Electronic Supplementary Material for CrystEngComm

A structural and spectroscopic investigation of the hydrochlorination of 4-benzylaniline: the interaction of anhydrous hydrogen chloride with chlorobenzene.

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Deposited Material

Table S1. Crystal data and structure refinement for 4-BA.

Identification code	4-BA	
Empirical formula	C13 H13 N	
Formula weight	183.24	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/c	
Unit cell dimensions	a = 9.5107(5) Å	α= 90°.
	b = 11.0673(6) Å	β= 108.888(2)°.
	c = 10.0425(6) Å	γ = 90°.
Volume	1000.13(10) $Å^3$	
Z	4	
Density (calculated)	1.217 Mg/m^3	
Absorption coefficient	0.071 mm^{-1}	
F(000)	392	
Crystal size	0.65 x 0.57 x 0.28 mm^3	
Theta range for data collection	2.26 to 27.48°.	
Index ranges	-11<=h<=12, -12<=k<=14, -13<=l<=9	
Reflections collected	11276	
Independent reflections	2265 [R(int) = 0.1061]	
Completeness to theta = 27.48°	98.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2265 / 0 / 135	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1273	
R indices (all data)	R1 = 0.0809, wR2 = 0.1386	
Largest diff. peak and hole	0.296 and -0.225 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 4-BA. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1087(2)	2264(2)	172(2)	24(1)
C(11)	2419(2)	2963(1)	1103(2)	21(1)
C(12)	2962(2)	3984(1)	629(2)	22(1)
C(13)	4182(2)	4613(2)	1489(2)	26(1)
C(14)	4900(2)	4241(2)	2871(2)	27(1)
C(15)	4359(2)	3217(2)	3359(2)	28(1)
C(16)	3145(2)	2600(2)	2488(2)	25(1)
C(21)	-110(2)	2106(1)	847(2)	22(1)
C(22)	-333(2)	1009(2)	1431(2)	26(1)
C(23)	-1421(2)	888(2)	2070(2)	31(1)
C(24)	-2305(2)	1870(2)	2139(2)	32(1)
C(25)	-2089(2)	2970(2)	1568(2)	32(1)
C(26)	-1006(2)	3083(2)	928(2)	28(1)
N(1)	6141(2)	4851(2)	3722(2)	42(1)

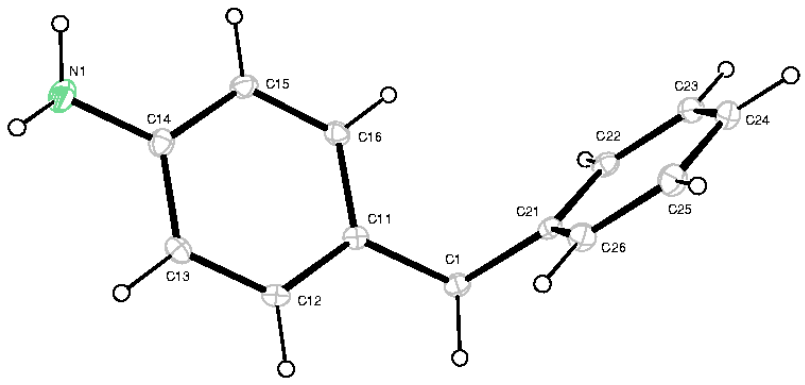


Table S3. Bond lengths [Å] and angles [°] for 4-BA.

