Supplementary Information

On the spontaneous carboxylation of 1-butyl-3methylimidazolium-acetate by carbon dioxide

Marcel Besnard ^a *, M. Isabel Cabaço ^{b,c}, Fabián Vaca Chávez ^d, Noël Pinaud ^e, Pedro J. Sebastião ^{b,d}, João A. P. Coutinho ^f, Yann Danten ^a

^a GSM Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération 33405 Talence Cedex, France

^b Departamento de Física, Instituto Superior Técnico, UTL, Av. Rovisco Pais 1049-001 Lisboa, Portugal

^c Centro de Física Atómica da UL, Av. Prof. Gama Pinto 2, 1649-003 Lisboa

^d Centro de Física da Matéria Condensada da UL, Av. Prof. Gama Pinto 2, 1694-003 Lisboa

^e CESAMO Institut des Sciences Moléculaires, CNRS (UMR 5255), Université Bordeaux I, 351, Cours de la Libération 33405 Talence Cedex, France.

^fCICECO, Departamento de Química, Universidade de Aveiro 3810-193 Aveiro, Portugal

Experimental conditions

The ionic liquid originated from Solvionic (purity greater than 98%), the CO_2 from Air Liquide (purity 99.995%) and the ¹³C labelled CO_2 from Aldrich (99 atom %). The IL was dried at 353 K under a primary vacuum during more than 48 hours under a continuous stirring. The water content measured by Karl-Fisher titration was 530ppm. Carbon dioxide was then introduced under a 0.1 MPa pressure and the solution was stirred about 30 hours.

The Raman spectra were measured with a resolution of 1.8 cm^{-1} in the spectral range 200 cm⁻¹ to 3400 cm⁻¹ on a Jobin-Yvon HR8000 spectrometer with a Spectra Physics krypton-ion laser source operating at a wavelength of 752.5 nm with a power of 6 mW using a back-scattering geometry. Typical spectra have been collected during 60 seconds and accumulated 100 times to improve the signal to noise ratio. In order to take accurate line positions the spectrometer has been calibrated by recording different emission lines of a neon bulb. Infrared absorption and ATR spectra have been measured on a Nicolet- Thermo Optek 6700 interferometer with a 4 cm⁻¹ resolution in the spectral range 400 cm⁻¹ to 4000 cm⁻¹ after collecting 50 scans. We use KRS5 windows for the absorption cell and a lead spacer to have a path-length of 25 micrometer which has been controlled on the empty cell using the standard method based upon interferences fringes.

DFT calculations have been carried out using the Gaussian-03 suite ¹. The optimized structures of an imidazolium carboxylate molecule interacting with a single Bmim Ac ion pair) have been achieved from the DFT procedure using the B3LYP functional using the 6-31+G(d,p) basis set. The optimized geometries have been obtained using a very tight criterion of convergence. The interaction energy values (ΔE_{int}) has been evaluated and corrected from the basis set superposition error (BSSE) according to the site-site function (SSFC) scheme ²⁻⁶. The vibrational analysis carried out from this structure using the standard Wilson FG matrix formalism based on the harmonic force field approximation ⁷ leads to the main fundamental calculated transitions displayed in Table 1. In this table the calculated transitions for the imidazolium carboxylate involving the labelled ¹³C in the COO group are also reported.

The NMR measurements were performed on Bruker AVANCE III spectrometer operating at 600 MHz Larmor frequency for ¹H, 150 MHz for ¹³C and 60 MHz for ¹⁵N (France). The ¹H spectra were collected after a 30° pulse with a 90° pulse (t_{90}) of 8 µs. The number of scans was ranging from 512 to 1024 with a relaxation delay (d1) of 1 s. The ¹³C spectra was acquired after a t_{90} =15 µs and d1=3 s. The ¹³C proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. Finally these measurements have been completed by performing 2D NMR measurements using the standard ¹³C -¹³C - INADEQUATE sequence on the AVANCE II 400 MHz with a BBO probe at 400 MHz and 100 MHz for ¹H and ¹³C. The samples were contained in standard 5 mm tubes filled with an external lock solvent of D₂O and calibrated with the H₂O signal at 4.8 ppm. The NMR spectra of the samples did not evolve in time as seen

from the comparison of the spectra recorded for fresh solutions, just after filling the tube, with those measured at regular interval period during more than 6 months, at exception of the line assigned to the acetic acid. In addition, spectra collected in the two different laboratories were always found in total agreement.

Measurements were also performed in a Bruker AVANCE II spectrometer at 300 MHz Larmor frequency for ¹H, 75 MHz for ¹³C (Portugal). The ¹H spectra were recorded after a single pulse, t_{90} =14 µs and d1=5 s. The number of scans has been ranging from 512 to 1024. The ¹³C spectra have been acquired after a single pulse with t_{90} =11 µs and d1=3 s. The ¹³C proton decoupled spectra was measured using the standard WALTZ-16 decoupling sequence. The temperature of the samples was regulated and stabilized to within ±0.5 K using gas flow.

