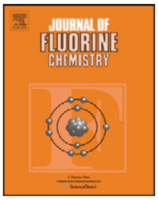
Journal of Fluorine Chemistry 133 (2012) 160–162

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor



Efficient synthesis of 1-alkyl-3-methylimidazolium fluorides and possibility of the existence of hydrogen bonding between fluoride anion and C(sp^3)–H

Zhi-Qiang Zhu [a], Ming-Yue Jiang [b], Chang-Ge Zheng [b], Ji-Chang Xiao [a,*]

[a] *Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*
[b] *School of Chemical and Material Engineering, Southern Yantze University, Wuxi 214122, China*

A R T I C L E I N F O

Article history:
Received 16 June 2011
Received in revised form 30 July 2011
Accepted 3 August 2011
Available online 10 August 2011

Keywords:
Imidazolium fluoride
Fluoride anion
Hydrogen bonding
X-ray diffraction analysis

Dedicated to Professor Wei-Yuan Huang on the occasion of his 90th birthday.

A B S T R A C T

1-Alkyl-3-methylimidazolium fluorides were successfully synthesized by the reaction of silver fluoride with the corresponding imidazolium iodides.

1. Introduction

Hydrogen bonding as one of the weak interactions plays an important role in life process and molecular assembly [1]. A hydrogen bond $D^{\delta-}–H^{\delta+}\cdots A^{\delta-}$ (donor–H···acceptor) generally involves a hydrogen atom with partial positive charge and an acceptor atom with partial negative charge, in which the acceptor atom usually refers to those electronegative elements such as F, O, N, Cl, and Br [2]. Although, on the one hand, more electronegative atoms are easier to form hydrogen bonds, on the other hand, higher electronegativity will make the atoms less inclined to share their electrons with a proton. This is the case with covalently bound halogens which rarely form hydrogen bonds. The great electronegativity and low polarizability of organic fluorine renders it a poorer hydrogen bond acceptor [3]. However, halide anions, especially fluoride ion, have been demonstrated to be good hydrogen bond acceptors [4]. For example, difluoride $[F–H\cdots F]^-$ showed a very short F–F distance of 2.25 Å and extremely strong bond energy of 39 kcal mol^{-1} [5]

In most cases, hydrocarbon compounds are weak hydrogen bond donors. However, the hybridization state of the central carbon and the substituents attached to it, to a great extent, will affect its ability to form hydrogen bond. Generally speaking, the proton-donating ability decreases as the carbon hybridization changes from sp to sp^2 to sp^3 [6]. Therefore, C(sp^3)–H is a very weak hydrogen bond donor. Just because of this, formation of hydrogen bond between C(sp^3)–H and fluoride anion is not easy in spite of the strong proton acceptor ability of fluoride ion. During our ongoing interest in the chemistry of ionic salts [7], an effective synthesis of the dialkylimidazolium fluoride was achieved with the accidental observation of weak interaction between C(sp^3)–H and F^- based on single crystal X-ray diffraction analysis.

2. Results and discussion

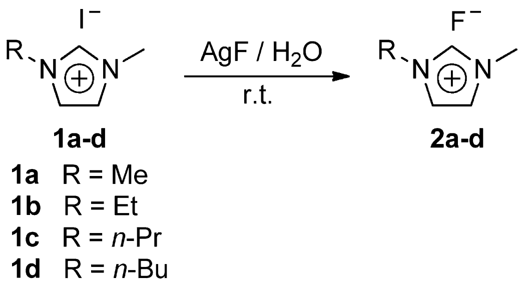
Different from other imidazolium halides which could be obtained readily by the quaternization of *N*-alkylimidazoles with alkyl halides, imidazolium fluorides can not be similarly synthesized because of the strong C–F bond in alkyl fluoride. To date, the only imidazolium fluoride, 1-butyl-3-methylimidazolium fluoride, was obtained as a decomposition product during purification of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [8]. Fortunately, dialkylimidazolium fluorides were successfully synthesized by the reaction of silver fluoride with the corresponding imidazolium iodides (Scheme 1). 1,3-Dimethylimidazolium fluoride was obtained as a white solid, whose structure was unambiguously assigned by single crystal X-ray diffraction analysis (Fig. 1) [9].

It shows that there are three water molecules, two fluoride anions and two dimethylimidazolium cations almost parallel to each other in a unit cell. The complicated hydrogen bonding framework exists among the cations, anions and water molecules,

---

[*] Corresponding author. Tel.: +86 21 54925340; fax: +86 21 64166128.
E-mail address: jchxiao@mail.sioc.ac.cn (J.-C. Xiao).

0022-1139/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2011.08.003



Scheme 1. Synthesis of **2a–d**.

