Supporting Information for the manuscript

Competing protonation sites in sulfadiazine: Answers from chemistry and electron density.

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Table S1. Data completeness for **1**

Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)

Theta	sin(th)/Lambda	Complete	Expected	Measured	Missing
20.82	0.500	0.999	1796	1794	2
23.01	0.550	0.999	2400	2398	2
25.24	0.600	0.999	3112	3110	2
				ACTA Min. Res.	---
27.51	0.650	0.999	3952	3950	2
29.84	0.700	1.000	4929	4927	2
32.21	0.750	1.000	6070	6068	2
34.65	0.800	1.000	7368	7366	2
37.17	0.850	1.000	8821	8819	2
39.77	0.900	1.000	10460	10458	2
42.47	0.950	1.000	12330	12326	4
45.29	1.000	1.000	14384	14380	4
48.27	1.050	0.999	16643	16630	13
51.43	1.100	0.997	19108	19052	56
51.77	1.105	0.992	19403	19247	156

Summary of Reflection Data in FCF - Note: Friedel Pairs Averaged

Total # of Reflections in FCF. 19247 (Hmax = 17, Kmax = 34, Lmax = 61) Obs
Number above Rep. Theta(Max) . 0
Actual Theta(Max) (Deg.) ... 51.767 (Hmax = 17, Kmax = 34, Lmax = 61) Exp
Reported Theta(Max) (Deg.) ... 51.770 (Hmax = 17, Kmax = 34, Lmax = 61) Rep
Actual Theta(Min) (Deg.) ... 2.563
Reported Theta(Min) (Deg.) ... 2.560

Unique (Expected) 19410
Unique (in FCF) 19247
Observed [I .gt. 2 Sig(I)] ... 12933
Less-Thans 6314
Negative Intensities 1395
Negative Intensities < - 2 SIG 0

Missing (Total) 156
Missing Below Th(Min) 1
Missing Th(Min) to STh/L=0.600 1
Missing STh/L=0.600 to Th(Max) 154
Missing Very Strong Refl. 0
Beamstop Effected Reflections 0

Table S2. Data completeness for **2**

Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)

Theta	sin(th)/Lambda	Complete	Expected	Measured	Missing
20.82	0.500	0.998	1118	1116	2
23.01	0.550	0.999	1501	1499	2
25.24	0.600	0.999	1927	1925	2
---------- ACTA Min. Res. ---					
27.51	0.650	0.999	2470	2468	2
29.84	0.700	0.999	3067	3065	2
32.21	0.750	0.999	3786	3783	3
34.65	0.800	0.999	4591	4587	4
37.17	0.850	0.999	5494	5490	4
39.77	0.900	0.999	6551	6545	6
42.47	0.950	0.999	7668	7658	10
45.29	1.000	0.998	8973	8959	14
48.27	1.050	0.997	10391	10363	28
51.43	1.100	0.994	11937	11870	67
54.16	1.141	0.978	13255	12966	289

Summary of Reflection Data in FCF - Note: Friedel Pairs Averaged

Total # of Reflections in FCF. 12966 (Hmax = 30, Kmax = 13, Lmax = 32) Obs
Number above Rep. Theta(Max) . 1
Actual Theta(Max) (Deg.) ... 54.161 (Hmax = 30, Kmax = 13, Lmax = 32) Exp
Reported Theta(Max) (Deg.) ... 54.160 (Hmax = 30, Kmax = 13, Lmax = 32) Rep
Actual Theta(Min) (Deg.) ... 2.771
Reported Theta(Min) (Deg.) ... 2.770

Unique (Expected) 13284
Unique (in FCF) 12966
Observed [I .gt. 2 Sig(I)] ... 8707
Less-Thans 4259
Negative Intensities 1123
Negative Intensities < - 2 SIG 0

Missing (Total) 289
Missing Below Th(Min) 1
Missing Th(Min) to STh/L=0.600 1
Missing STh/L=0.600 to Th(Max) 287
Missing Very Strong Refl. 0
Beamstop Effected Reflections 0

Table S3. Data completeness for **3b**

Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)

