

SUPPLEMENTARY MATERIAL

Experimental and Theoretical Characterization of the Zn-Zn Bond in $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$.

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Table S1. Bond distances (Å) and (selected) angles (°) involving the Zn atoms from the neutron diffraction experiment.

Atom-Atom	Distance(esd)	Atom-Atom-Atom	Angle(esd)
Zn(1)-Zn(2)	2.292(1)	Zn(2)-Zn(1)-C(1)	145.2(4)
Zn(1)-C(1)	2.306(5)	Zn(2)-Zn(1)-C(2)	146.3(3)
Zn(1)-C(2)	2.304(5)	Zn(2)-Zn(1)-C(3)	149.4(3)
Zn(1)-C(3)	2.272(4)	Zn(2)-Zn(1)-C(4)	149.9(5)
Zn(1)-C(4)	2.272(5)	Zn(2)-Zn(1)-C(5)	147.8(2)
Zn(1)-C(5)	2.284(3)	Zn(1)-Zn(2)-C(6)	146.4(3)
Zn(2)-C(6)	2.326(3)	Zn(1)-Zn(2)-C(7)	147.2(3)
Zn(2)-C(7)	2.308(4)	Zn(1)-Zn(2)-C(8)	150.2(4)
Zn(2)-C(8)	2.308(3)	Zn(1)-Zn(2)-C(9)	149.3(5)
Zn(2)-C(9)	2.304(3)	Zn(1)-Zn(2)-C(10)	147.2(3)
Zn(2)-C(10)	2.305(5)		

Table S2. Bond distances (Å) and (selected) angles (°) involving the Zn atoms from the synchrotron X-ray diffraction experiment.

Atom-Atom	Distance(esd)	Atom-Atom-Atom	Angle(esd)
Zn(1)-Zn(2)	2.3186(3)	Zn(2)-Zn(1)-C(1)	148.91(5)
Zn(1)-C(1)	2.2909(12)	Zn(2)-Zn(1)-C(2)	150.65(4)
Zn(1)-C(2)	2.2756(12)	Zn(2)-Zn(1)-C(3)	148.36(4)
Zn(1)-C(3)	2.2794(11)	Zn(2)-Zn(1)-C(4)	145.12(6)
Zn(1)-C(4)	2.3124(14)	Zn(2)-Zn(1)-C(5)	145.72(3)
Zn(1)-C(5)	2.3132(9)	Zn(1)-Zn(2)-C(6)	147.77(5)
Zn(2)-C(6)	2.2892(13)	Zn(1)-Zn(2)-C(7)	146.45(5)
Zn(2)-C(7)	2.2811(11)	Zn(1)-Zn(2)-C(8)	147.02(4)
Zn(2)-C(8)	2.2859(10)	Zn(1)-Zn(2)-C(9)	148.52(6)
Zn(2)-C(9)	2.3027(14)	Zn(1)-Zn(2)-C(10)	149.12(3)
Zn(2)-C(10)	2.3060(10)		

Table S3. Monopole populations, radial parameters and net atomic charges from the multipole refinement.