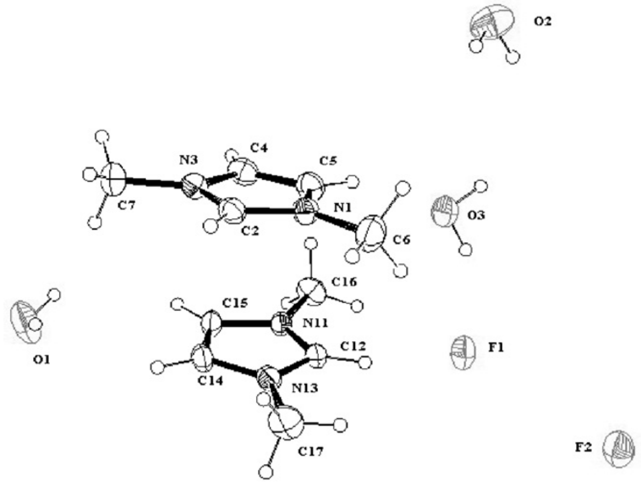


Fig. 1. Single crystal X-ray structure of **2a**.

which constructs the three dimensional structure (Fig. 2). The hydrogen bonding interactions in the crystal are list in Table 1. It can be seen that the shortest F···H distance is from F^- to the acidic C(2)–H (sp^2-hybridized C–H) of one imidazolium ring (1.92 Å), which is shorter than the shortest F···H distance in 1-butyl-3-methylimidazolium fluoride (1.96(2) Å). The observed distance between fluoride anion and C(sp^2)–H on the imidazolium ring is 1.92 Å for C(2)–H···F(2), 2.04 Å for C(12)–H···F(1), 2.20 Å for C(14)–H···F(1) and 2.20 Å for C(15)–H···F(2). The increase in the bond length of D–H···A corresponds to the decrease in proton donating ability of the C–H group.

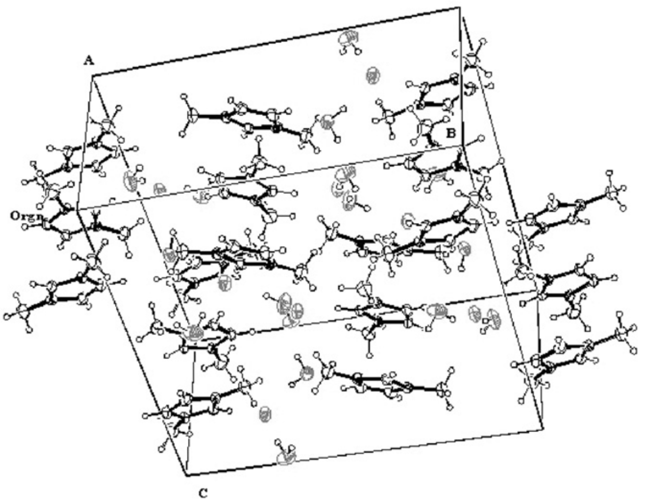


Fig. 2. Molecular packing diagram of **2a**.

In spite of the poor ability of a C(sp^3)–H group as proton donors in hydrogen bonding, under relatively few specific circumstances, short C(sp^3)–H···F contacts was observed. Grushin and Marshall have reported very short C(sp^3)–H···F distance, which could be as low as 2.083 Å [10]. We have also investigated the C(sp^3)–H···F interaction in the crystal structure of 1,3-dimethylimidazolium fluoride. And it was observed that the bond length is 2.53 Å for C(17)–H···F(2) and 2.57 Å for C(7)–H···F(1), slightly less than the sum of the van der Waals radii of hydrogen (1.20 Å) and fluorine (1.47 Å) [11]. These data suggests the weak C(sp^3)–H···F interaction and the possibility of the existence of hydrogen bond between fluoride anion and C(sp^3)–H. As for other dialkylimidazolium fluorides, our attempts to obtain single crystals failed mainly because of their lower melting points.

3. Conclusion

In summary, 1-alkyl-3-methylimidazolium fluorides have been efficiently synthesized. Weak interactions between fluoride anion

Table 1
Summary of hydrogen bonding interactions.