C(1)-C(21)	1.511(2)	C(16)-H(16)	0.9500
C(1)-C(11)	1.521(2)	C(21)-C(22)	1.394(2)
C(1)-H(1A)	0.9900	C(21)-C(26)	1.395(2)
C(1)-H(1B)	0.9900	C(22)-C(23)	1.389(3)
C(11)-C(12)	1.390(2)	C(22)-H(22)	0.9500
C(11)-C(16)	1.396(2)	C(23)-C(24)	1.389(3)
C(12)-C(13)	1.388(2)	C(23)-H(23)	0.9500
C(12)-H(12)	0.9500	C(24)-C(25)	1.388(3)
C(13)-C(14)	1.396(2)	C(24)-H(24)	0.9500
C(13)-H(13)	0.9500	C(25)-C(26)	1.386(3)
C(14)-N(1)	1.388(2)	C(25)-H(25)	0.9500
C(14)-C(15)	1.397(2)	C(26)-H(26)	0.9500
C(15)-C(16)	1.383(2)	N(1)-H(111)	0.94(3)
C(15)-H(15)	0.9500	N(1)-H(112)	0.91(3)
C(21)-C(1)-C(11)	112.43(13)	C(11)-C(16)-H(16)	119.0
C(21)-C(1)-H(1A)	109.1	C(22)-C(21)-C(26)	118.11(16)
C(11)-C(1)-H(1A)	109.1	C(22)-C(21)-C(1)	121.89(15)
C(21)-C(1)-H(1B)	109.1	C(26)-C(21)-C(1)	119.98(15)
C(11)-C(1)-H(1B)	109.1	C(23)-C(22)-C(21)	121.05(16)
H(1A)-C(1)-H(1B)	107.8	C(23)-C(22)-H(22)	119.5
C(12)-C(11)-C(16)	117.16(15)	C(21)-C(22)-H(22)	119.5
C(12)-C(11)-C(1)	122.12(14)	C(22)-C(23)-C(24)	120.05(16)
C(16)-C(11)-C(1)	120.72(14)	C(22)-C(23)-H(23)	120.0
C(13)-C(12)-C(11)	121.56(15)	C(24)-C(23)-H(23)	120.0
C(13)-C(12)-H(12)	119.2	C(25)-C(24)-C(23)	119.50(16)
C(11)-C(12)-H(12)	119.2	C(25)-C(24)-H(24)	120.3
C(12)-C(13)-C(14)	120.81(15)	C(23)-C(24)-H(24)	120.3
C(12)-C(13)-H(13)	119.6	C(26)-C(25)-C(24)	120.14(16)
C(14)-C(13)-H(13)	119.6	C(26)-C(25)-H(25)	119.9
N(1)-C(14)-C(13)	120.92(17)	C(24)-C(25)-H(25)	119.9
N(1)-C(14)-C(15)	120.99(17)	C(25)-C(26)-C(21)	121.15(16)
C(13)-C(14)-C(15)	118.07(15)	C(25)-C(26)-H(26)	119.4
C(16)-C(15)-C(14)	120.39(15)	C(21)-C(26)-H(26)	119.4
C(16)-C(15)-H(15)	119.8	C(14)-N(1)-H(111)	114.7(17)
C(14)-C(15)-H(15)	119.8	C(14)-N(1)-H(112)	115.8(18)
C(15)-C(16)-C(11)	122.01(15)	H(111)-N(1)-H(112)	118(2)
C(15)-C(16)-H(16)	119.0		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3)for 4-BA. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	27(1)	24(1)	22(1)	-2(1)	6(1)	1(1)
C(11)	23(1)	19(1)	22(1)	-1(1)	8(1)	5(1)
C(12)	29(1)	20(1)	19(1)	1(1)	9(1)	6(1)
C(13)	31(1)	21(1)	30(1)	1(1)	15(1)	-1(1)
C(14)	24(1)	28(1)	28(1)	-4(1)	9(1)	-1(1)
C(15)	28(1)	30(1)	22(1)	4(1)	3(1)	2(1)
C(16)	28(1)	20(1)	26(1)	5(1)	9(1)	1(1)
C(21)	22(1)	22(1)	18(1)	-2(1)	1(1)	-1(1)
C(22)	29(1)	21(1)	23(1)	-2(1)	2(1)	0(1)
C(23)	35(1)	28(1)	26(1)	1(1)	6(1)	-10(1)
C(24)	25(1)	41(1)	28(1)	-3(1)	8(1)	-7(1)
C(25)	26(1)	33(1)	36(1)	0(1)	10(1)	6(1)
C(26)	29(1)	23(1)	31(1)	4(1)	7(1)	2(1)
N(1)	38(1)	41(1)	39(1)	-1(1)	1(1)	-14(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for 4-BA.

	x	y	z	U(eq)
H(1A)	665	2696	-733	29
H(1B)	1419	1458	-33	29
H(12)	2488	4259	-305	27
H(13)	4532	5305	1132	31
H(15)	4829	2944	4295	33
H(16)	2793	1908	2843	30
H(22)	269	334	1392	31
H(23)	-1561	133	2459	37
H(24)	-3052	1790	2573	38
H(25)	-2685	3646	1618	38
H(26)	-872	3838	536	34
H(111)	6190(30)	5670(30)	3490(30)	76(9)
H(112)	6440(30)	4650(30)	4650(30)	77(9)

Table S6. Torsion angles [°] for 4-BA.