Theta	sin(th)/Lambda	Complete	Expected	Measured	Missing
20.82	0.500	0.999	1392	1391	1
23.01	0.550	0.999	1850	1849	1
25.24	0.600	1.000	2405	2404	1
ACTA Min. Res. ---					
27.51	0.650	0.998	3060	3053	7
29.84	0.700	0.995	3812	3792	20
32.21	0.750	0.990	4689	4643	46
34.65	0.800	0.988	5672	5603	69
37.17	0.850	0.984	6842	6734	108
39.77	0.900	0.982	8113	7968	145
42.47	0.950	0.978	9549	9338	211
45.29	1.000	0.974	11135	10844	291
48.27	1.050	0.969	12873	12472	401
51.43	1.100	0.961	14811	14227	584
54.10	1.140	0.938	16455	15441	1014

Summary of Reflection Data in FCF - Note: Friedel Pairs Averaged

Total # of Reflections in FCF. 15441 (Hmax = 12, Kmax = 25, Lmax = 27) Obs
Number above Rep. Theta(Max) . 1
Actual Theta(Max) (Deg.) ... 54.104 (Hmax = 12, Kmax = 25, Lmax = 27) Exp
Reported Theta(Max) (Deg.) ... 54.100 (Hmax = 12, Kmax = 25, Lmax = 27) Rep
Actual Theta(Min) (Deg.) ... 1.903
Reported Theta(Min) (Deg.) ... 1.900

Unique (Expected) 16453
Unique (in FCF) 15441
Observed [I .gt. 2 Sig(I)] ... 11851
Less-Thans 3590
Negative Intensities 841
Negative Intensities < - 2 SIG 0

Missing (Total) 1014
Missing Below Th(Min) 0
Missing Th(Min) to STh/L=0.600 1
Missing STh/L=0.600 to Th(Max) 1013
Missing Very Strong Refl. 0
Beamstop Effected Reflections 1

Table S4. Properties of bond critical points in **1**. ρ is the electron density, $\nabla^2\rho$ is the Laplacian of the electron density in the bond critical point, D_{ij} the interatomic distance, R_{ij} the length of the bond path, d_1 the distance from the first atom to the (3,-1) critical point and λ_1 - λ_3 the eigenvalues of the Laplacian in the bond critical point.