Electronic Supplementary Material (ESI) for Chemical Communications This journal is The Royal Society of Chemistry 2011

NMR spectra



Fig. 1 Comparison of the ¹H NMR spectra (600 MHz, 14.1 T, 16 scans) of the pure Bmim Ac (a) with that of the CO₂-Bmim Ac mixture (b). The time evolution of the resonance line of the proton of the COOH group of the nascent acetic in the mixture is displayed (c): 3 days (red), 30 days (black) and 40 days (blue) after preparation



Fig. 2 Comparison of the ¹H decoupled ¹³C NMR spectrum of pure Bmim Ac (a) with the ¹H decoupled (b) and the ¹H non-decoupled (c) ¹³C NMR spectra of the CO₂-Bmim Ac mixture. The spectra have been performed at 600 MHz, 14.1 T, 4096 scans.

Table SI1: Assignment of the Raman bands of the acetate anion in Bmim Ac (pure and mixture) and in aqueous solution of sodium acetate (1 mol dm⁻³). The assignment of the bands of the anion have been taken from ⁸⁻¹⁵ and for the cation from ¹⁶⁻¹⁹. Only the perturbed bands of the cation in the mixture are presented here.

Acetate anion			Bmim cation			
xCO2=0	xCO2=0.49	Assignement	xCO2=0	xCO2=0.49 Assignement		
454 (w P)	454 (ww)	rock // COO	328 (m,P) 418(m,P)		b (CH ₃ (N), CH ₂ (N)), δ CCCC b (CH ₃ (N), CH ₂ (N),CH ₃)	
434 (w,1)	434 (VW)	rock \perp COO	603 (m,P)		b (ring op), v iph ($CH_2(N)$, $CH_3(N)$)	
637 (m,P)	637 (w,P)	b OCO				
			627 (w,P)		b (ring op), v iph ($CH_2(N)$, $CH_3(N)$)	
			659 (vw)		b Ring op), ν (CH ₃ (N))	
			700 (vw)		v oph ($CH_2(N), CH_3(N)$)	
	794(w,P)	b OCO ^[a]	811 (w,P)		v sym (chain CC), b iph (ring (HCCH,	
			828 (m,P)		b iph (ring HCHH, NC(H)N op), v sym (chain CC)	
902 (s,P)	910 (m,P)	v CC	882 (m,P)		v sym ($CH_2CH_2CH_3CCC$)	
			907(w,P) 1020 (vs,P)	1020 (s,P)	v sym (CH ₂ CH ₂ CH ₃ CCC) v (ring CN ip iph, CH ₂ (N), CH ₂ CH ₂ CC)	
			1056 (w)		v asym (chain CCC)	
			1096 (w)		b ((N)CH ₃ CH),v asym (ring CN)	
			1117 (m,P)		v sym (chain CCC)	
			1132(vw) 1307 (sh.w)	1206(sh m)	v (chain CC), b (butyl CH)	
	1323(s.P)	v sym COO ^[a]	1507 (sii,w)	1300(811,111)		
1326 (m,P)	1323(s,P)	b CH ₃				
1382 (vs,P)	1381 (s,P) ^[b]	v sym COO	1339 (s,P)	1336(s,P)	v CH_3 (N), v CH_2 (N), v sym ip ring	
			1390 (m,P)	1390(m,P)	v CCCC	
			1416 (vs,P)	1417 (m,P)	v asym ip ring, v CH_3 (N)	
			1429 (w,P)	1433 (m,P)	v asym ip ring, v CH_3 (N)	
			1447 (m,P)	1445 (vs,P)	v sym ip ring	
			1461 (s,P)	1458 (vs,P)	v ring CH ₃ CN	
			1479 (III,F)	1470 (III,F) 1510 (vw)		
			1568 (w,P)	1568 (w,P)	v CH ₃ (N), v CH ₂ (N), v asym ip ring	
1582(sh,w)	1672 (w,D)	v asymCOO v asymCOO ^[a]				
			2833 (w,P)	2838(vw,P)		
			2874 (s,P)	2876 (s,P)	v sym CH ₃ HCH (terminal), v sym $CH_{3}HCH$	
2917(vs,P)	2936(vs,P)	ν sym CH ₃	2917 (vs,P)	2917 (s,P)	v asym ethyl HCH	
			2941 (m,P)	2939 (vs,P)	v sym CH ₃ (N) HCH	
			2961 (s,P) ^[d]	2968(s,P)	v asym propyl HCH	
			2995(m,P)	2999(w,P)		
			3027 (w,D) $3074 (w,D)^{[e]}$	3023(m,D) ~ $3097(m,P)$	v asym CH ₂ (N)HCH ^[g]	
			$3150(vw.P)^{[f]}$	~3155(w,P)	v sym ring HCCH, v NC(H)N CH ^[g]	

Reported values are cm⁻¹. P-polarised and D-depolarised profiles; rock \perp and rock //, rocking perpendicular and parallel to the CCOO plane; b, bending; v stretching; sym and asym, symmetric and asymmetric vibrations, respectively; ip and op, in-plane and out-of-plane; iph and oph, in-phase and outof-phase vibrations, respectively.

