1-propargyl-3-methyl-	-20	117	192
4	1-(2-butyne)-3-methyl-	-5	131	254
5	1-(2-pentyne)-3-methyl-	-18	66	216

Table 2 Crystal and structure refinement data for substituted -imidazolium bromides.

Compound	1-allyl-3-methyl-	1-propargyl-3-methyl-	1-(2-butynyl)-3-mehtly-
Formula	$C_7H_{11}N_2Br$	$C_7H_9N_2Br$	$C_8H_{11}N_2Br$
Space group	$P2_1$ monoclinic	Pbca ortho.	P212121ortho.
a (Å)	5.893(1)	12.593(2)	6.951(1)
b (Å)	9.721(2)	11.969(2)	9.317(1)
c (Å)	7.939(2)	21.745(3)	14.088(2)
α (°)	90.000	90.000	90.000
β (°)	108.997(3)	90.000	90.000
γ (°)	90.000	90.000	90.000
V/Å^3	430.1(2)	3277.5(8)	912.4(2)
$\rho_{calc.}$/g cm^{-3}	1.568	1.630	1.566
Z	2	16	4
Formula weight	203.08	201.06	215.09
μ/mm^{-1}	4.709	4.943	4.445
Temperature (K)	100	100	100
λ(MoKα)	0.71073	0.71073	0.71073
Crystal size	0.20x0.15x0.10	0.25x0.20x0.20	0.86x0.40x0.35
Theta range θ/°	2.71 to 28.20	1.87 to 28.29	2.62 to 26.32
Index range	-7≤h≤7, -12≤k≤12, -10≤l≤10	-16≤h≤16, -15≤k≤15, -27≤l≤28	-8≤h≤8, -11≤k≤11, -17≤l≤17
Reflection collected	4861	35673	9413
Independent [R(int)]/	1976 [0.018]	3989 [0.032]	1854 [0.030]
Obs. refl. ([I > 2.0 σ(I)])	1881	3497	1807
F(000)	204	1600	432
GooF	1.015	1.043	1.092
R_1, wR [I > 2σ(I)]	0.0176, 0.0391	0.0223, 0.0515	0.0165, 0.452
R_1, wR_2 (all data)	0.0188, 0.0393	0.0281, 0.0535	0.0171, 0.455
L.diff. peak/hole eÅ^3	0.54 and -0.22	0.58 and -0.24	0.51 and -0.35
Absorption correct.	SADABS	SADABS	SADABS
Data/restraints/param.	1976/1/135	3989/0/253	1854/0/145
Refinement method	Full-matrix least squares on F^2		

$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{½}$

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk

Scheme 1.

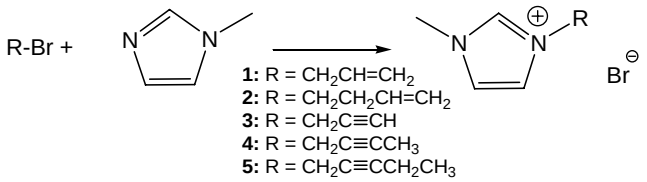
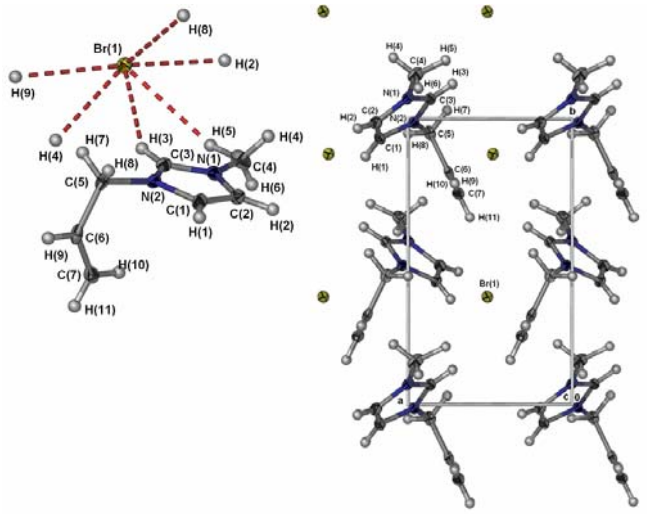