Atom	P_{val}	κ	P_{co}	κ_0'	Net charge
ZN (1)	11.49 (13)	0.998 (7)	0.000	1.050 (9)	+0.508
ZN (2)	11.55 (13)	0.998 (7)	0.000	1.050 (9)	+0.450
C (1)	4.0 (3)	0.900 (7)	0.000	0.776 (9)	-0.034
C (2)	4.6 (3)	0.900 (7)	0.000	0.776 (9)	-0.553
C (3)	4.3 (3)	0.900 (7)	0.000	0.776 (9)	-0.312
C (4)	4.6 (3)	0.900 (7)	0.000	0.776 (9)	-0.605
C (5)	4.2 (3)	0.900 (7)	0.000	0.776 (9)	-0.200
C (6)	3.6 (3)	0.900 (7)	0.000	0.776 (9)	+0.430
C (7)	4.8 (3)	0.900 (7)	0.000	0.776 (9)	-0.835
C (8)	3.7 (3)	0.900 (7)	0.000	0.776 (9)	+0.286
C (9)	3.3 (3)	0.900 (7)	0.000	0.776 (9)	+0.740
C (10)	6.2 (3)	0.900 (7)	0.000	0.776 (9)	-2.236
C (11)	5.3 (2)	0.900 (7)	0.000	0.776 (9)	-1.324
C (12)	5.3 (2)	0.900 (7)	0.000	0.776 (9)	-1.264
C (13)	4.9 (2)	0.900 (7)	0.000	0.776 (9)	-0.909
C (14)	5.2 (2)	0.900 (7)	0.000	0.776 (9)	-1.199
C (15)	4.6 (2)	0.900 (7)	0.000	0.776 (9)	-0.623
C (16)	4.8 (2)	0.900 (7)	0.000	0.776 (9)	-0.781
C (17)	4.9 (2)	0.900 (7)	0.000	0.776 (9)	-0.890
C (18)	5.0 (2)	0.900 (7)	0.000	0.776 (9)	-1.006
C (19)	5.3 (2)	0.900 (7)	0.000	0.776 (9)	-1.305
C (20)	5.6 (2)	0.900 (7)	0.000	0.776 (9)	-1.571
H (11A) [#]	1.000	1.200	-0.579 (51)	1.200	+0.579
H (12A)	1.000	1.200	-0.271 (55)	1.200	+0.271
H (13A)	1.000	1.200	-0.364 (55)	1.200	+0.364
H (14A) [‡]	0.12 (4)	1.200	-0.331 (569)	1.200	+0.040
H (14D)	0.88 (4)	1.200	-0.467 (76)	1.200	+0.411
H (15A)	0.67 (4)	1.200	-0.679 (97)	1.200	+0.455
H (15D)	0.33 (4)	1.200	0.083 (194)	1.200	-0.027
H (16A)	0.28 (4)	1.200	-0.802 (241)	1.200	+0.225
H (16D)	0.72 (4)	1.200	-0.187 (95)	1.200	+0.135
H (17A)	1.000	1.200	-0.362 (54)	1.200	+0.362
H (18A)	1.000	1.200	-0.604 (55)	1.200	+0.604
H (19A)	0.30 (4)	1.200	-0.770 (254)	1.200	+0.231
H (19D)	0.70 (4)	1.200	-0.248 (109)	1.200	+0.174
H (20A)	1.000	1.200	-0.589 (53)	1.200	+0.589

[#] Only one hydrogen atom is included in the table for each methyl group.

[‡] Some of the methyl groups were split into two components for treating the disorder problems.

Table S4. Dipole population parameters.