- ^[a] new bands (see Table 1)
- ^[b] band contributing to the intense upper component of the Fermi dyad
- ^[c] band contributing to the broad feature observed in the domain of the water bending
- ^[d] 2970 cm⁻¹ for $\operatorname{Bmim} \operatorname{PF}_6$ and $\operatorname{Bmim} \operatorname{BF}_4$

^[e] 3120 cm⁻¹ for Bmin PF₆ and Bmin BF₄ ^[f] 3175 cm⁻¹ for Bmin PF₆ and Bmin BF₄ ^[g] This assignment is commonly accepted, however it has been revisited recently and a new kind of assignment ^[g] This assignment is commonly accepted, however it has been revisited recently and a new kind of assignment has been proposed: ^[d] is assigned to the v iph $C_{(4,5)}$ H, v $C_{(2)}$ H and v oph $C_{(4,5)}$ H modes; ^[e] is assigned to overtones and combination of the ring modes in Fermi resonance ¹⁹⁻²¹

Table SI2. ¹H NMR and ¹³C NMR chemical shifts (δ , ppm) of the pure 1-butyl-3methylimidazolium acetate (Bmim Ac) and of the solution obtained by mixing CO₂ with Bmim Ac at 298K under 0.1MPa. The coupling constants J (Hz) are given in parentheses.

atom	Bmim Ac		CO ₂ -Bmim Ac				
	¹ H	¹³ C	$^{1}\mathrm{H}$	$^{1}\mathrm{H}$	¹³ C	¹³ C	
				secondar lines	у	secondary lines	
9	0.72	13.10 (124)	0.72		13.10 (125)	13.25 (124)	
8	1.13	19.14 (126)	1.13		19.16 (127)	19.32 (125)	
12	1.64	25.53 (124)	1.69		24.81 (125)		
7	1.74	32.22 (128)	1.75		32.13 (128)	32.88 (127)	
10	4.11	35.49 (143)	4.08	4.13	35.43 (143)	36.65 (143)	
6	4.37	48.54 (143)	4.35	4.60	48.54 (143)	48.8 (138)	
4	8.52	124.1 (204)	8.36	8.31	124.2 (204)	123.4 (204)	
5	8.67	123.1 (204)	8.51	8.40	123.1 (204)	122.2 (204)	
2	10.88	138.6 (220)	10.67		138.9 (222)	141.6	
11		175.07			174.69	174. 7	
<i>C</i> OO ^a						155.3	
COOH ^b				15.95 -			
				12.3 ^c			

^a COO group of the carboxylate formed upon the reaction

^b COOH group of the acetic acid formed upon the reaction

^c The position of this resonance line evolves from 15.95 ppm (3 days after preparation) to 12.3 ppm (40 days after preparation of the mixture)

References

- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. V. Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. C. A., G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, in 'Gaussian 03 package', 2004.
- 2 S. F. Boys and F. Bernardi, *Mol. Phys*, 1970, **19**, 553.
- 3 K. Mierzwicki and Z. Latajka, Chem. Phys. Lett., 2003, 380, 654.
- 4 L. Tury and J. J. Dannenberg, J. Phys. Chem., 1993, 97, 2488.
- 5 P. Valiron and I. Mayer, Chem. Phys. Lett., 1997, 1997, 46.
- 6 J. C. White and E. R. Davidson, J. Chem. Phys., 1990, 93, 8029.
- 7 E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations', 1955.
- 8 K. Ito and H. J. Bernstein, Can. J. Chem., 1956, 34, 170.
- 9 E. Spinner, J. Chem. Soc. 1964, 4217.
- 10 M. Kakihana, M. Kotaka, and M. Okamoto, J. Phys. Chem, 1982, 86, 4385.
- 11 I. Paul, S. Kang, and E. Spinner, Aust. J. Chem., 1986, 39, 465.
- 12 M. Kakihana, T. Nagumo, M. Okamoto, and H. Kakihana, J. Phys. Chem, 1987, 91, 6128.
- 13 F. Quilès and A. Burneau, Vib. Spectrosc., 1998, 16, 105.
- 14 F. Quilès and A. Burneau, Vib. Spectrosc., 1998, 18, 61.
- 15 R. L. Frost and J. T. Kloprogge, J Mol. Struct., 2000, 526, 131.
- 16 R. Talaty, S. Raja, V. J. Storhaug, A. Dölle, and W. R. Carper, J. Phys. Chem. B, 2004, 108, 13177.
- 17 N. E. Heimer, R. E. D. Sesto, Z. Meng, J. S. Wilkes, and W. R. Carper, J. Mol. Liq., 2006, 124, 84.
- 18 R. Holomb, A. Martinelli, I. Albinsson, J. C. Lassègues, P. Johansson, and P. Jacobsson, J. Raman Spectrosc., 2008, 39, 793.
- 19 J.-C. Lassègues, J. Grondin, D. Cavagnat, and P. Johansson, J. Phys. Chem. A Lett., 2009, 113, 6419.
- 20 A. Wulf, K. Fumino, and R. Ludwig, J. Phys. Chem. A, 2010, 114, 685.
- 21 J. C. Lassègues, J. Grondin, D. Cavagnat, and P. Johansson, J. Phys. Chem. A, 2010, 114, 687.