**An XRD and NMR crystallographic investigation of the structure of 2,6-lutidinium hydrogen fumarate**

*Emily K. Corletta, Helen Bladeb, Leslie P. Hughesb, Philip J. Sidebottomc, David Walkera, Richard I. Waltond and Steven P. Browna*

aDepartment of Physics, University of Warwick, Coventry, CV4 7AL;

bPharmaceutical Development AstraZeneca, Macclesfield, SK10 2NA;

cSyngenta, Jealott’s Hill, RG42 6EY;

dDepartment of Chemistry, University of Warwick, Coventry, CV4 7AL

Correspondence email: S.P.Brown@warwick.ac.uk

In the following, the names of all raw data files from the solid-state NMR measurements and different calculations are presented:

1. **Raw files for the PXRD experiments**

**Figure 2:** PXRD data of 2,6-lutidinium hydrogen fumarate recorded at 300 K with a MAC detector at the I11 beamline, λ = 0.8249 Å: **731249-mac-001.dat, 731250-mac-001.dat,** **RT-mac-summed.dat** (recorded on 27/04/2018)

**Figure 6:** PXRD data of 2,6-lutidinium hydrogen fumarate recorded at 100 K with a MAC detector at the I11 beamline, λ = 0.8249 Å: **732167-mac-001.dat, 732168-mac-001.dat,** **100-mac-summed.dat** (recorded on 27/04/2018)

**Figure 8:** Static transmission PXRD of 2,6-lutidinium hydrogen fumarate recorded with a 2D detector, λ = 1.5406 Å, screen shot of the 2D pattern: **WAXS.tiff** (recorded on 29/11/2017)

**Figure 10:** PXRD data of 2,6-lutidinium hydrogen fumarate recorded with a Panalytical X’Pert Pro MPD diffractometer, λ = 1.5406 Å, more than a week after first being ground to powder**: EC\_6-60\_2hr22\_1.xrdml** (recorded 23/08/2017)

1. **Raw files from NMR experiments**

**Figure 3:** MAS NMR spectra of 2,6-lutidinium hydrogen fumarate recorded immediately after grinding into a powder (a and b) and after storage as a powder for several weeks (c and d):

1. 1H (600 MHz) one-pulse MAS (60 kHz): **Fig3-H-clean [1]** (recorded 30/03/2018)
2. 1H (500 MHz)-13C CP MAS (12.5 kHz): **Fig3-HC-clean [2]** (recorded 25/08/2017)
3. 1H (600 MHz) one-pulse MAS (60 kHz): **Fig3-H-fum [3]** (recorded 29/03/2018)
4. 1H (500 MHz)-13C CP MAS (12.5 kHz): **Fig3-HC-fum [4]** (recorded 05/04/2017)

**Figure 4:** 1H (500 MHz)-13C CP (200 μs) HETCOR MAS (12.5 kHz) NMR spectra of 2,6-lutidinium hydrogen fumarate: **Fig4-HETCOR [1]** (recorded 25/08/2017)

**Figure 5:** 1H (600 MHz) DQ MAS (60 kHz) NMR spectrum of 2,6-lutidinium hydrogen fumarate recorded with one rotor period of BaBa recoupling: **Fig5-HDQ [1]** (recorded 30/03/2018)

**Figure 9:** 2D MAS (60 kHz) NMR spectra of 2,6-lutidinium hydrogen fumarate after storage as a powder for several weeks:

**(a)** 1H (600 MHz) DQ spectrum recorded with one rotor period of BaBa recoupling: **Fig8-HDQ-fum [1]** (recorded 24/08/2017)

**(b)** 14N-1H (600 MHz) HMQC spectrum with 8 rotor periods of R3 recoupling: **Fig8-HMQC-fum [2]** (recorded 28/05/2017)

**(a)** 1H (600 MHz) SQ NOESY spectrum with tmix = 300 ms: **Fig8-HSQ-fum [3]** (recorded 15/12/2017)

**Figure S5:** 1H (500 MHz)-13C CP (200 μs) HETCOR MAS (12.5 kHz) NMR spectra of 2,6-lutidinium hydrogen fumarate with fumaric acid present: **FigS5-HETCOR [1]** (recorded 25/08/2017)

**Figure S6:** 1H (400 MHz, one pulse) NMR spectra of 2,6-lutidinium hydrogen fumarate dissolved in d6-DMSO:

**(blue)** old powder: **FigS6-sol-gr [1]** (recorded 06/06/2018)

**(red)** block crystal: **FigS6-sol-block [2]** (recorded 06/06/2018)

1. **For the calculations, the initial CIF file, the CIF file after geometry optimisation (with and without varying unit cell) and the magres-files for the full crystal structure and isolated molecules**

MIBYEB.cif (as determined by single-crystal X-ray diffraction)

MIBYEB\_opt.cif

MIBYEB\_opt\_var-uc.cif

MIBYEB\_NMR.magres

MIBYEB\_isolated\_fumarate.magres

MIBYEB\_isolated\_26lutidinium.magres

LF26nw.cif (as determined by single-crystal X-ray diffraction)

LF26nw\_opt.cif

LF26nw\_opt\_var-uc.cif

LF26nw\_NMR.magres

1. **TGA and DSC data**

**Figure S7:** DSC of small plate crystals of 2,6-lutidinium hydrogen fumarate: **DSC\_plates.001** (recorded 07/02/2018)

**Figure 11:** TGA of 2,6-lutidinium hydrogen fumarate powder recorded at 70°C: **blank\_25-70\_N2.txt, 26lf\_powder.txt** (recorded 16/06/2018)