Atom	D_{11+}	D_{11-}	D_{10}	κ_1'
ZN(1)	-0.062 (21)	0.249 (39)	-0.020 (22)	1.283 (71)
ZN(2)	0.040 (21)	0.339 (43)	-0.115 (22)	1.283 (71)
C(1)	0.088 (81)	0.199 (137)	-0.034 (168)	0.776
C(2)	0.149 (83)	0.220 (133)	0.205 (177)	0.776
C(3)	0.100 (85)	-0.043 (133)	-0.345 (174)	0.776
C(4)	-0.233 (84)	0.134 (163)	0.284 (159)	0.776
C(5)	0.097 (78)	-0.184 (134)	-0.038 (158)	0.776
C(6)	0.173 (82)	-0.457 (184)	-0.165 (138)	0.776
C(7)	-0.075 (82)	0.426 (141)	0.290 (181)	0.776
C(8)	0.194 (83)	0.091 (138)	-0.229 (176)	0.776
C(9)	0.131 (87)	0.246 (168)	-0.485 (170)	0.776
C(10)	0.074 (81)	-0.121 (155)	0.464 (153)	0.776
C(11)	0.303 (92)	0.197 (71)	0.214 (93)	0.776
C(12)	0.054 (105)	0.167 (76)	0.054 (67)	0.776
C(13)	0.330 (76)	0.180 (61)	0.010 (94)	0.776
C(14)	0.239 (116)	0.255 (98)	0.173 (76)	0.776
C(15)	0.133 (70)	0.038 (74)	0.142 (61)	0.776
C(16)	-0.263 (102)	0.114 (94)	0.077 (83)	0.776
C(17)	-0.230 (87)	0.050 (100)	0.098 (64)	0.776
C(18)	0.345 (75)	0.264 (66)	0.017 (95)	0.776
C(19)	-0.339 (122)	0.016 (88)	0.021 (87)	0.776
C(20)	-0.351 (71)	0.187 (82)	-0.018 (62)	0.776
H(11A) #	0.000	0.000	0.005 (25)	1.200
H(12A)	0.000	0.000	0.013 (30)	1.200
H(13A)	0.000	0.000	0.035 (30)	1.200
H(14A)	0.000	0.000	-0.078 (223)	1.200
H(14D)	0.000	0.000	-0.027 (32)	1.200
H(15A)	0.000	0.000	0.030 (43)	1.200
H(15D)	0.000	0.000	0.264 (81)	1.200
H(16A)	0.000	0.000	-0.061 (97)	1.200
H(16D)	0.000	0.000	-0.010 (38)	1.200
H(17A)	0.000	0.000	0.039 (29)	1.200
H(18A)	0.000	0.000	0.039 (30)	1.200
H(19A)	0.000	0.000	-0.068 (99)	1.200
H(19D)	0.000	0.000	0.028 (42)	1.200
H(20A)	0.000	0.000	-0.022 (28)	1.200

Same values for the other hydrogen atoms of the same methyl group.

Table S5. Quadrupole population parameters.

Atom	Q_{20}	Q_{21+}	Q_{21-}	Q_{22+}	Q_{22-}	κ_2'
ZN(1)	1.696(22)	0.029(21)	0.425(43)	-2.710(9)	1.270(7)	0.888(28)
ZN(2)	-0.146(68)	-2.512(75)	-1.579(88)	-0.251(89)	-1.157(76)	0.888(28)
C(1)	0.175(21)	0.028(15)	0.537(21)	-0.060(26)	-0.229(21)	0.776
C(2)	0.243(50)	0.217(32)	-0.252(60)	0.062(54)	-0.149(45)	0.776
C(3)	0.426(9)	0.248(9)	-0.139(9)	0.037(7)	0.031(7)	0.776
C(4)	-0.002(21)	-0.172(9)	0.336(22)	-0.216(7)	0.032(43)	0.776
C(5)	0.026(75)	0.020(89)	-0.238(68)	0.108(8)	0.145(88)	0.776
C(6)	-0.043(15)	0.344(26)	0.426(21)	-0.070(22)	-0.020(21)	0.776
C(7)	0.273(32)	0.180(54)	0.296(50)	-0.099(58)	-0.205(60)	0.776
C(8)	0.040(9)	0.087(9)	-0.023(9)	0.079(8)	0.282(8)	0.776
C(9)	-0.285(9)	-0.334(9)	0.232(21)	-0.310(7)	0.185(22)	0.776
C(10)	0.315(89)	-0.220(9)	-0.767(75)	-0.216(9)	-0.183(68)	0.776
C(11)	0.025(26)	-0.002(22)	0.044(15)	0.046(9)	-0.236(21)	0.776
C(12)	0.142(54)	-0.009(58)	-0.063(32)	0.289(61)	-0.082(50)	0.776
C(13)	0.152(9)	-0.048(9)	0.108(9)	-0.284(7)	-0.139(8)	0.776
C(14)	0.062(9)	-0.272(9)	0.259(9)	0.052(7)	-0.245(21)	0.776
C(15)	0.100(9)	-0.033(9)	-0.032(89)	-0.398(7)	-0.022(75)	0.776
C(16)	0.117(22)	0.241(9)	-0.142(26)	-0.090(8)	0.075(15)	0.776
C(17)	-0.025(58)	0.238(61)	-0.015(54)	-0.132(7)	0.002(32)	0.776
C(18)	0.207(9)	0.100(7)	0.116(9)	-0.300(9)	-0.283(9)	0.776
C(19)	0.142(9)	0.084(9)	-0.022(9)	0.012(9)	-0.066(9)	0.776
C(20)	0.342(9)	0.108(9)	-0.019(9)	-0.206(9)	0.077(89)	0.776

Table S6. Octupole population parameters.