C(21)-C(1)-C(11)-C(12)	-126.15(16)	C(1)-C(11)-C(16)-C(15)	179.98(15)
C(21)-C(1)-C(11)-C(16)	53.4(2)	C(11)-C(1)-C(21)-C(22)	-104.22(17)
C(16)-C(11)-C(12)-C(13)	0.6(2)	C(11)-C(1)-C(21)-C(26)	74.27(19)
C(1)-C(11)-C(12)-C(13)	-179.88(14)	C(26)-C(21)-C(22)-C(23)	0.3(2)
C(11)-C(12)-C(13)-C(14)	-0.5(2)	C(1)-C(21)-C(22)-C(23)	178.83(15)
C(12)-C(13)-C(14)-N(1)	178.42(16)	C(21)-C(22)-C(23)-C(24)	-0.2(2)
C(12)-C(13)-C(14)-C(15)	0.2(2)	C(22)-C(23)-C(24)-C(25)	-0.1(3)
N(1)-C(14)-C(15)-C(16)	-178.32(17)	C(23)-C(24)-C(25)-C(26)	0.4(3)
C(13)-C(14)-C(15)-C(16)	-0.1(3)	C(24)-C(25)-C(26)-C(21)	-0.4(3)
C(14)-C(15)-C(16)-C(11)	0.3(3)	C(22)-C(21)-C(26)-C(25)	0.0(2)
C(12)-C(11)-C(16)-C(15)	-0.5(2)	C(1)-C(21)-C(26)-C(25)	-178.56(15)

Table S7. Crystal data and structure refinement for 4-BA.HCl.

Identification code	4-BA.HCl	
Empirical formula	$C_{13}H_{14}ClN$	
Formula weight	219.70	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.5504(2) Å	α= 90°.
	b = 22.0930(8) Å	β= 106.4360(10)°.
	c = 9.7906(4) Å	γ = 90°.
Volume	1151.51(8) $Å^3$	
Z	4	
Density (calculated)	1.267 Mg/m^3	
Absorption coefficient	0.297 mm^{-1}	
F(000)	464	
Crystal size	0.53 x 0.25 x 0.10 mm^3	
Theta range for data collection	1.84 to 27.22°.	
Index ranges	-7<=h<=6, -24<=k<=28, -12<=l<=10	
Reflections collected	12278	
Independent reflections	2504 [R(int) = 0.0479]	
Completeness to theta = 27.22°	97.5 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9709 and 0.7150	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2504 / 0 / 148	
Goodness-of-fit on F^2	1.011	
R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0761	
R indices (all data)	R1 = 0.0550, wR2 = 0.0817	
Largest diff. peak and hole	0.29 and -0.23 e.$Å^{-3}$	

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for 4-BA.HCl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4244(3)	1603(1)	-1696(2)	22(1)
C(11)	4850(3)	1214(1)	-359(2)	16(1)
C(12)	3044(3)	822(1)	-129(2)	17(1)
C(13)	3575(3)	438(1)	1042(2)	17(1)
C(14)	5946(3)	452(1)	1991(2)	15(1)
C(15)	7772(3)	842(1)	1807(2)	18(1)
C(16)	7218(3)	1223(1)	632(2)	20(1)
C(21)	5641(3)	2197(1)	-1533(2)	18(1)
C(22)	5218(3)	2646(1)	-628(2)	23(1)
C(23)	6547(4)	3183(1)	-453(2)	29(1)
C(24)	8320(4)	3282(1)	-1182(2)	31(1)
C(25)	8717(3)	2846(1)	-2102(2)	30(1)
C(26)	7384(3)	2307(1)	-2279(2)	23(1)
Cl(1)	8214(1)	607(1)	6298(1)	18(1)
N(1)	6554(3)	46(1)	3230(2)	17(1)

Table S9. Bond lengths [Å] and angles [°] for 4-BA.HCl.