Compound **1**								
Bond	ρ(e/Å^3)	$\nabla^2\rho$(e/Å^5)	D_{ij}(Å)	R_{ij}(Å)	d_1(Å)	λ_1	λ_2	λ_3
ZN(1)-N(5)	0.443(8)	6.87(3)	2.1747(9)	2.1747	1.0648	-2.02	-1.99	10.89
ZN(1)-N(6)	0.406(8)	5.45(4)	2.1973(11)	2.1975	1.0531	-1.71	-1.63	8.79
ZN(1)-N(7)	0.427(8)	5.72(4)	2.1864(13)	2.1865	1.0384	-1.86	-1.81	9.39
S(1)-O(1)	2.45(8)	-15.7(5)	1.4653(11)	1.4569	0.6112	-18.97	-17.36	20.64
S(1)-O(2)	2.38(8)	-20.4(5)	1.4663(13)	1.4687	0.636	-17.81	-16.68	14.10
S(1)-N(3)	2.02(7)	-18.3(3)	1.5775(12)	1.5836	0.717	-15.14	-12.65	9.54
S(1)-C(5)	1.43(4)	-6.57(9)	1.7597(10)	1.7602	1.0019	-8.83	-8.60	10.85
O(3)-H(3O)	2.09(11)	-28.8(9)	0.9830(13)	0.9836	0.7739	-34.52	-30.85	36.58
N(1)-C(1)	2.44(7)	-26.5(3)	1.3561(17)	1.3565	0.7955	-21.24	-18.23	12.97
N(1)-C(2)	2.61(9)	-29.0(4)	1.333(2)	1.3336	0.7524	-22.99	-20.69	14.67
N(2)-C(1)	2.54(7)	-27.8(3)	1.3505(14)	1.3506	0.7725	-22.82	-19.37	14.4
N(2)-C(4)	2.64(7)	-27.3(3)	1.3349(16)	1.3363	0.7286	-23.75	-20.56	17.00
N(3)-C(1)	2.44(7)	-27.5(3)	1.3617(15)	1.3629	0.7808	-22.33	-18.70	13.55
N(4)-C(8)	2.42(7)	-29.5(3)	1.3693(18)	1.3694	0.7894	-22.50	-19.39	12.40
N(4)-H(4A)	2.18(13)	-33.6(10)	1.01	1.0101	0.7976	-33.41	-31.98	31.75
N(4)-H(4B)	2.05(13)	-26.7(8)	1.01	1.0102	0.7516	-27.72	-25.07	26.13
N(5)-C(11)	1.84(6)	-13.88(19)	1.4741(15)	1.4743	0.8338	-13.96	-13.5	13.58
N(5)-H(5A)	2.12(9)	-26.2(5)	1.01	1.0105	0.7425	-27.05	-25.85	26.68
N(5)-H(5B)	2.05(9)	-21.9(5)	1.01	1.01	0.7526	-26.20	-25.24	29.54
N(6)-C(12)	1.80(7)	-13.96(19)	1.4649(14)	1.4656	0.8325	-13.45	-13.03	12.52
N(6)-H(6A)	1.99(9)	-28.6(7)	1.01	1.0109	0.7867	-28.82	-27.55	27.82
N(6)-H(6B)	2.23(11)	-26.1(6)	1.01	1.0105	0.7512	-28.98	-27.79	30.64
N(7)-C(13)	1.67(8)	-9.0(3)	1.478(2)	1.4787	0.8483	-12.44	-9.85	13.25
N(7)-H(7A)	1.91(10)	-26.8(7)	1.01	1.01	0.795	-27.78	-27.21	28.2
N(7)-H(7B)	2.06(11)	-29.9(7)	1.01	1.01	0.775	-28.52	-27.98	26.61
C(2)-C(3)	2.28(7)	-22.46(19)	1.388(2)	1.388	0.7334	-18.45	-15.45	11.45
C(2)-H(2)	2.03(15)	-22.8(5)	1.083	1.0831	0.6953	-20.94	-17.98	16.08
C(3)-C(4)	2.36(7)	-23.93(18)	1.3878(18)	1.3879	0.6694	-20.15	-16.00	12.22
C(3)-H(3)	1.99(12)	-19.7(3)	1.083	1.0831	0.6482	-18.08	-16.46	14.85
C(4)-H(4)	2.05(11)	-24.2(3)	1.083	1.0854	0.6566	-20.05	-17.98	13.78
C(5)-C(6)	2.23(6)	-20.97(15)	1.3946(13)	1.3948	0.6903	-18.25	-14.91	12.19
C(5)-C(10)	2.26(6)	-21.24(16)	1.3947(15)	1.3950	0.7152	-18.39	-14.89	12.04
C(6)-C(7)	2.24(6)	-22.44(17)	1.3843(16)	1.3843	0.6677	-18.55	-14.82	10.93
C(6)-H(6)	1.95(11)	-19.7(3)	1.083	1.0833	0.6765	-18.9	-16.65	15.84
C(7)-C(8)	2.22(7)	-21.07(16)	1.4080(19)	1.4082	0.7087	-19.18	-13.63	11.74
C(7)-H(7)	1.92(10)	-19.0(4)	1.083	1.0833	0.6914	-18.82	-16.43	16.29
C(8)-C(9)	2.18(7)	-21.0(3)	1.4051(19)	1.4052	0.7684	-17.24	-14.29	10.5
C(9)-C(10)	2.17(7)	-19.26(19)	1.3914(16)	1.3915	0.647	-17.07	-13.55	11.37