Atom	O_{30}	O_{31+}	O_{31-}	O_{32+}	O_{32-}	O_{33+}	O_{33-}	κ_3'
ZN (1)	0.127 (22)	-0.010 (15)	-0.047 (22)	0.180 (25)	-0.055 (21)	-0.103 (24)	-0.116 (24)	1.050 (9)
ZN (2)	0.174 (21)	-0.019 (15)	-0.047 (21)	0.267 (26)	0.067 (21)	0.133 (22)	-0.147 (26)	1.050 (9)
C (1)	0.285 (141)	0.041 (86)	0.010 (143)	0.139 (101)	-0.029 (89)	0.107 (64)	-0.049 (71)	0.776
C (2)	0.452 (161)	0.416 (95)	-0.370 (143)	0.274 (101)	0.226 (90)	0.065 (65)	-0.029 (70)	0.776
C (3)	0.410 (169)	0.227 (93)	-0.017 (145)	0.261 (106)	-0.021 (92)	0.208 (68)	0.035 (75)	0.776
C (4)	0.358 (128)	-0.031 (79)	-0.115 (146)	0.316 (120)	-0.111 (96)	0.122 (73)	-0.053 (87)	0.776
C (5)	0.392 (151)	0.072 (85)	-0.241 (138)	0.368 (105)	-0.075 (91)	-0.103 (63)	-0.083 (74)	0.776
C (6)	0.269 (125)	0.207 (79)	-0.216 (138)	-0.019 (111)	-0.108 (88)	0.002 (82)	-0.025 (10)	0.776
C (7)	0.438 (163)	0.082 (92)	-0.252 (145)	0.373 (102)	0.072 (90)	0.050 (64)	0.048 (72)	0.776
C (8)	0.306 (171)	0.156 (94)	-0.521 (150)	0.269 (108)	-0.039 (92)	-0.037 (66)	-0.047 (74)	0.776
C (9)	-0.139 (132)	0.009 (84)	0.409 (151)	0.137 (119)	-0.053 (97)	-0.070 (75)	-0.046 (87)	0.776
C (10)	1.074 (145)	0.063 (81)	-0.468 (148)	0.648 (121)	0.121 (10)	-0.011 (71)	-0.324 (91)	0.776
C (11)	-0.101 (91)	0.339 (81)	-0.443 (65)	-0.473 (73)	-0.410 (73)	0.178 (54)	-0.465 (71)	0.776
C (12)	0.233 (81)	-0.071 (71)	0.013 (56)	-0.159 (75)	0.394 (69)	-0.007 (76)	-0.296 (90)	0.776
C (13)	-0.010 (100)	0.125 (77)	-0.186 (69)	-0.136 (64)	-0.208 (66)	0.125 (52)	-0.305 (67)	0.776
C (14)	0.069 (105)	0.046 (70)	0.301 (63)	-0.046 (82)	-0.397 (104)	-0.178 (82)	-0.165 (10)	0.776
C (15)	0.045 (97)	0.376 (62)	-0.317 (56)	-0.566 (96)	0.141 (69)	0.099 (70)	-0.266 (68)	0.776
C (16)	0.104 (106)	0.003 (72)	0.352 (66)	0.140 (86)	0.285 (97)	0.250 (72)	-0.186 (89)	0.776
C (17)	0.022 (78)	-0.018 (55)	0.628 (63)	-0.149 (67)	0.476 (74)	0.117 (79)	-0.029 (91)	0.776
C (18)	0.134 (104)	-0.109 (76)	0.354 (71)	-0.004 (63)	-0.420 (68)	-0.173 (54)	-0.367 (68)	0.776
C (19)	0.094 (118)	-0.183 (86)	-0.338 (60)	-0.500 (11)	-0.068 (87)	0.286 (99)	-0.320 (87)	0.776
C (20)	0.041 (78)	-0.012 (54)	0.500 (62)	-0.035 (65)	0.541 (63)	0.148 (68)	-0.205 (81)	0.776

Table S7. Hexadecapole population parameters.