Entry	D–H···A	D–H/Å	H···A/Å	D···A/Å	D–H···A/deg
1	C(5)–H(5)···O(3)	0.93	2.27	3.159(4)	160.1
2	C(12)–H(12)···F(1)	0.93	2.04	2.906(3)	154.6
3	C(16)–H(16 C)···F(1)	0.96	2.67	3.450(3)	138.4
4	O(3)–H(3Y)···F(1)	0.836(19)	1.98(3)	2.735(3)	150(4)
5	C(2)–H(2)···F(2)^{a}	0.93	1.92	2.846(3)	174.4
6	C(7)–H(7B)···O(2)^{b}	0.96	2.67	3.499(4)	144.7
7	C(4)–H(4)···O(2)^{b}	0.93	2.66	3.237(4)	121.1
8	C(16)–H(16A)···O(3)^{c}	0.96	2.68	3.371(4)	129.7
9	C(16)–H(16B)···O(2)^{c}	0.96	2.60	3.509(4)	157.2
10	O(2)–H(2Y)···F(1)^{d}	0.834(17)	1.98(2)	2.690(3)	142(3)
11	C(17)–H(17A)···O(1)^{e}	0.96	2.59	3.501(5)	159.1
12	C(12)–H(12)···O(1)^{e}	0.93	2.78	3.535(4)	138.4
13	C(6)–H(6C)···O(1)^{f}	0.96	2.54	3.499(4)	178.3
14	C(7)–H(7A)···F(1)^{g}	0.96	2.57	3.459(4)	153.3
15	O(1)–H(1X)···F(1)^{g}	0.832(19)	1.87(2)	2.680(4)	163(4)
16	O(1)–H(1Y)···F(2)^{g}	0.831(17)	1.864(18)	2.691(3)	172(3)
17	C(15)–H(15)···F(2)^{g}	0.93	2.20	3.107(3)	165.1
18	C(14)–H(14)···F(1)^{g}	0.93	2.20	3.059(4)	153.4
19	C(14)–H(14)···O(2)^{h}	0.93	2.81	3.544(4)	136.6
20	C(17)–H(17B)···F(2)^{i}	0.96	2.53	3.415(4)	153.3
21	O(3)–H(3X)···F(2)^{j}	0.863(17)	1.809(18)	2.658(3)	167(3)
22	O(2)–H(2X)···F(2)^{j}	0.853(18)	1.88(2)	2.716(4)	166(3)

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

and sp^3-hybridized C–H groups were observed as determined by single crystal X-ray diffraction analysis. From these results, it seems likely that similar interactions might also be found in other imidazolium fluorides. Further work is currently being investigated in our laboratories.

4. Experimental

4.1. General information

All the reagents used were purchased from commercial sources and used without further purification. ^1H, ^{19}F, ^{13}C NMR spectra were recorded in D_2O on a spectrometer operating at 300, 282 and 75 MHz, respectively. Chemical shifts are reported in parts per million relative to the appropriate standard: TMS for ^1H and ^{13}C NMR spectra and $CFCl_3$ for ^{19}F NMR spectra. High Resolution Mass spectra were recorded on a IonSpec 4.7 Tesla FTMS instrument. The IR spectra were recorded on a Shimadzu IR-440 spectrometer.

4.2. General procedure for the synthesis of 1-alkyl-3-methylimidazolium fluorides

To a stirred solution of 1-alkyl-3-methylimidazolium iodides (1 mmol) in H_2O (10 ml) was added slowly a solution of AgF (1 mmol) in H_2O (10 ml). After stirring at room temperature for 2 h, the mixture was filtrated and the water was evaporated under reduced pressure at room temperature. The crude residue was dissolved in anhydrous methanol. The subsequent filtration and the evaporation of the solvent under reduced pressure to give the corresponding product in quantitative yields.

1,3-Dimethylimidazolium fluoride (**2a**): ^1H NMR (300 MHz, D_2O) δ 8.61 (s, 1H), 7.37 (s, 2H), 3.85 (s, 6H); ^{19}F NMR (282 MHz, D_2O) δ −122.7 (s, 1F); ^{13}C NMR (75 MHz, D_2O) δ 136.42, 123.22, 35.45; IR (KBr): ν = 3400 (br), 1667, 2111, 1577, 1526, 1257, 1175, 622 cm^{-1}; HRMS (EI, m/z): calcd for $[cation]^+$, 97.0760; found 97.0763. Anal. calcd for $[DMIM]F{\cdot}1.4H_2O$: C, 42.48; H, 8.41; N, 19.82. Found: C, 42.53; H, 8.55; N, 19.46.

1-Ethyl-3-methylimidazolium fluoride (**2b**): ^1H NMR (300 MHz, D_2O) δ 8.67 (s, 1H), 7.44 (s, 1H), 7.37 (s, 1H), 4.18 (q, J = 7.4 Hz, 2H), 3.84 (s, 3H), 1.45 (t, J = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, D_2O) δ −122.6 (s, 1F); ^{13}C NMR (75 MHz, D_2O) δ 135.44, 123.25, 121.66, 44.55, 35.42, 14.36; IR (KBr): ν = 3435, 3083, 2057, 1837, 1573, 1458, 1388, 1338, 1227, 1171, 1031, 960, 838, 760, 647, 621 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 130.0906; found 130.0900.

