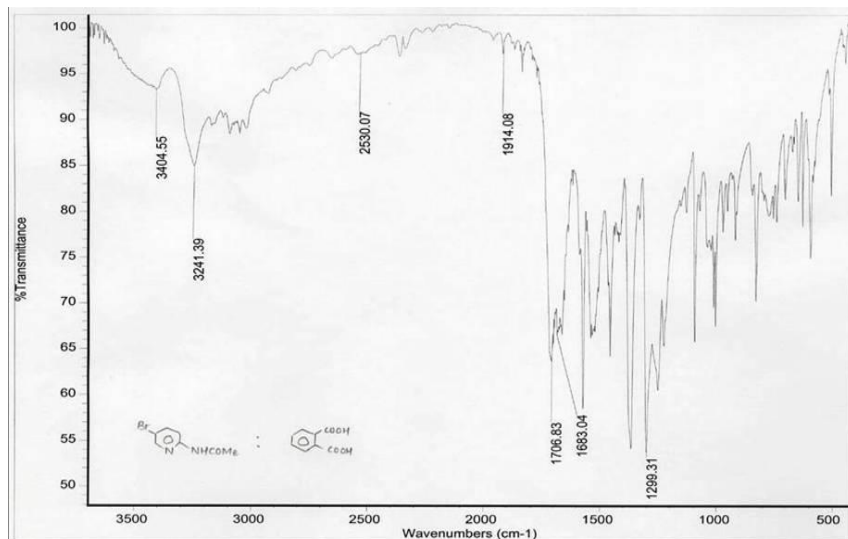
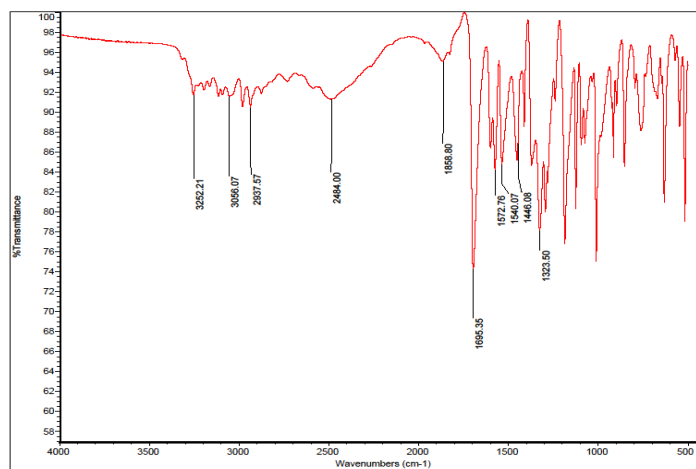


Two representative IR spectra



IR spectrum of the attempted co-crystallization of 2-acetamido-5-bromopyridine & phthalic acid, **f12** (no reaction).



IR spectrum of the successful 2-propionamido-5-bromopyridine & succinic acid, **d14**.

X-ray crystallography

All datasets were collected on Bruker Kappa APEX II system, with the exception of **D13**, which was collected on a SMART APEX II system. All datasets were collected at 120 K, with the exception of **D11** and **F14**, which were collected at 100 K. Oxford Cryostream low-temperature devices were used to control temperature. MoK α radiation was used for all datasets. Data were collected using APEX2 software.^(a) Initial cell constants were found by small widely separated “matrix” runs. Data collection strategies were determined using COSMO.^(b) Scan speed and scan width were chosen based on scattering power and peak rocking curves.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,^(b) using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Unless otherwise indicated, datasets were corrected for absorption using the multi-scan procedure of SADABS.^(c)

Data were reduced with SHELXTL.^(d) The structures were solved in all cases by direct methods without incident. Unless otherwise noted, the coordinates for all amine, ammonium, and carboxylic acid hydrogens were allowed to refine; all other hydrogens were assigned to idealized positions and were allowed to ride. Unless otherwise noted, carboxylic acids were observed in the difference electron density map to retain their protonated state. All structures were fully ordered and none contained solvent or water of hydration.

A3 The difference electron density map clearly indicated that the 2-aminopyridine group was protonated. An absorption correction was attempted but did not significantly improve the fit. The material crystallizes in the noncentrosymmetric space group *Pn*. Friedel opposites were not merged; the value of 0.02(4) for the Flack parameter suggests that the correct enantiomorph has been chosen.

A15 The diacid sits on a crystallographic inversion center. The amine sits on a general position, giving overall stoichiometry 1 : 2 diacid : amine. The difference electron density map clearly indicated that the 2-aminopyridine group was protonated.

B1 The difference electron density map clearly indicated that the 2-aminopyridine group was protonated. The material crystallizes in the noncentrosymmetric space group *Pca2₁*. Friedel opposites were not merged; the value of -0.006(7) for the Flack parameter suggests that the correct enantiomorph has been chosen.

B5 The difference electron density map clearly indicated that the 2-aminopyridine group was protonated.

D13 The diacid sits on a crystallographic inversion center. The amine sits on a general position, giving overall stoichiometry 1 : 2 diacid : amine.

D11 The diacid sits on a crystallographic inversion center. The amine sits on a general position, giving overall stoichiometry 1 : 2 diacid : amine.

D6 The material crystallizes in a 1 : 1 mixture of acid : amine.

E9 The asymmetric unit contains two acid : amide pairs. For labelling purposes, each pair was included into one SHELXL RESIDUE.

E13 The diacid sits on a crystallographic inversion center. The amine sits on a general position, giving overall stoichiometry 1 : 2 diacid : amine.

F14 The diacid sits on a crystallographic inversion center. The amine sits on a general position, giving overall stoichiometry 1 : 2 diacid : amine.

- (a) APEXII v2009. 5-1, © 2009, Bruker Analytical X-ray Systems, Madison, WI.
- (b) COSMO v1. 60, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.
- (c) SAINT v7. 60a, © 1997 - 2008, Bruker Analytical X-ray Systems, Madison, WI.
- (d) SADABS v2008/1, © 2008, , Bruker Analytical X-ray Systems, Madison, WI.
- (e) SHELXTL v2008/4, © 2008, , Bruker Analytical X-ray Systems, Madison, WI.