Atom	H_{40}	H_{41+}	H_{41-}	H_{42+}	H_{42-}	H_{43+}	H_{43-}	H_{44+}	H_{44-}	κ_4'
ZN(1)	0.005(46)	-0.630(37)	0.524(68)	0.185(49)	0.320(43)	0.770(59)	-0.177(60)	0.327(59)	0.092(63)	0.983(38)
ZN(2)	0.032(50)	0.308(32)	0.726(60)	-0.179(54)	0.250(45)	-0.728(58)	-0.162(67)	-0.148(61)	-0.343(53)	0.983(38)
C(1)	-0.008(167)	-0.099(90)	-0.193(170)	-0.066(130)	0.071(124)	-0.014(90)	-0.063(104)	-0.046(78)	0.091(69)	0.776
C(2)	0.186(183)	0.142(97)	0.064(172)	0.040(131)	-0.032(129)	-0.127(88)	0.041(103)	0.016(79)	0.020(73)	0.776
C(3)	-0.170(184)	0.014(96)	0.223(167)	-0.306(136)	0.253(134)	0.092(87)	-0.050(107)	-0.054(81)	0.021(75)	0.776
C(4)	0.465(158)	0.106(85)	0.041(176)	0.074(142)	0.200(127)	0.140(99)	-0.146(127)	0.252(91)	0.101(79)	0.776
C(5)	0.174(166)	0.071(86)	-0.390(164)	0.013(132)	0.101(127)	0.041(88)	0.124(103)	-0.079(79)	-0.240(70)	0.776
C(6)	-0.214(155)	0.106(85)	-0.178(176)	-0.167(141)	0.039(125)	-0.010(91)	-0.288(121)	0.132(106)	0.070(87)	0.776
C(7)	0.185(186)	-0.108(96)	-0.141(181)	-0.037(136)	0.261(128)	-0.070(86)	0.016(106)	-0.053(80)	0.087(73)	0.776
C(8)	-0.035(183)	0.062(96)	0.025(179)	-0.052(138)	0.121(134)	0.221(88)	-0.079(108)	-0.022(81)	-0.101(74)	0.776
C(9)	-0.193(167)	0.153(88)	0.312(183)	-0.105(148)	-0.142(138)	0.490(100)	0.075(127)	0.233(91)	-0.140(80)	0.776
C(10)	0.708(157)	0.055(86)	0.263(174)	0.374(143)	0.128(132)	0.146(99)	0.368(120)	0.206(90)	-0.125(79)	0.776
C(11)	-0.229(91)	0.072(86)	-0.231(72)	0.059(79)	-0.152(78)	-0.125(68)	-0.148(85)	0.185(56)	0.323(65)	0.776
C(12)	-0.222(83)	-0.018(80)	-0.025(65)	0.094(80)	-0.138(70)	-0.119(77)	0.127(90)	-0.172(86)	-0.200(86)	0.776
C(13)	-0.046(110)	-0.191(93)	-0.090(87)	0.165(78)	-0.061(79)	0.053(67)	-0.008(80)	0.059(58)	-0.012(61)	0.776
C(14)	-0.017(90)	-0.052(81)	0.333(72)	-0.265(71)	0.011(73)	-0.049(81)	-0.154(109)	-0.062(84)	0.101(93)	0.776
C(15)	-0.169(96)	-0.006(69)	-0.130(72)	0.116(68)	-0.398(69)	-0.352(92)	-0.012(81)	0.057(74)	-0.074(78)	0.776
C(16)	-0.173(99)	0.264(82)	0.148(75)	-0.487(76)	0.056(79)	-0.158(85)	-0.136(105)	0.068(80)	0.145(86)	0.776
C(17)	-0.049(75)	0.207(67)	0.171(68)	-0.251(74)	-0.041(74)	0.159(77)	-0.109(88)	-0.244(80)	0.082(89)	0.776
C(18)	-0.022(109)	-0.152(91)	-0.033(82)	-0.028(75)	0.271(84)	0.166(65)	0.085(79)	-0.065(60)	-0.211(63)	0.776
C(19)	-0.120(107)	-0.089(94)	0.069(71)	-0.046(81)	0.191(76)	-0.039(106)	0.302(94)	-0.096(90)	0.014(86)	0.776
C(20)	-0.196(75)	0.320(63)	0.164(76)	-0.038(72)	-0.143(69)	0.059(73)	0.008(90)	-0.203(74)	0.049(78)	0.776