R-Br +
N
N
1: R = CH2CH=CH2
2: R = CH2CH2CH=CH2
3: R = CH2C≡CH
4: R = CH2C≡CCH3
5: R = CH2C≡CCH2CH3
N
N
R
Br

Figure 1.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H(2)
H(9)
H(4)
H(7)
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H(8)
C(4)
C(5)
H(6)
N(2)
C(1)
C(2)
H(2)
H(1)
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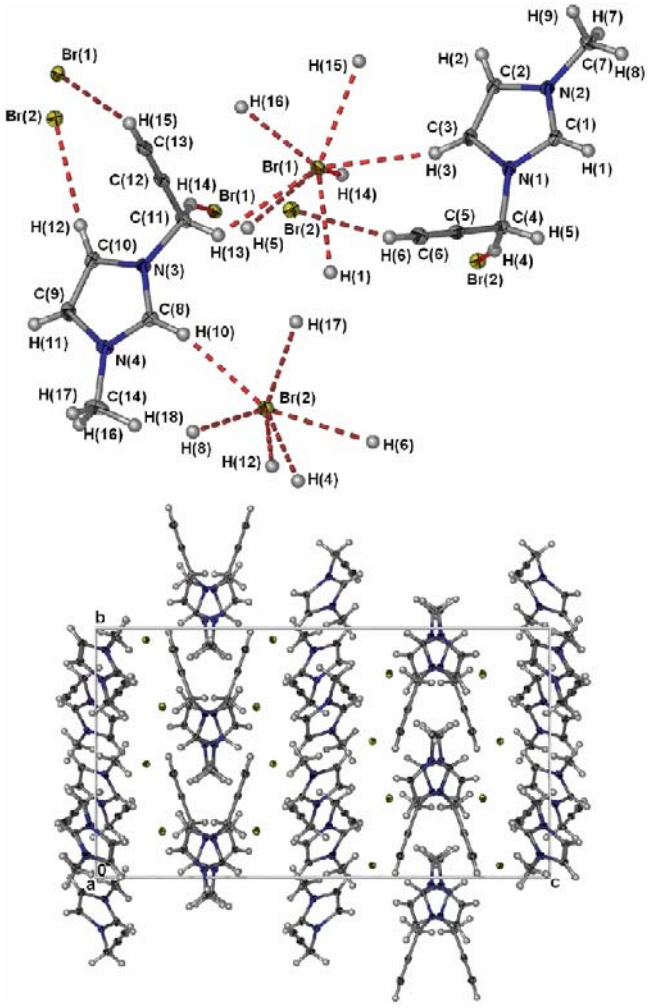
H(10)
C(7)
H(11)
Br(1)
a
b
c
0

Figure 2.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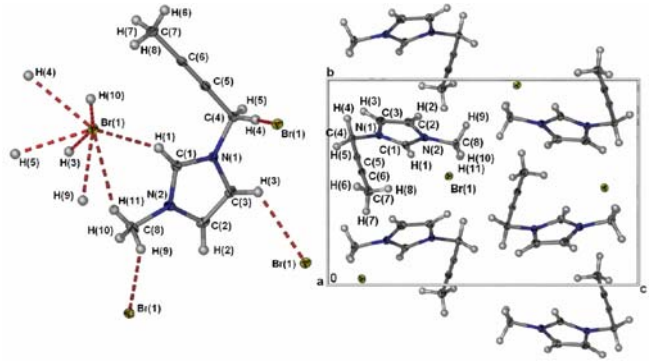
b
0
a
c

Figure 3.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C(6)
H(6)
H(8)
Br(1)
C(7)
H(7)

Scheme 1. Synthesis of compounds **1**-**5**

Figure 1. ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-allyl-3-methylimidazolioum bromide (**1**) along the *c* axis.

Figure 2. ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-propargyl-3-methylimidazolioum bromide (**3**) along the *a* axis.

Figure 3. ORTEP diagram showing connectivity, conformation, and the atom numbering scheme of the individual cations and anions present in the asymmetric unit and packing diagram of 1-(2-butynyl)-3-methylimidazolioum bromide (**4**) along the *a* axis.