C(9)-H(9)	1.71(9)	-14.3(3)	1.083	1.0832	0.7112	-16.47	-14.61	16.80
C(10)-H(10)	1.87(10)	-18.9(3)	1.083	1.0833	0.6879	-18.01	-16.34	15.45
C(11)-C(12)	1.77(5)	-13.69(11)	1.5219(15)	1.5226	0.7369	-12.78	-12.12	11.21
C(11)-H(11A)	1.80(9)	-16.9(3)	1.091	1.0919	0.7344	-17.57	-17.10	17.72
C(11)-H(11B)	1.81(8)	-17.7(3)	1.091	1.0912	0.7394	-17.81	-17.06	17.19
C(12)-H(12A)	1.86(9)	-18.9(4)	1.091	1.0919	0.7477	-18.69	-18.20	17.97
C(12)-H(12B)	1.75(8)	-16.8(4)	1.091	1.0911	0.7896	-18.6	-17.93	19.74
C(13)-H(13A)	1.64(10)	-13.9(3)	1.091	1.0921	0.7002	-15.06	-14.18	15.34
C(13)-H(13B)	1.80(11)	-17.7(3)	1.091	1.0932	0.6118	-15.56	-13.07	10.93
H(30)…O(2)^{i}	0.16(6)	4.41(6)	1.76	1.7672	0.5816	-0.82	-0.79	6.01
H(5A)…N(3)^{i}	0.044(17)	1.189(2)	2.280	2.3795	0.8638	-0.19	-0.14	1.53
H(5B)…O(1)^{ii}	0.073(15)	1.383(2)	2.230	2.255	0.8749	-0.29	-0.28	1.95
H(6A)…N(1)	0.092(18)	1.639(4)	2.200	2.2335	1.4251	-0.39	-0.36	2.39
H(6B)…O(3)^{iii}	0.10(3)	2.138(8)	2.051	2.0772	0.7807	-0.49	-0.40	3.02
H(7A)…O(2)^{i}	0.07(3)	1.414(5)	2.170	2.1797	0.8111	-0.28	-0.28	1.97
H(7B)…O(1)^{iv}	0.063(12)	1.192(3)	2.210	2.287	0.9108	-0.25	-0.20	1.64
H(4A)…N(1)^{v}	0.031(19)	0.684(4)	2.448	2.4727	0.9559	-0.10	-0.09	0.87
H(4B)…N(2)^{vi}	0.045(11)	0.865(3)	2.396	2.4785	0.9766	-0.20	-0.13	1.20

Symmetry operations: ^{i} –x, +y, 1/2-z; ^{ii} x-1, +y, +z; ^{iii} 1/2+, y-1/2, 1/2-z; ^{iv} 1-x, +y, 1/2-z; ^{v} 1/2+x, 1/2-y, -z; ^{vi} x-1/2, 1/2-y, -z;

Table S5. Properties of bond critical points in **2**. ρ is the electron density, $\nabla^2\rho$ is the Laplacian of the electron density in the bond critical point, D_{ij} the interatomic distance, R_{ij} the length of the bond path, d_1 the distance from the first atom to the (3,-1) critical point and λ_1 - λ_3 the eigenvalues of the Laplacian in the bond critical point.

Compound **2**								
Bond	ρ(e/Å^3)	$\nabla^2\rho$(e/Å^5)	D_{ij}(Å)	R_{ij}(Å)	d_1(Å)	λ_1	λ_2	λ_3
S(1)-O(1)	2.85(8)	-27.9(4)	1.4310(11)	1.4314	0.6678	-23.07	-21.57	16.71
S(1)-O(2)	2.61(7)	-23.5(4)	1.4393(11)	1.4403	0.6624	-23.78	-16.88	17.20
S(1)-N(3)	2.09(4)	-12.22(10)	1.6506(8)	1.6512	0.8967	-17.64	-15.31	20.73
S(1)-C(5)	1.57(4)	-7.52(11)	1.7376(9)	1.7402	1.0369	-11.00	-9.59	13.06
N(1)-C(1)	2.72(6)	-28.31(18)	1.3446(9)	1.3451	0.7227	-25.38	-22.04	19.11
N(1)-C(2)	2.57(6)	-28.0(3)	1.3371(11)	1.3377	0.7560	-22.86	-21.02	15.84
N(2)-C(1)	2.67(6)	-26.6(2)	1.3334(11)	1.3337	0.7299	-24.16	-20.75	18.33
N(2)-C(4)	2.51(6)	-22.6(3)	1.3387(12)	1.3396	0.7318	-21.28	-19.59	18.30
N(3)-C(1)	2.33(5)	-20.69(18)	1.3805(11)	1.3807	0.7590	-21.61	-16.61	17.53
N(3)-H(3A)	1.95(8)	-25.9(6)	1.027	1.0274	0.8032	-28.15	-27.20	29.45
N(4)-C(8)	2.31(6)	-18.96(18)	1.3810(11)	1.3812	0.7576	-19.71	-17.26	18.01
N(4)-H(4A)	2.10(10)	-25.1(6)	1.01	1.0103	0.7470	-27.04	-26.18	28.13
N(4)-H(4B)	2.10(10)	-28.5(7)	1.01	1.0103	0.7730	-29.13	-28.48	29.13
C(2)-C(3)	2.23(6)	-21.28(16)	1.3928(13)	1.3929	0.7418	-18.79	-15.02	12.53
C(2)-H(2)	1.96(8)	-24.3(4)	1.083	1.0837	0.7606	-21.78	-20.40	17.84
C(3)-C(4)	2.35(5)	-23.72(14)	1.3878(13)	1.3879	0.6826	-20.08	-16.67	13.03
C(3)-H(3)	1.85(9)	-19.5(4)	1.083	1.0832	0.7397	-19.23	-17.87	17.56
C(4)-H(4)	1.81(8)	-20.4(4)	1.083	1.0838	0.7811	-20.60	-18.95	19.17

