

## “Pro-fragrant ionic liquids with stable hemiacetal motifs: Water triggered release of fragrances” by H. Q. Nimal Gunaratne, \* Peter Nockemann and K. R. Seddon

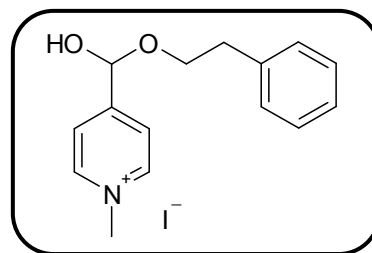
### Electronic supplementary information

Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich and used without further purification.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III 400 spectrometer (400 MHz). ESMS-mass spectroscopy measurements were carried out on a Waters LCT Premier instrument with an Advion TriVersa NanoMate injection system (cone voltage 50 V, source 120 °C). Both positive and negative ions were detected, with an  $m/z$  range of 50 to 1500. Samples were injected as dilute solutions in acetonitrile. All DSC scans were obtained using a TA DSC Q2000 model with a TA Refrigerated Cooling System 90 (RCS) and an autosampler. For each sample, three scans were run with scan rates of 5 °C  $\text{min}^{-1}$ .

### Synthesis of pro-fragrant ionic liquids

#### Synthesis of 2-phenylethanol tagged ionic liquid (2a):



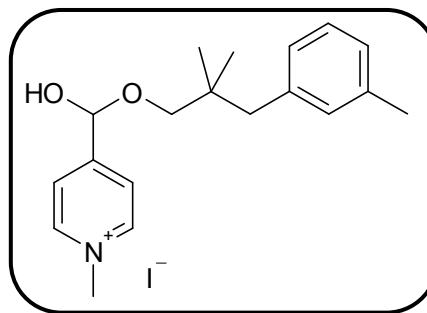
1-Methylpyridinium methiodide (0.5 g, 2 mmol) was dissolved in dry acetonitrile (5  $\text{cm}^3$ ) and treated with 2-phenylethanol (0.74 g, 6 mmol) at room temperature for 4 h. After careful evaporation of the solvent, the residue was washed with dry ether, with sonication, several times to yield (2a) as an off white solid (0.63 g, 85% yield). X-ray quality crystals were obtained by dissolving the material in dry acetonitrile followed by slow diffusion of dry ether.

$^1\text{H}$  NMR (in  $\text{dms}\text{-}d_6$ , 400 MHz):  $\delta$  8.92(d, PyH, 2H), 8.0(d, PyH, 2H), 7.54(d, OH, 1H), 7.20-7.32 (brm, ArH, 5H), 5.80(d,  $\text{CH}\text{OH}$ , 1H), 4.30(s,  $\text{N}^+\text{-Me}$ , 3H), 4.0-3.75{2xm,  $\text{OCH}_2$ {diastereotopic protons), 2H}, 2.85(t,  $\text{PhCH}_2$ , 2H)

ESMS: Cation;  $\text{C}_{15}\text{H}_{18}\text{NO}_2$  Calc. 244.1337, observed 244.1327

