Supplementary Material (ESI) for Chemical Communications

Constitutional dynamic systems of ionic and molecular liquids

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SUPPLEMENTAL INFORMATION

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I. Synthesis of IL 1

II. Representative NMRs

  a. 2:40% H2O at 35^{o} C

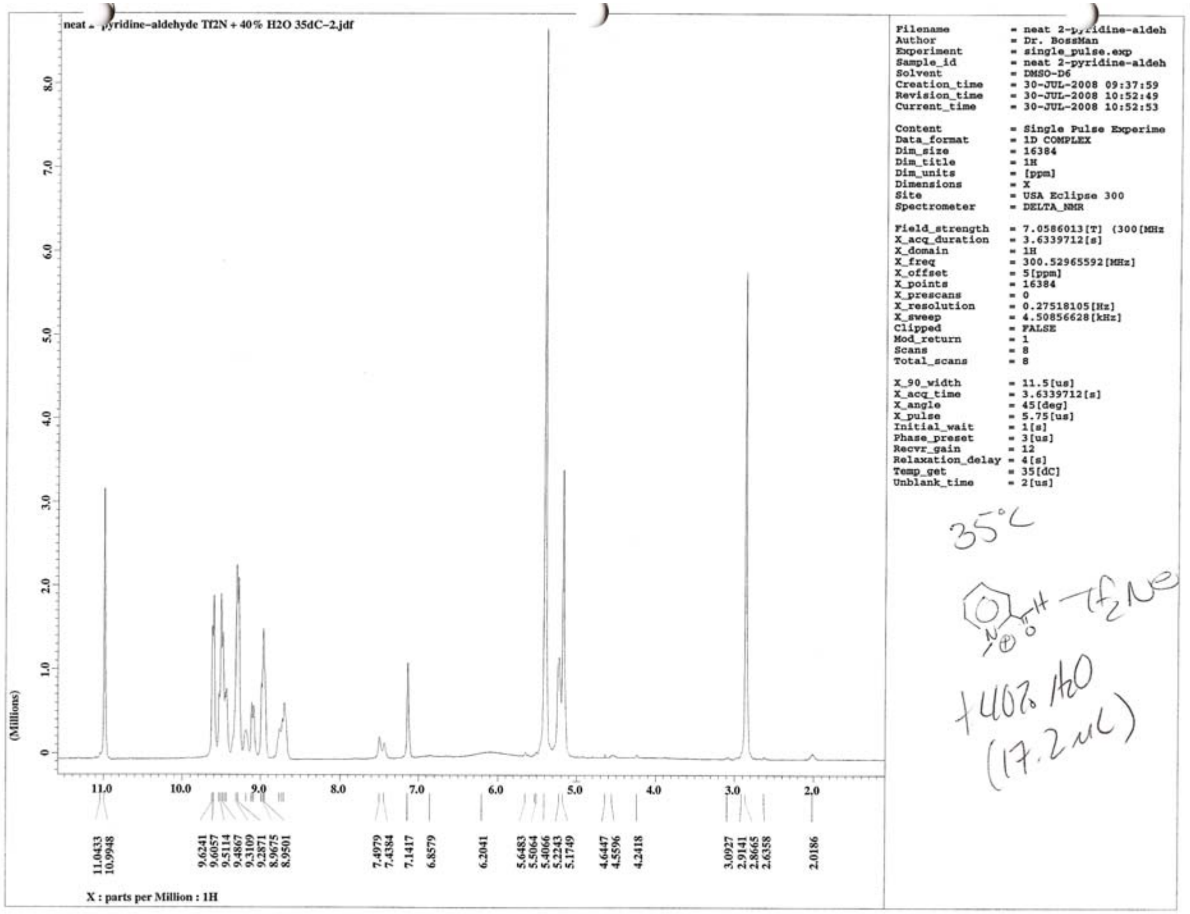
  b. 2:40% H2O at 85^{o} C

Synthesis of **1**.

A 100 mL, long-necked glass pressure bottle was charged with a magnetic stirbar, 10.0 g (93.4 mmol) of pyridine-2-carboxaldehyde (Aldrich, 99%), 25 mL of acetone (Fisher, reagent grade) and 39.8 g (280 mmol) of iodomethane (Aldrich, ReagentPlus, 99.5+%). The vessel was sealed and heated to 60^{o} C for 48h while stirring continuously [Caution! Heating a closed vessel – especially a glass one – is hazardous. Make sure the glass vessel is rated for pressure before use. Perform the heating operation in a fume hood and behind an approved safety shield.]. During the initial 24h period the initially yellow solution gradually became orange then wine red, and began to deposit a dark solid. The solid gradualy becomes so copious as to preclude further stirring. The pressure bottle was then cooled to room temperature, and the suspended solid quickly isolated by vacuum filtration. It was collected immediately and transferred to a flask for drying under vacuum and then storage under an atmosphere of dry N_2. [Solid left exposed to the atmosphere will gradually become mustard yellow as the iodide salt reacts with atmospheric moisture to form the corresponding *gem* diol.] Meanwhile, the acetone was stripped from the supernatent solution to recover an additional modest quantity of the desired N-methyl pyridinium 2- carboxaldehyde iodide salt. Collectively 22.2 grams (89.2 mmol, 95.5% yield) was recovered.