C(5)-C(6)	2.16(5)	-18.19(13)	1.3997(11)	1.3997	0.6864	-17.41	-14.10	13.32
C(5)-C(10)	2.29(5)	-21.19(14)	1.3949(11)	1.3960	0.7151	-18.66	-16.14	13.61
C(6)-C(7)	2.31(5)	-22.62(14)	1.3872(12)	1.3874	0.6973	-19.24	-16.38	12.99
C(6)-H(6)	1.89(8)	-19.5(3)	1.083	1.0831	0.7342	-19.40	-18.45	18.40
C(7)-C(8)	2.23(5)	-20.60(14)	1.4093(12)	1.4093	0.6801	-18.98	-14.94	13.32
C(7)-H(7)	1.85(8)	-17.3(3)	1.083	1.0830	0.7168	-18.63	-16.96	18.25
C(8)-C(9)	2.27(5)	-21.06(14)	1.4046(12)	1.4047	0.7181	-18.61	-15.82	13.37
C(9)-C(10)	2.33(6)	-21.83(14)	1.3851(11)	1.3851	0.6946	-19.33	-16.23	13.73
C(9)-H(9)	1.90(8)	-17.5(3)	1.083	1.0831	0.6616	-17.92	-15.40	15.82
C(10)-H(10)	1.91(9)	-19.2(3)	1.083	1.0834	0.7002	-18.71	-17.38	16.86
H(3A)…N(1)^{i}	0.17(4)	3.12(4)	1.895	1.8986	0.6293	-0.95	-0.88	4.95
H(4B)…O(2)^{ii}	0.09(5)	2.69(3)	1.972	1.9765	0.6829	-0.38	-0.36	3.43
H(4A)…O(1)^{iii}	0.067(2)	1.026(3)	2.465	2.5590	1.1527	-0.21	-0.19	1.42
H(4A)…N(4)^{iv}	0.018(8)	0.481(3)	2.566	2.7071	1.0515	-0.08	-0.05	0.61

Symmetry operations: ^{i} –x, 2-y, 1-z; ^{ii} x, 5/2-y, z-1/2; ^{iii} x, 3/2-y, z-1/2; ^{iv} 1-x, y-1/2, 1/2-z

Table S6. Properties of bond critical points in **3b**. ρ is the electron density, $\nabla^2\rho$ is the Laplacian of the electron density in the bond critical point, D_{ij} the interatomic distance, R_{ij} the length of the bond path, d_1 the distance from the first atom to the (3,-1) critical point and λ_1 - λ_3 the eigenvalues of the Laplacian in the bond critical point.