Anion; I, Calc. 126.9045, observed 126.9037

### Synthesis of majantol tagged ionic liquid (2b) :



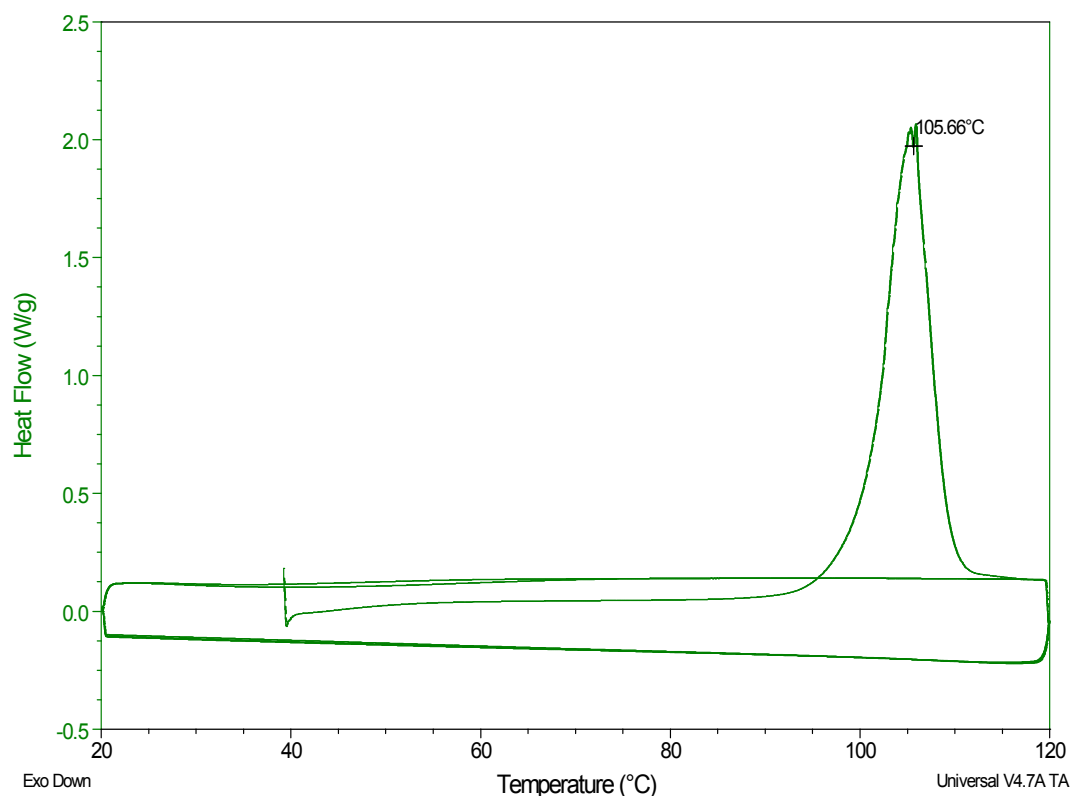
1-Methylpyridinium methiodide (0.5 g, 2 mmol) was dissolved in dry acetonitrile (5 cm<sup>3</sup>) and treated with majantol (1.07 g, 4 mmol) at room temperature for 4 h. After careful evaporation of the solvent, the residue was washed with dry ether, with sonication, several times to yield (2a) as a light brown viscous liquid (0.69 g, 81% yield).

<sup>1</sup>H NMR (in dms<sub>o</sub>-d<sub>6</sub>, 400 MHz): d 8.80(d, PyH, 2H), 8.20(d, PyH, 2H), 7.20-6.90 (brm, ArH, 5H), 5.80(broad signal, CHOH and OH, 2H), 4.35(s, N<sup>+</sup>-Me, 3H), 3.60 & 3.30 {2xd, OCH<sub>2</sub>(diastereotopic protons), 2H}, 2.65 (m, ArCH<sub>2</sub>, 2H), 2.30 (s, ArCH<sub>3</sub>, 3H), 0.90 (2xs, CH(CH<sub>3</sub>)<sub>2</sub>, 6H).

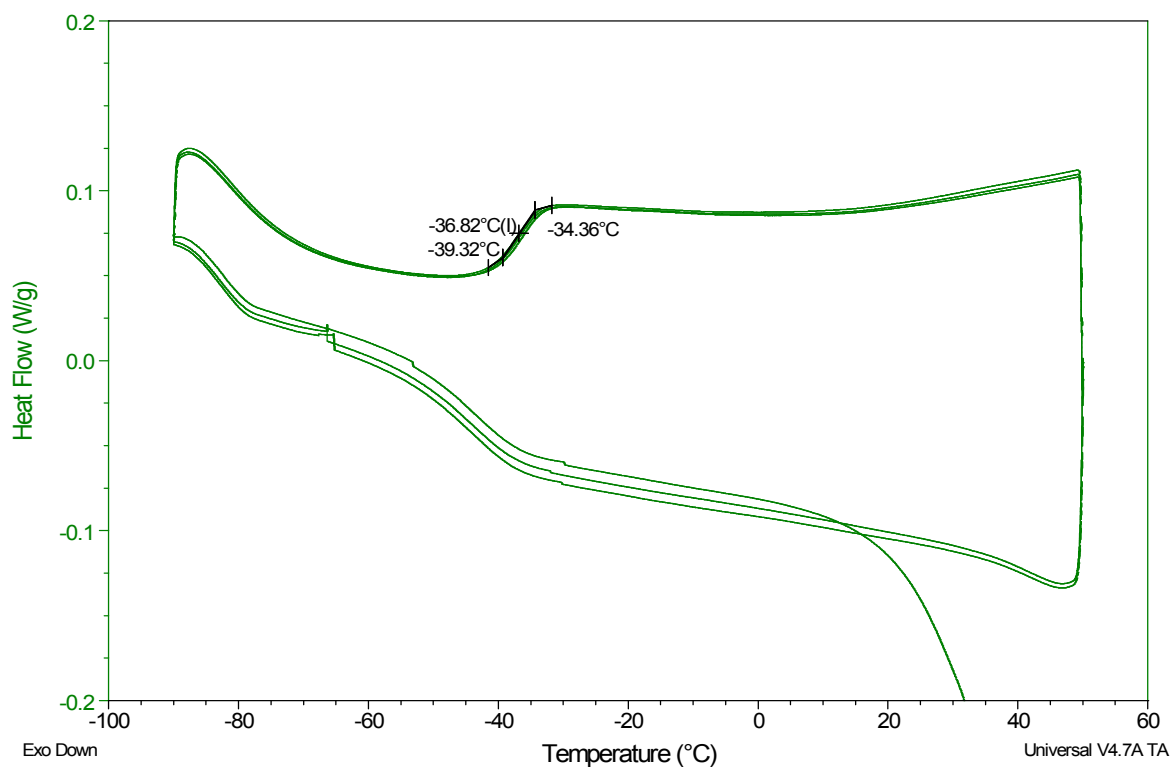
**ESMS:** Cation; C<sub>19</sub>H<sub>26</sub>NO<sub>2</sub> Calc. 300.1964, observed 300.1955

