

Electronic Supplementary Information for Multi-Component Crystals of 4-phenylpyridine: Competing Co-Crystal and Salt Formation.

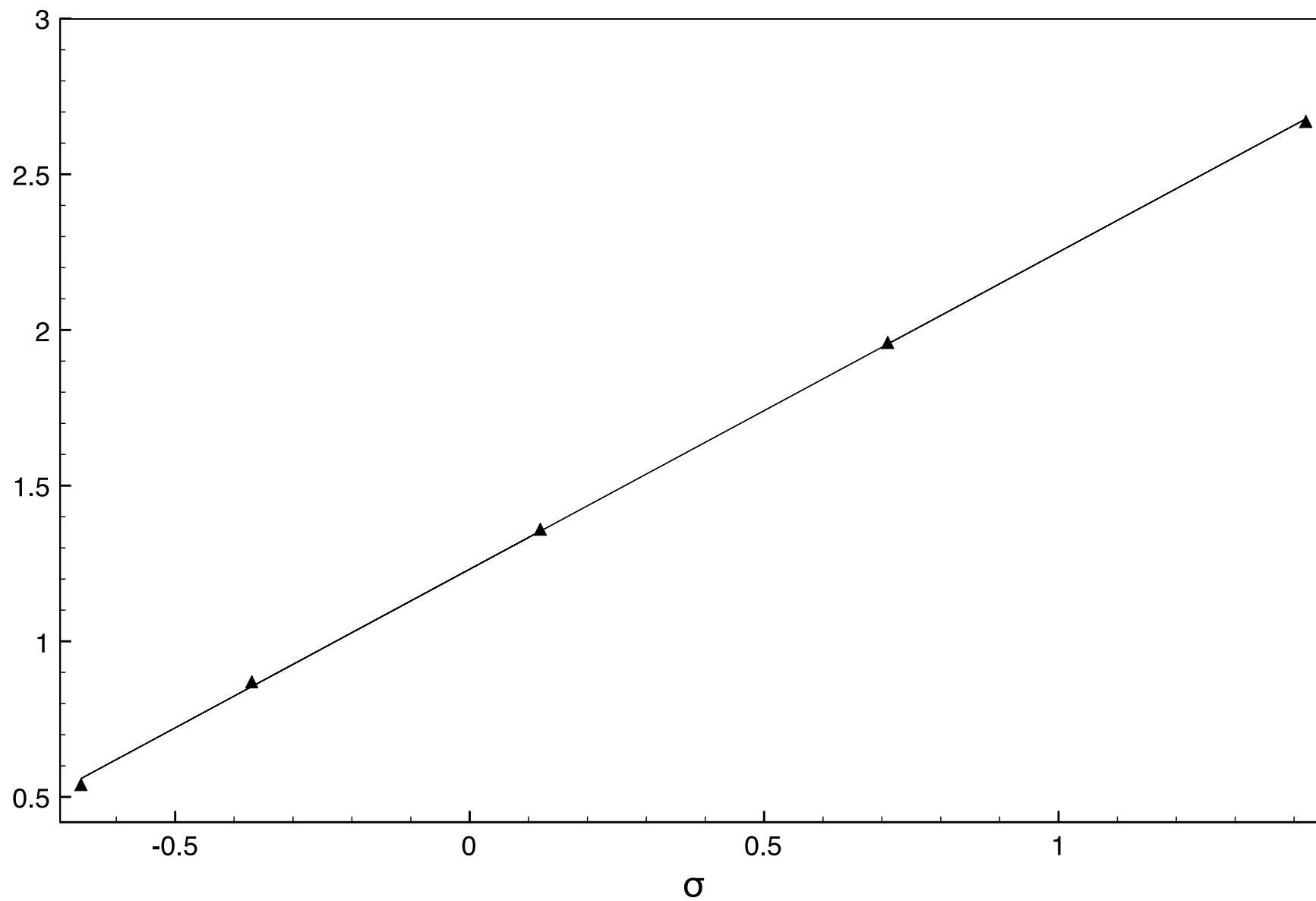


Figure S1. Plot of ΔpK_a of complex against the Hammett constant of the benzoic acid. Line of best fit to the data is plotted.