Under an atmosphere of dry nitrogen, 5.0g (20.0 mmol) of N-methyl pyridinium 2- carboxaldehyde iodide was dissolved/suspended in 50.0 mL of dry acetonitrile. To this was added, in one portion, 7.8 g (20.0 mmol) of $Ag(CF_3SO_2)_2N$ as a solid. A copious amount of solid AgI immediately precipitated, this being accompanied by a change to near-colorless on the part of the solution. The AgI was removed by filtration, and the supernatent allowed to stand exposed to fluorescent lighting (under N_2) for 3 days to allow traces of excess silver ion to be photolytically reduced. After this time, the greyish solution was filted through a small plug of celite and the solvent stripped in vacuo to afford **1** as a colorless, slightly viscous liquid in essentially quantitative yield (7.8 g).

Ionic liquid **2** is prepared in an analogous fashion using pyridine 3-carboxaldehyde.



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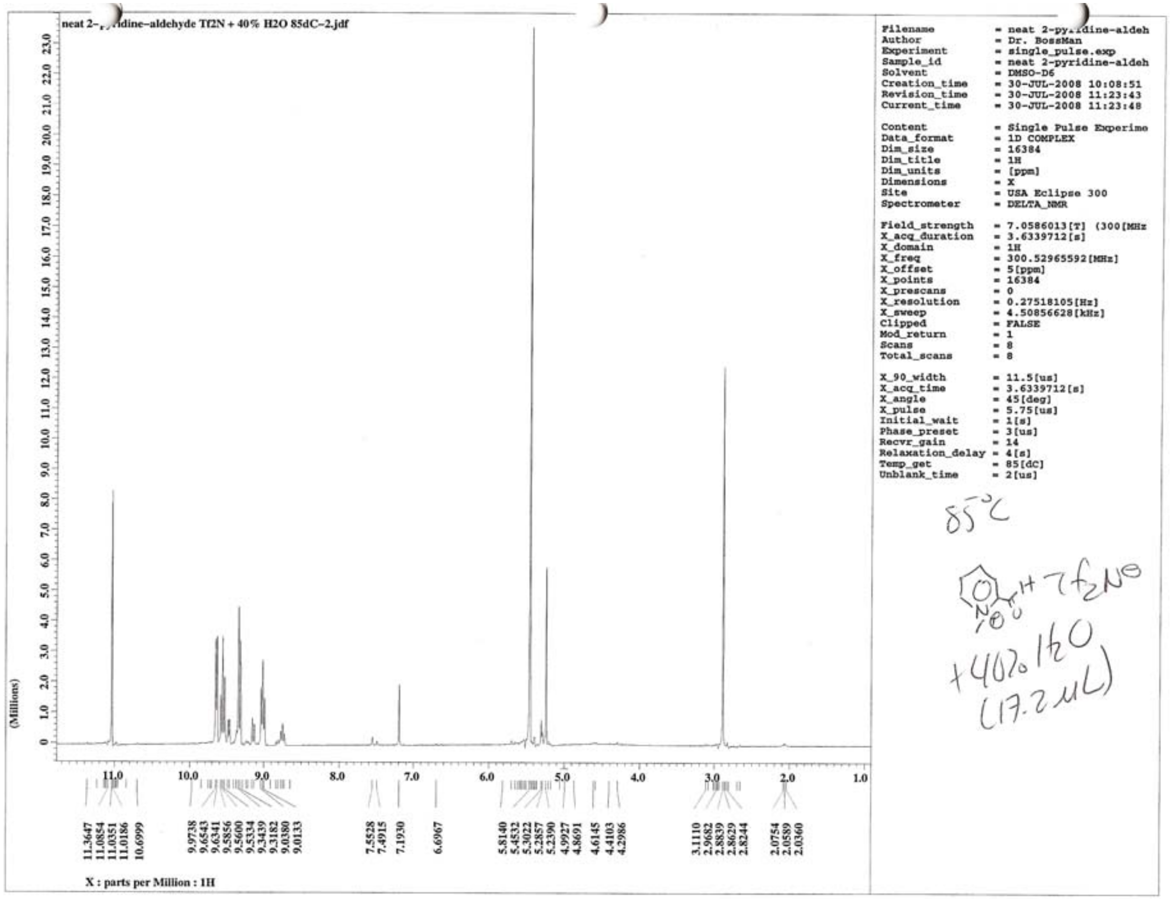
35°C

+40% H2O
(17.2 uL)

Note: (a) Large singlet @ 2.73 (uncorrected) => residual proton in the external d^6-dmso lock & reference; (b) Large singlets between 5-5.6 ppm which are the N-Me groups of the aldehyde, gem diol and bis(hemialdal). Broad resonance @ 6 ppm of ‘free’ water; (c) singlets between 7-7.5 ppm from the unique C-H of the gem diol and diastereomeric bis(hemialdal)s; (d) 8.5 – 9.8 aromatic H resonances from pyridinium ring, and (e) singlet at ca. 11 from aldehyde H.



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85°C

$Tf_2N^{\ominus}$

+40% H_2O
(17.2 µL)

Note the shift of the ‘free’ water peak to ca. 4.6 (uncorrected) and the general sharpening of all resonances; also note the relative decrease in peak sizes of the gem diol and bis(hemialdal) C-H resonances relative to the aldehydic C-H.