

Intramolecular Cation- π Interactions Control the Conformation of Nonrestricted (Phenylalkyl)Pyridines

Isabella Richter, Jusaku Minari, Philip Axe, John P. Lowe, Kazuo Sakurai, Tony D. James, Steven D. Bull* and John S. Fossey*

E.Mail: s.d.bull@bath.ac.uk; j.fossey@bath.ac.uk

General

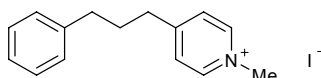
Solvents and reagents were reagent grade and were used without further purification. All melting points were measured using a Büchi 535 melting point apparatus and are reported uncorrected. Nuclear magnetic resonance spectra were run in chloroform-*d* using Bruker AVANCE 300 and Bruker AVANCE^{II} 500 spectrometers to acquire ¹H and ¹³C NMR spectra. All nOesy data were acquired using a Bruker AVANCE^{II} 500 spectrometers. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak as an internal standard in ¹H and ¹³C{¹H} NMR spectra, with coupling constants (*J*) expressed in Hertz. All Mass spectrums were recorded on a micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH) coupled to an Agilent Technologies 1200 LC system. Fluorescence measurements were performed using a Perkin-Elmer Luminescent Spectrophotometer LS50B, utilising Starna Silica (quartz) cuvetts with 10mm path lengths, four faces polished. Data was collected using the Perkin-Elmer FL Winlab software package. All solvents used in fluorescence measurements were HPLC or fluorescent grade, with samples analysed at a concentration of 10⁻⁶M.

Experimental

Representative procedure for *N*-methylation of pyridines **5**

Methyl iodide (0.5 mL, 8 mmol) was added to a solution of pyridine **5b** (0.5 mL, 2.6 mmol) dissolved in acetone (10 mL) and the resultant solution stirred at reflux for 1hr. After cooling to room temperature, the resultant precipitate was filtered off, washed with cold acetone and dried *in vacuo* to afford the desired *N*-methyl-pyridinium salt **6b** (0.89g, 2.61mmol, 99% yield) which was then recrystallised from EtOH/diethylether.

Representative data for 1-methyl-4-(3-phenylpropyl) pyridinium iodide **6b**



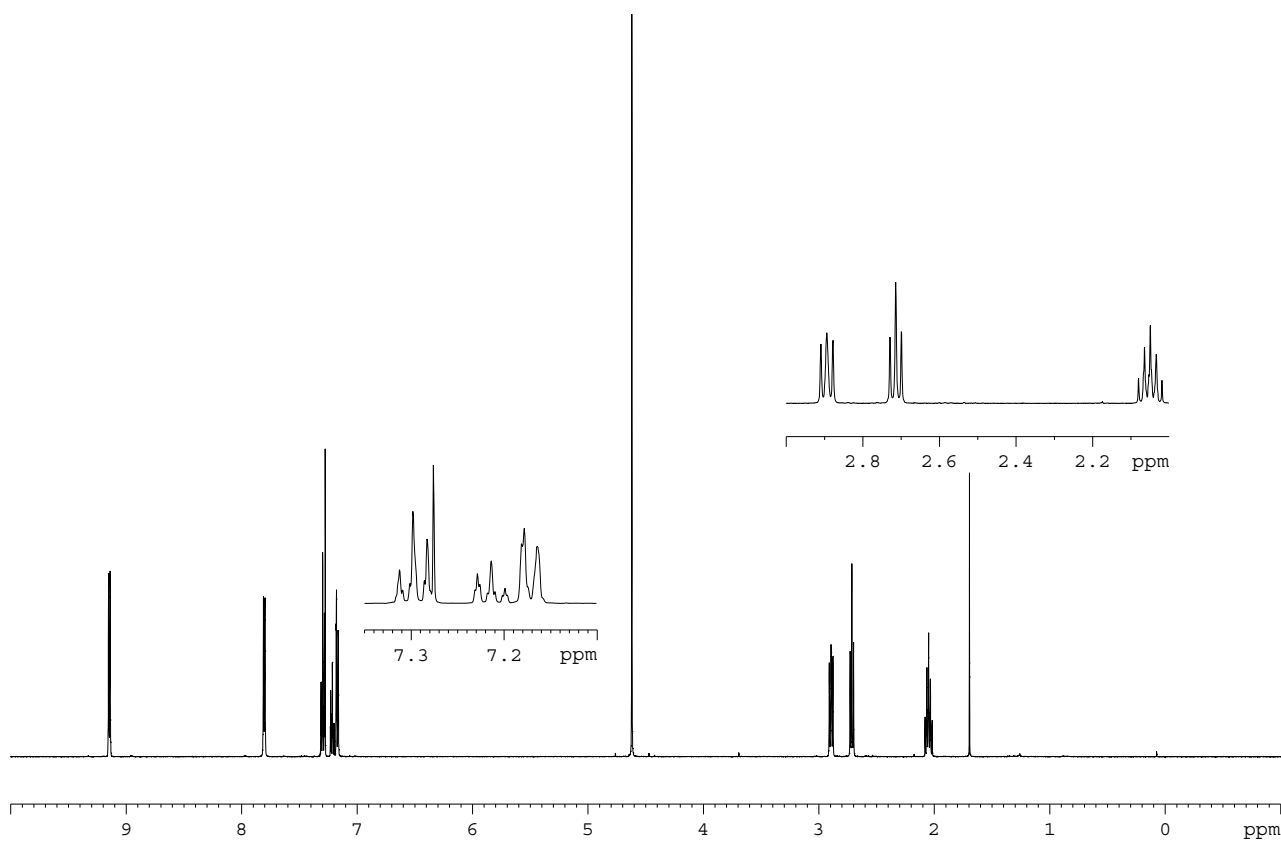
Yellow solid; yield 94%; mp 90-92 °C; ¹H NMR (δ ; 500 MHz; CDCl₃) 9.21 (2H, d, *J* = 6.6, Py-H₂), 7.77 (2H, d, *J* = 6.6, Py-H₃), 7.29 (2H, t, *J* = 7.4, Ph-H_{3'}), 7.21 (1H, t, *J* = 7.4, Ph-H_{4'}), 7.07 (2H, d, *J* = 7.5, Ph-H_{2'}), 4.60 (3H, s, N-CH₃), 2.82 (2H, t, *J* = 7.9, CH₂), 2.63 (2H, t, *J* = 7.3, CH₂), 2.06