C(1)-C(21)	1.510(2)	C(21)-C(26)	1.388(2)
C(1)-C(11)	1.521(2)	C(21)-C(22)	1.393(2)
C(1)-H(1A)	0.9900	C(22)-C(23)	1.383(3)
C(1)-H(1B)	0.9900	C(22)-H(22)	0.9500
C(11)-C(12)	1.391(2)	C(23)-C(24)	1.386(3)
C(11)-C(16)	1.396(2)	C(23)-H(23)	0.9500
C(12)-C(13)	1.389(2)	C(24)-C(25)	1.378(3)
C(12)-H(12)	0.9500	C(24)-H(24)	0.9500
C(13)-C(14)	1.380(2)	C(25)-C(26)	1.387(2)
C(13)-H(13)	0.9500	C(25)-H(25)	0.9500
C(14)-C(15)	1.380(2)	C(26)-H(26)	0.9500
C(14)-N(1)	1.470(2)	N(1)-H(111)	0.94(2)
C(15)-C(16)	1.388(2)	N(1)-H(112)	0.90(2)
C(15)-H(15)	0.9500	N(1)-H(113)	0.93(2)
C(16)-H(16)	0.9500		
C(21)-C(1)-C(11)	114.72(13)	C(26)-C(21)-C(22)	118.61(15)
C(21)-C(1)-H(1A)	108.6	C(26)-C(21)-C(1)	120.62(15)
C(11)-C(1)-H(1A)	108.6	C(22)-C(21)-C(1)	120.77(15)
C(21)-C(1)-H(1B)	108.6	C(23)-C(22)-C(21)	120.66(16)
C(11)-C(1)-H(1B)	108.6	C(23)-C(22)-H(22)	119.7
H(1A)-C(1)-H(1B)	107.6	C(21)-C(22)-H(22)	119.7
C(12)-C(11)-C(16)	118.40(14)	C(22)-C(23)-C(24)	120.12(16)
C(12)-C(11)-C(1)	119.82(14)	C(22)-C(23)-H(23)	119.9
C(16)-C(11)-C(1)	121.74(14)	C(24)-C(23)-H(23)	119.9
C(13)-C(12)-C(11)	121.32(14)	C(25)-C(24)-C(23)	119.71(16)
C(13)-C(12)-H(12)	119.3	C(25)-C(24)-H(24)	120.1
C(11)-C(12)-H(12)	119.3	C(23)-C(24)-H(24)	120.1
C(14)-C(13)-C(12)	118.75(14)	C(24)-C(25)-C(26)	120.19(17)
C(14)-C(13)-H(13)	120.6	C(24)-C(25)-H(25)	119.9
C(12)-C(13)-H(13)	120.6	C(26)-C(25)-H(25)	119.9
C(13)-C(14)-C(15)	121.49(14)	C(25)-C(26)-C(21)	120.69(16)
C(13)-C(14)-N(1)	119.60(14)	C(25)-C(26)-H(26)	119.7
C(15)-C(14)-N(1)	118.92(13)	C(21)-C(26)-H(26)	119.7
C(14)-C(15)-C(16)	119.18(14)	C(14)-N(1)-H(111)	111.8(12)
C(14)-C(15)-H(15)	120.4	C(14)-N(1)-H(112)	111.0(12)
C(16)-C(15)-H(15)	120.4	H(111)-N(1)-H(112)	106.9(16)
C(15)-C(16)-C(11)	120.85(15)	C(14)-N(1)-H(113)	113.6(12)
C(15)-C(16)-H(16)	119.6	H(111)-N(1)-H(113)	103.9(16)
C(11)-C(16)-H(16)	119.6	H(112)-N(1)-H(113)	109.2(16)

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 4-BA.HCl. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	24(1)	24(1)	16(1)	2(1)	3(1)	-2(1)
C(11)	19(1)	17(1)	14(1)	-2(1)	6(1)	2(1)
C(12)	15(1)	22(1)	14(1)	-4(1)	2(1)	0(1)
C(13)	14(1)	21(1)	16(1)	-3(1)	6(1)	-3(1)
C(14)	18(1)	15(1)	12(1)	-1(1)	6(1)	3(1)
C(15)	13(1)	21(1)	19(1)	-3(1)	1(1)	0(1)
C(16)	17(1)	18(1)	24(1)	0(1)	7(1)	-3(1)
C(21)	18(1)	20(1)	14(1)	3(1)	1(1)	3(1)
C(22)	26(1)	28(1)	15(1)	3(1)	6(1)	6(1)

C(23)	44(1)	20(1)	17(1)	-1(1)	-2(1)	7(1)
C(24)	37(1)	23(1)	25(1)	7(1)	-6(1)	-9(1)
C(25)	26(1)	37(1)	27(1)	6(1)	7(1)	-6(1)
C(26)	23(1)	26(1)	19(1)	-1(1)	6(1)	2(1)
Cl(1)	16(1)	21(1)	16(1)	0(1)	4(1)	0(1)
N(1)	15(1)	22(1)	15(1)	0(1)	4(1)	1(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 4-BA.HCl.

	x	y	z	U(eq)
H(1A)	4633	1369	-2468	26
H(1B)	2418	1688	-1993	26
H(12)	1414	817	-785	21
H(13)	2330	170	1187	20
H(15)	9389	850	2477	22
H(16)	8466	1493	501	24
H(22)	4004	2582	-127	28
H(23)	6245	3486	168	35
H(24)	9257	3647	-1048	38
H(25)	9908	2915	-2617	36
H(26)	7667	2009	-2917	27
H(111)	7010(30)	263(9)	4100(20)	31(5)
H(112)	7860(40)	-196(9)	3230(20)	30(5)
H(113)	5210(40)	-191(9)	3300(20)	31(5)

Table S12. Torsion angles [°] for 4-BA.HCl.