Compound **3b**								
Bond	ρ(e/Å^3)	$\nabla^2\rho$(e/Å^5)	D_{ij}(Å)	R_{ij}(Å)	d_1(Å)	λ_1	λ_2	λ_3
S(1)-O(1)	2.95(7)	-16.3(2)	1.4486(9)	1.4488	0.8077	-25.57	-20.66	29.92
S(1)-O(2)	2.89(8)	-23.2(4)	1.4402(9)	1.4409	0.6744	-22.31	-20.19	19.34
S(1)-N(3)	2.09(6)	-11.30(13)	1.5986(7)	1.5997	0.8578	-17.65	-14.17	20.52
S(1)-C(5)	1.33(4)	-4.24(8)	1.7704(8)	1.7714	0.9691	-8.91	-8.21	12.88
O(3)-C(11)	1.80(8)	-16.1(3)	1.4249(16)	1.4278	0.8389	-13.73	-12.56	10.15
O(3)-H(3O)	2.06(12)	-19.7(8)	0.98	0.9804	0.7551	-29.00	-28.66	37.93
N(1)-C(1)	2.40(7)	-23.4(3)	1.3670(9)	1.3673	0.7592	-22.25	-17.89	16.79
N(1)-C(2)	2.41(8)	-27.3(3)	1.3449(10)	1.3451	0.7798	-21.84	-18.96	13.55
N(1)-H(1A)	1.83(10)	-27.7(8)	1.027	1.0302	0.8236	-28.03	-27.03	27.41
N(2)-C(1)	2.52(7)	-23.2(3)	1.3444(9)	1.3445	0.7389	-23.01	-18.72	18.57
N(2)-C(4)	2.42(8)	-21.5(3)	1.3318(11)	1.3333	0.7553	-20.84	-17.38	16.71
N(3)-C(1)	2.45(7)	-20.8(3)	1.3419(10)	1.3421	0.7152	-21.41	-18.08	18.71
N(4)-C(8)	1.77(6)	-12.2(3)	1.4594(10)	1.4596	0.8498	-14.13	-12.23	14.18
N(4)-H(4A)	1.89(10)	-27.0(7)	1.036	1.0379	0.8070	-26.57	-26.05	25.58
N(4)-H(4B)	1.87(11)	-29.4(8)	1.036	1.0441	0.8238	-27.31	-27.06	25.00
N(4)-H(4C)	1.88(10)	-26.8(7)	1.036	1.0386	0.8137	-26.81	-26.39	26.44
C(2)-C(3)	2.43(7)	-24.72(18)	1.3750(11)	1.3751	0.7131	-21.58	-16.51	13.38
C(2)-H(2)	2.05(12)	-25.1(4)	1.083	1.0853	0.7205	-21.94	-19.46	16.34
C(3)-C(4)	2.19(7)	-19.96(17)	1.3988(11)	1.3991	0.6731	-18.11	-15.10	13.26
C(3)-H(3)	1.84(11)	-16.9(4)	1.083	1.0832	0.7065	-18.44	-16.17	17.66
C(4)-H(4)	1.92(12)	-22.1(5)	1.083	1.0832	0.7338	-20.21	-18.62	16.72
C(5)-C(6)	2.28(6)	-20.38(17)	1.3918(9)	1.3919	0.6693	-19.16	-15.39	14.17
C(5)-C(10)	2.25(6)	-19.51(16)	1.393	1.3934	0.7061	-18.57	-15.41	14.47

C(6)-C(7)	2.12(6)	-20.38(18)	1.3917(10)	1.392	0.6449	-17.68	-14.51	11.8
C(6)-H(6)	1.83(9)	-21.6(4)	1.083	1.0838	0.7574	-20.03	-18.33	16.71
C(7)-C(8)	2.37(6)	-22.56(17)	1.3905(10)	1.3906	0.6763	-20.37	-16.22	14.03
C(7)-H(7)	1.95(10)	-20.5(4)	1.083	1.0832	0.7211	-19.72	-18.49	17.69
C(8)-C(9)	2.37(7)	-24.02(19)	1.3908(10)	1.3912	0.7596	-21.01	-15.85	12.84
C(9)-C(10)	2.20(6)	-21.70(17)	1.3944(10)	1.3948	0.7353	-18.62	-15.63	12.54
C(9)-H(9)	1.83(10)	-19.5(5)	1.083	1.083	0.7751	-20.22	-18.88	19.64
C(10)-H(10)	1.94(10)	-21.8(4)	1.083	1.0831	0.7537	-20.60	-19.61	18.48
C(11)-H(111)	1.56(10)	-12.5(5)	1.091	1.097	0.8052	-16.63	-15.53	19.68
C(11)-H(112)	1.51(8)	-13.4(3)	1.091	1.1074	0.7088	-13.59	-13.30	13.48
H(1A)...N(3)^{i}	0.21(4)	2.47(3)	1.89	1.915	0.6762	-1.19	-1.10	4.76
H(4A)…O(1)^{ii}	0.12(5)	2.85(3)	1.89	1.9272	0.6763	-0.64	-0.48	3.96
N(4)…CL(1)^{iii}	0.068(6)	0.826(4)	3.2187(10)	3.2555	1.6271	-0.22	-0.15	1.20
H(4B)…CL(1)	0.15(4)	1.875(12)	2.19	2.2261	0.7563	-0.79	-0.59	3.25
H(4C)…CL(1)^{iv}	0.14(4)	2.18(2)	2.15	2.1823	0.7038	-0.76	-0.61	3.56
H(3O)…CL(1)^{iv}	0.14(4)	1.916(13)	2.23	2.2374	0.7622	-0.62	-0.56	3.09

Symmetry operations: ^{i} 1-x,-y, 1-z; ^{ii} 1-x, 1-y, -z; ^{iii} 1-x, 2-y, -z; ^{iv} x-1, y, z

Table S7. Integrated net charges q [e] and volumes V [Å^3] of the atomic basins by QTAIM partitioning for the sulfadiazine groups in **1**, **2** and **3b**.