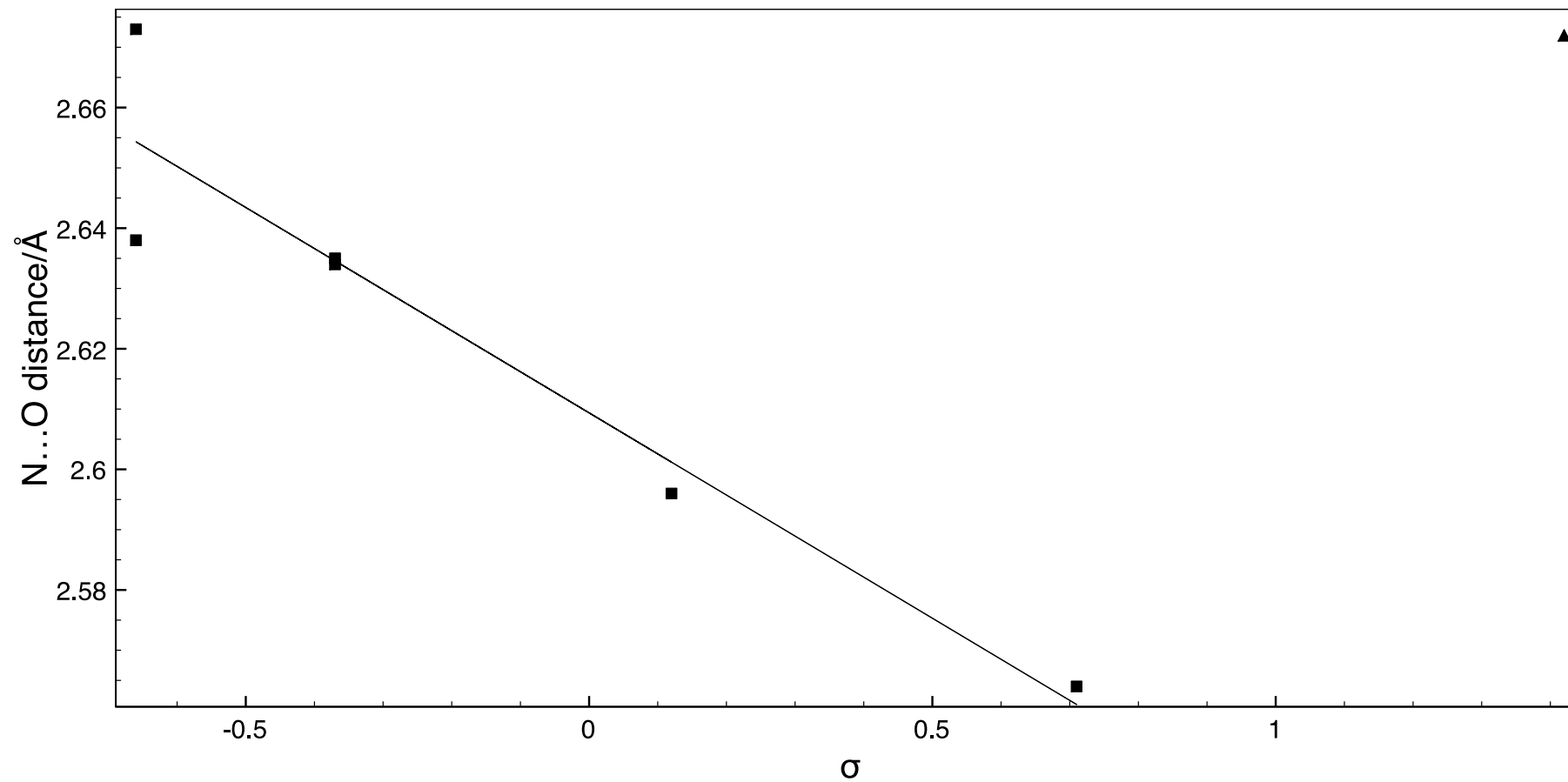


Figure S2. Plot of N...O distance against Hammett constant of the benzoic acids. Co-crystal forming systems marked by as squares, salt forming systems as triangles.

Table S1. OH and O...N distances in acid/pyridine interaction containing systems determined at multiple temperatures

System (REFCODE)	D _{OH} /Å (X-Ray Data)	D _{O...N} /Å (X-ray Data)	D _{OH} /Å (Neutron Data)	D _{O...N} /Å (Neutron Data)
3-fluorobenzoic acid/4-methoxypyridine (HOLJAU) [†]	Form I (100 K): 0.97(2) Form I (200 K): 1.02(3) Form II (100 K): 1.01(3) Form II (200 K): 1.00(3)	Form I (100 K): 2.643(2) Form I (200 K): 2.649(2) Form II (100 K): 2.621(2) Form II (200 K): 2.625(2)	Form I (30 K): 1.051(3) Form I (RT): 1.04(2) Form II (150 K): 1.063(7)	Form I (30 K): 2.629(2) Form I (RT): 2.66(1) Form II (150 K): 2.635(4)
4-aminosalicylic acid/isoniazid (URUDER, Z' = 2)	100 K: 0.97(3), 1.25(5) 120 K: 1.04(3), 1.13(5) 140 K: 0.9(5), 1.21(5) 150 K: 0.89(5), 1.24(5) 160 K: 0.97(5), 1.18(5) 180 K: 1.02(5), 1.15(5) 200 K: 0.88(3), 1.21(7) 220 K: 1.01(7), 1.01(5) 240 K: 1.02(5), 1.01(5) 260 K: 1.03(7), 1.03(7) 280 K: 0.96(5), 1.11(7)	100 K: 2.548(2), 2.574(2) 120 K: 2.547(2), 2.575(2) 140 K: 2.553(3), 2.575(3) 150 K: 2.554(3), 2.576(3) 160 K: 2.559(3), 2.580(3) 180 K: 2.562(3), 2.577(3) 200 K: 2.564(3), 2.580(3) 220 K: 2.560(3), 2.583(3) 240 K: 2.566(3), 2.581(3) 260 K: 2.568(3), 2.582(3) 280 K: 2.576(3), 2.585(3)	N/A	N/A
3,5-dinitrobenzoic acid/2,4-dimethylpyridine (PUHRIT, PUHROZ) [§]	H form (RT): 0.9(6) H form (80 K): 0.98(6) D form (RT): 0.9(5) D form (80K): 0.91(5)	H form (RT): 2.551(3) H form (80 K): 2.529(3) D form (RT): 2.563(3) D form (80K): 2.531(2)	N/A	N/A
3,5-dinitrobenzoic acid/4-(dimethylamino)benzoic acid/4,4'-bipyridine (QUQCUB)	100 K: 1.04(2) 200 K: 1.05(3) RT: 1.01(3)	100 K: 2.547(2) 200 K: 2.553(2) RT: 2.566(2)	40 K: 1.102(6) 100 K: 1.086(9) 200 K: 1.09(1) RT: 1.07(2)	40 K: 2.551(3) 100 K: 2.550(6) 200 K: 2.564(6) RT: 2.54(1)

[†]polymorphic system, [§]room temperature form classified as a salt in CSD (PUHRIT), low temperature and deuterated systems as co-crystals (PUHROZ).