Supplementary Material (ESI) for Chemical Communications

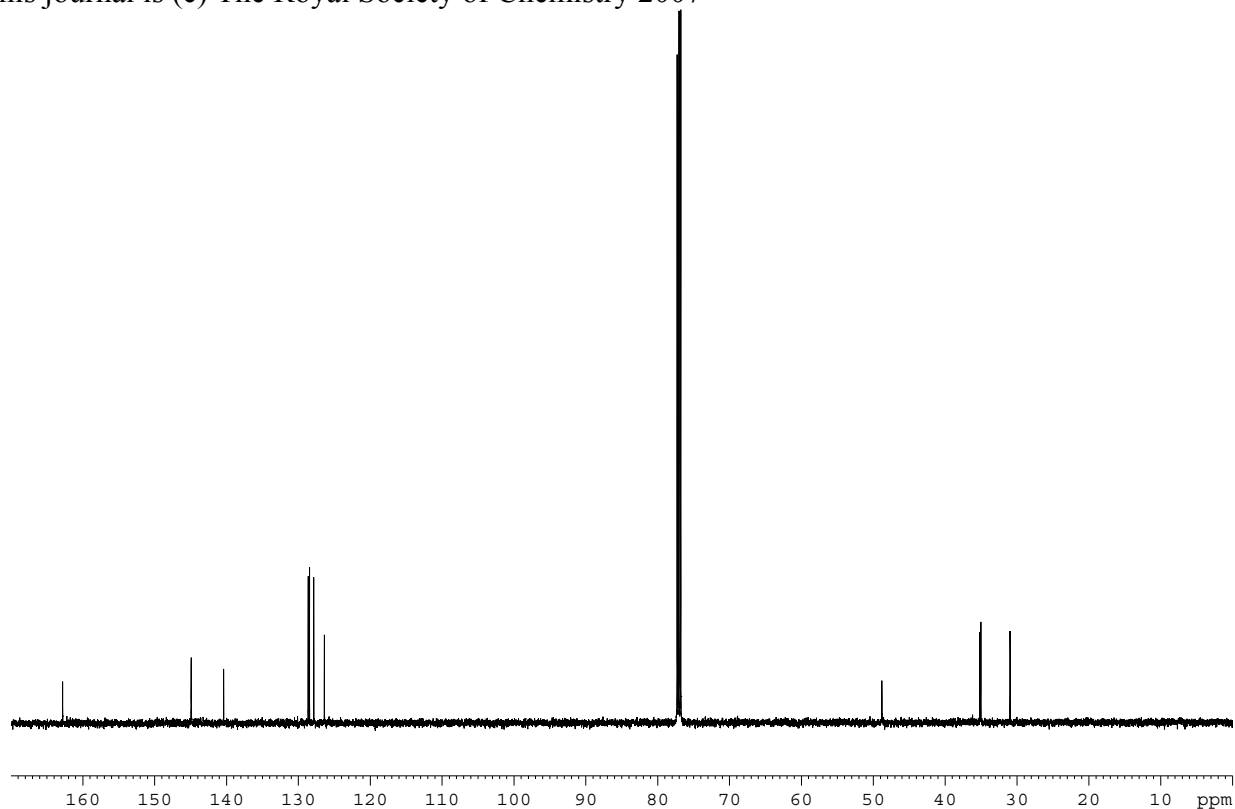
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(2H, app quin, $J = 7.7$, CH_2); ^{13}C NMR (δ ; 125 MHz; CDCl_3) 162.8 (Py- C_2), 144.9 (Py- C_4), 142.0 (Ph- $\text{C}_{1'}$), 128.65, 128.45, 127.87, 126.40, 48.81 (CH_3), 35.16 (2 x CH_2), 30.97 (CH_2); MS: $[\text{M}+\text{H}]^+$, m/z , (ESI, positive) found 198.1282. $\text{C}_{15}\text{H}_{18}\text{N}$ requires 198.1273.

^1H NMR spectrum of 1-methyl-4-(3-phenylpropyl) pyridinium iodide 6b



^{13}C NMR Spectrum of 1-methyl-4-(3-phenylpropyl) pyridinium iodide 6b



Details of nOesy Experiments on pyridines 5a-c and N-methyl-pyridinium salts 6a-c

General Procedure: nOesy spectra were acquired using a standard Bruker gradient selected 2D pulse sequence, with a mixing time of 1 s. Data were acquired with 2048 point in F2, 640 increments, and 20 scans per increment.

nOesy spectrum of N-methyl-pyridiniums 6a and 6c – See paper for nOesy spectra of N-methyl-pyridinium **6b**

<i>nOesy plot for 6a</i>	<i>nOesy plot for 6c</i>