	1		**2**		**3**	
Atom	Q_{001} **[e]**	V_{001} **[Å^3]**	Q_{001} **[e]**	**Atom**	Q_{001} **[e]**	V_{001} **[Å^3]**
S1	2.25	7.35	1.59	S1	2.25	7.35
O1	-1.31	16.54	-1.24	O1	-1.31	16.54
O2	-1.25	17.25	-1.20	O2	-1.25	17.25
N1	-1.08	15.57	-0.87	N1	-1.08	15.57
N2	-0.96	14.23	-0.94	N2	-0.96	14.23
N3	-1.26	14.52	-1.13	N3	-1.26	14.52
N4	-1.20	17.28	-1.16	N4	-1.20	17.28
C1	1.22	5.81	0.96	C1	1.22	5.81
C2	0.37	10.72	0.30	C2	0.37	10.72
C3	0.10	11.44	-0.01	C3	0.10	11.44
C4	0.45	9.81	0.25	C4	0.45	9.81
C5	-0.11	9.71	-0.04	C5	-0.11	9.71
C6	0.07	11.00	-0.07	C6	0.07	11.00
C7	-0.13	11.82	-0.04	C7	-0.13	11.82
C8	0.28	8.91	0.27	C8	0.28	8.91
C9	0.02	12.62	-0.02	C9	0.02	12.62
C10	-0.05	11.58	0.03	C10	-0.05	11.58
H2	0.10	5.52	0.34	H2	0.10	5.52
H3	-0.04	5.83	0.33	H3	-0.04	5.83
H4	-0.01	5.35	0.36	H4	-0.01	5.35
H6	0.03	5.49	0.22	H6	0.03	5.49
H7	0.08	5.43	0.14	H7	0.08	5.43
H9	0.21	5.54	0.08	H9	0.21	5.54
H10	0.12	5.28	0.17	H10	0.12	5.28
H1A				H1A		
H3A			0.59	H3A		
H4A	0.58	2.86	0.53	H4A	0.58	2.86
H4B	0.57	2.23	0.57	H4B	0.57	2.23
H4C				H4C		

Fig. S1: Residual electron density after the multipole refinement of **1** with contour intervals at 0.1 e Å^{-3} in the plane of the pyrimidine (left) and the aniline (right); positive values shown in red, negative values in blue.

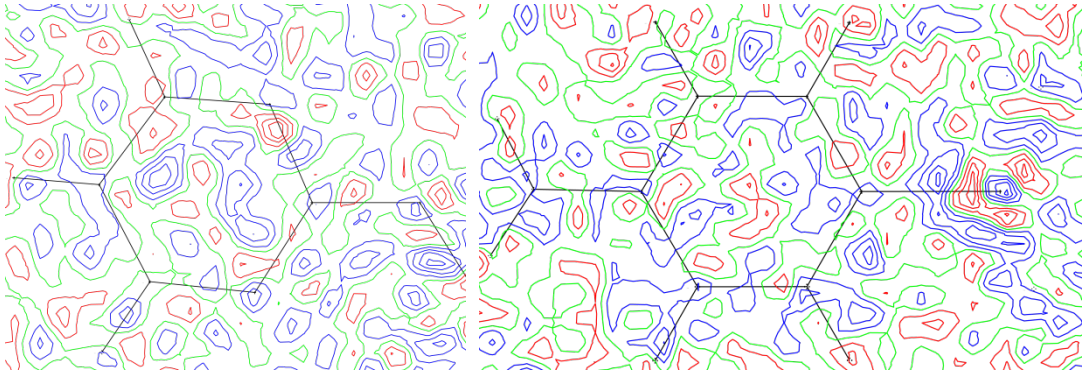

Fig. S2: Residual electron density after the multipole refinement of **2** with contour intervals at 0.1 e Å^{-3} in the plane of the pyrimidine (left) and the aniline (right); positive values shown in red, negative values in blue.