1-Methyl-3-propylimidazolium fluoride (**2c**): ^1H NMR (300 MHz, D_2O) δ 8.69 (s, 1H), 7.45 (s, 1H), 7.41 (s, 1H), 4.13 (t, J = 7.4 Hz, 2H), 3.87(s, 3H), 1.86 (m, 2H), 0.88 (t, J = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, D_2O) δ −122.7 (s, 1F); ^{13}C NMR (75 MHz, D_2O) δ 135.88, 123.47, 122.16, 51.00, 35.60, 22.82, 9.81; IR (KBr): ν = 3442, 3074, 2967, 2879, 2046, 1836, 1570, 1459, 1230, 1172, 846, 751, 651, 622 cm^{-1}; HRMS (EI, m/z): calcd for $[M]^+$, 144.1063; found 144.1070.

1-Butyl-3-methylimidazolium fluoride (**2d**): ^1H NMR (300 MHz, D_2O) δ 8.63 (s, 1H), 7.37 (s, 1H), 7.32 (s, 1H), 4.07 (t, J = 7.1 Hz, 2H), 3.77 (s, 3H), 1.71 (m, 2H), 1.17 (m, 2H), 0.77 (t, J = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, D_2O) δ −122.7 (s, 1F); ^{13}C NMR (75 MHz, D_2O) δ 135.73, 123.38, 122.08, 49.09, 35.51, 31.11, 18.59, 12.54; IR (KBr): ν = 3448, 3082, 2961, 2935, 2874, 2046, 1836, 1743, 1571, 1465, 1378, 1236, 1169, 846, 753, 652, 622 cm^{-1}; HRMS (EI, m/z): calcd for $[cation]^+$, 139.1230; found 139.1237.

Acknowledgements

We thank the Chinese Academy of Sciences (Hundreds of Talents Program) and the National Natural Science Foundation (20972179, 21032006) for financial support. We thank Dr. Shubin Liu of University of North Carolina for proofreading of the manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.08.003.

References

[1] (a) S.K. Chang, D.V. Engen, E. Fan, A.D. Hamilton, J. Am. Chem. Soc. 113 (1991) 7640–7645;
(b) C.Y. Hung, T. Höphner, R.P. Thummel, J. Am. Chem. Soc. 115 (1993) 12601–12602;
(c) C.-Y. Huang, L.A. Cabell, E.V. Anslyn, J. Am. Chem. Soc. 116 (1994) 2778–2792;
(d) J.T. Koh, V.W. Cornish, P.G. Schultz, Biochemistry 36 (1997) 11314–11322;
(e) L.J. Prins, J.J. Verhage, F. Jong, P. Timmerman, D.N. Reinhoudt, Chem. Eur. J. 8 (2002) 2302–2313;
(f) J.S. Nowick, Acc. Chem. Res. 41 (2008) 1319–1330;
(g) K. Ariga, T. Kunitake, Acc. Chem. Res. 31 (1998) 371–378.

[2] (a) P.A. Kollman, L.C. Allen, Chem. Rev. 72 (1972) 283–303;
(b) G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441–449.

[3] (a) L. Shimoni, J.P. Glusker, Struct. Chem. 5 (1994) 383–397;
(b) J.A.K. Howard, V.J. Hoy, D. O'Hagan, G.T. Smith, Tetrahedron 52 (1996) 12613–12622;
(c) J.D. Dunitz, R. Taylor, Chem. Eur. J. 3 (1997) 89–98;
(d) L. Brammer, E.A. Bruton, P. Sherwood, Cryst. Growth Des. 1 (2001) 277–290;
(e) A.R. Choudhury, R.G. Bhat, T.N. Guru Row, S. Chandrasekaran, Cryst. Growth Des. 7 (2007) 844–846.

[4] A. Allerhand, P.R. Schleyer, J. Am. Chem. Soc. 85 (1963) 1233–1237.

[5] E.V. Anslyn, D.A. Dougherty, Modern Physical Organic Chemistry, University Science Books, Sausalito, California, 2006 (Chapter 3).

[6] (a) A. Allerhand, P.R. Schleyer, J. Am. Chem. Soc. 85 (1963) 1715–1723;
(b) C.J. Creswell, A.L. Allred, J. Am. Chem. Soc. 85 (1963) 1723–1726.

[7] (a) Z-Q. Zhu, S. Xiang, Q.-Y. Chen, C. Chen, Z. Zeng, Y.-P. Cui, J.-C. Xiao, Chem. Commun. (2008) 5016–5018;
(b) C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, Eur. J. Inorg. Chem. (2010) 3419–3422.

[8] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, Green Chem. 5 (2003) 361–363.

[9] CCDC 709062 contains the supplementary crystallographic data for the compound **2a**. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

[10] V.V. Grushin, W.J. Marshall, Angew. Chem. Int. Ed. 41 (2002) 4476–4479.

[11] A. Bondi, J. Phys. Chem. 68 (1964) 441–451.