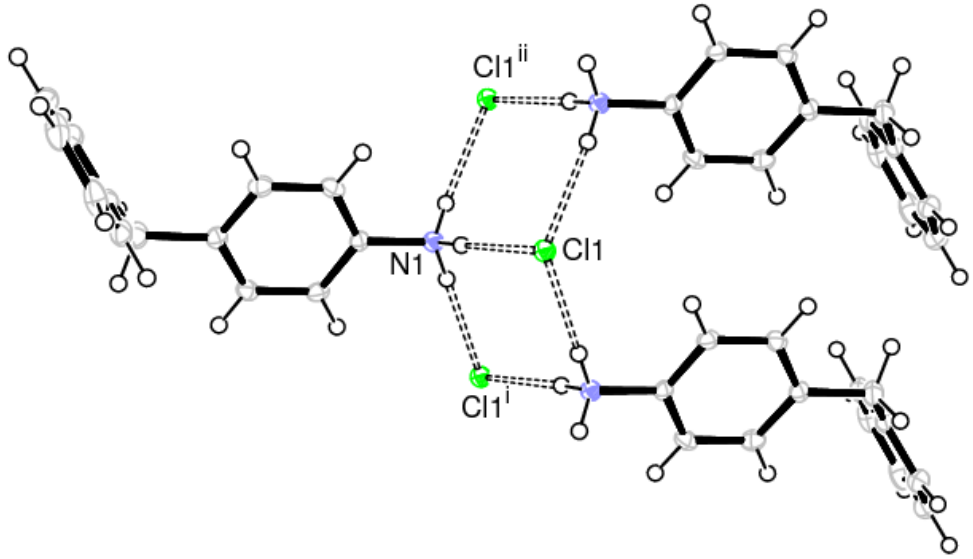
C(21)-C(1)-C(11)-C(12)	150.95(15)	C(1)-C(11)-C(16)-C(15)	-176.69(14)
C(21)-C(1)-C(11)-C(16)	-31.3(2)	C(11)-C(1)-C(21)-C(26)	114.17(17)
C(16)-C(11)-C(12)-C(13)	-1.1(2)	C(11)-C(1)-C(21)-C(22)	-65.6(2)
C(1)-C(11)-C(12)-C(13)	176.63(15)	C(26)-C(21)-C(22)-C(23)	-1.4(2)
C(11)-C(12)-C(13)-C(14)	0.3(2)	C(1)-C(21)-C(22)-C(23)	178.31(14)
C(12)-C(13)-C(14)-C(15)	0.7(2)	C(21)-C(22)-C(23)-C(24)	0.1(2)
C(12)-C(13)-C(14)-N(1)	-179.47(14)	C(22)-C(23)-C(24)-C(25)	1.2(2)
C(13)-C(14)-C(15)-C(16)	-0.8(2)	C(23)-C(24)-C(25)-C(26)	-1.2(3)
N(1)-C(14)-C(15)-C(16)	179.38(14)	C(24)-C(25)-C(26)-C(21)	-0.1(3)
C(14)-C(15)-C(16)-C(11)	-0.1(2)	C(22)-C(21)-C(26)-C(25)	1.4(2)
C(12)-C(11)-C(16)-C(15)	1.0(2)	C(1)-C(21)-C(26)-C(25)	-178.30(15)

Table S13. Hydrogen bonds for 4-BA.HCl[Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(111)...Cl(1)	0.94(2)	2.20(2)	3.1369(15)	169.7(17)
N(1)-H(113)...Cl(1)#1	0.93(2)	2.24(2)	3.1603(15)	168.6(16)
N(1)-H(112)...Cl(1)#2	0.90(2)	2.29(2)	3.1571(15)	163.1(16)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 #2 -x+2,-y,-z+1

Fig. S1. The N-H...Cl hydrogen bonding in 4-BA.HCl. Symmetry codes are as defined in Table 3, footnote c of the main text, so that Cl^{i} and Cl^{ii} are related by translation along the *a*-axis.


Cl1ii
N1
Cl1
Cl1i