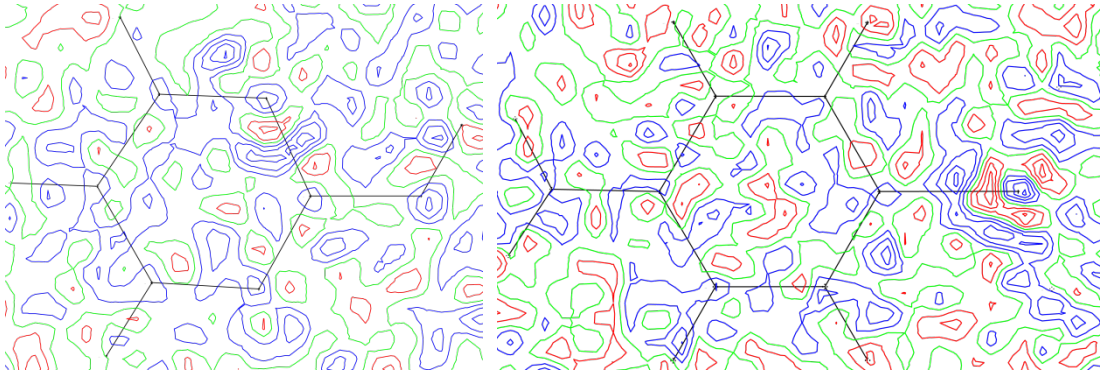

Fig. S3: Residual electron density after the multipole refinement of **3b** with contour intervals at 0.1 e Å^{-3} in the plane of the pyrimidine (left) and the aniline (right); positive values shown in red, negative values in blue.

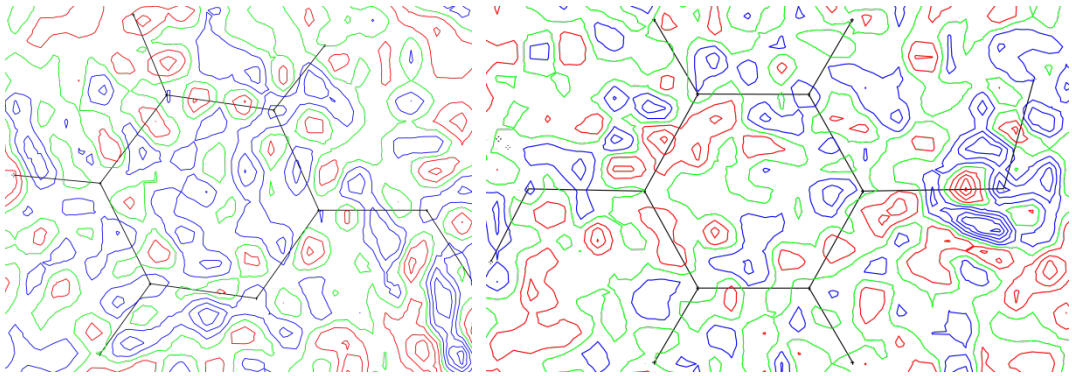

Table S8. IAM refinement results for alternative protonation patterns in **3a** and **3b**.

	correct assignment: site I (N1) protonated	no H assigned	incorrect assignment: site II (N3) protonated
3a			
*wR*2	0.1220	0.1259	0.1287
R(all)	0.0629	0.0635	0.0641
$R[F^2 > 2\sigma(F^2)]$	0.0466	0.0472	0.0478
ρ_{max}, ρ_{min} (e Å^{-3})	1.02 (around S1) -0.54 (around S1)	1.04 (around N1) -0.53 (around S1)	1.02 (around N1) -1.11 (around H3)
3b			
*wR*2	0.1364	0.1387	0.1423
R(all)	0.0654	0.0659	0.0664
$R[F^2 > 2\sigma(F^2)]$	0.0497	0.0502	0.0506
ρ_{max}, ρ_{min} (e Å^{-3})	1.20 (around S1), -0.66 (around S1)	1.21 (around S1), -0.67 (around S1)	1.23 (around S1), -1.20 (around H3)

Fig. S4: Laplacian of the experimental charge density in **3b**; positive values shown in blue. The representations are based on the correct structure model with protonated pyridine N, i.e. site I in Scheme 1, (left) and based on the alternative incorrect assumption of protonated amidic N, site II in Scheme 1, (right); note the obvious artefacts in the region of the wrongly assigned H atoms in the latter model.