Anion; I, Calc. 126.9045, observed 126.9036

### Differential Scanning Calorimetry of pro-fragrant ionic liquids



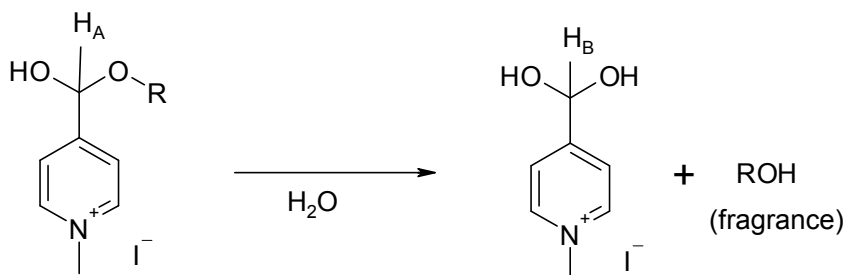
**Figure 1:** Second DSC scan of **2a** (solid), carried out with a scan rate of 5 °C m<sup>-1</sup>



**Figure 2:** DSC scans of **2b** (liquid), carried out with a scan rate of  $5\text{ }^{\circ}\text{C m}^{-1}$ ; A glass transition is seen at  $-36.8\text{ }^{\circ}\text{C}$ .

### Reaction profile plots (Figures 4 and 5)

These plots were constructed using time dependant NMR spectrometry. The  $^1\text{H}$  NMR integrals of protons  $\text{H}_\text{A}$  (in the starting materials, **SM**) and protons  $\text{H}_\text{B}$  (in the products, **P**) were obtained (see below).



Assuming the Integral of proton  $\text{H}_\text{A} = \text{I}_\text{A}$  and Integral of proton  $\text{H}_\text{B} = \text{I}_\text{B}$

$$\% \text{ Reaction (or Product) } = \text{I}_\text{B} / (\text{I}_\text{A} + \text{I}_\text{B})$$

### X-ray crystallographic data

Crystal Data for  $C_{15}H_{18}INO_2$  ( $M = 343.19$ ): monoclinic, space group  $P2_1/n$  (no. 14),  $a = 9.3649(2)$  Å,  $b = 15.0028(4)$  Å,  $c = 11.1821(7)$  Å,  $\beta = 92.996(7)^\circ$ ,  $V = 1568.93(11)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 100.15$  K,  $\mu(\text{MoK}\alpha) = 2.026$  mm<sup>-1</sup>,  $D_{\text{calc}} = 1.453$  g/mm<sup>3</sup>, 17143 reflections measured ( $6.16 \leq 2\theta \leq 54.9$ ), 3585 unique ( $R_{\text{int}} = 0.0152$ ,  $R_{\text{sigma}} = 0.0110$ ) which were used in all calculations. The final  $R_1$  was 0.0134 ( $>2\sigma(I)$ ) and  $wR_2$  was 0.0341 (all data). The crystal was kept at 100.15 K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.

2. Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.

3. Sheldrick, G.M. (2008). *Acta Cryst.* A64, 112-122.