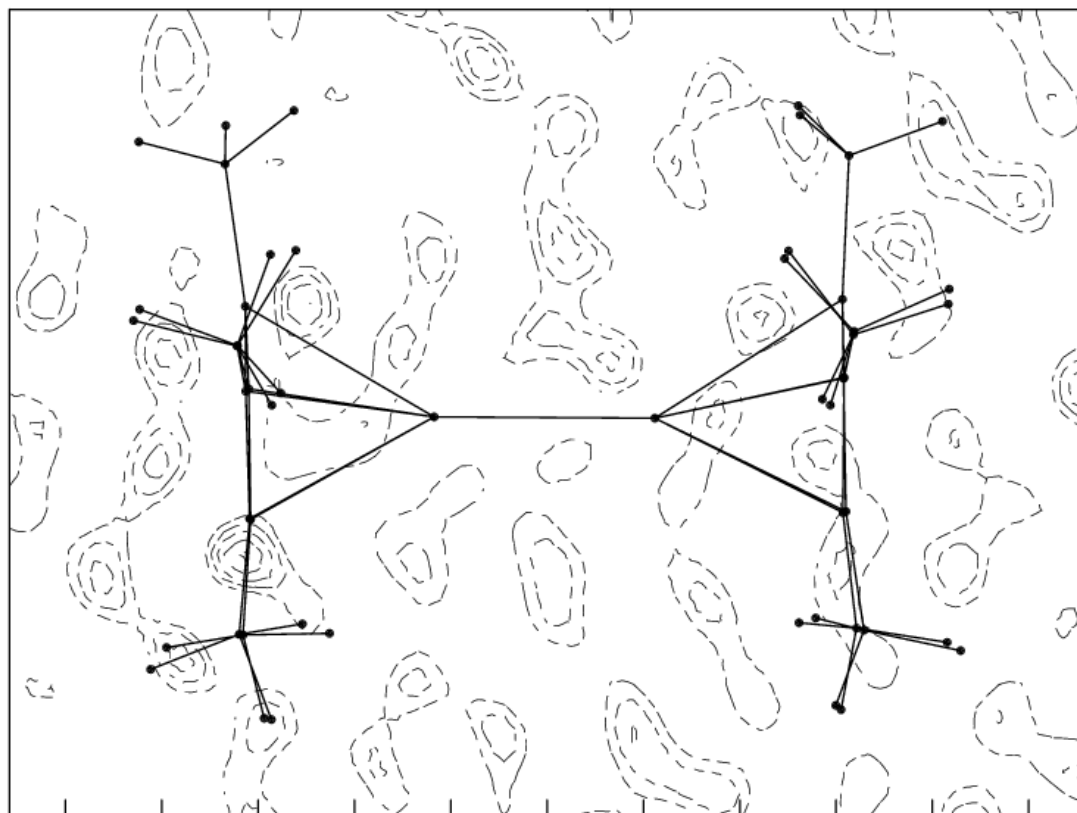


Figure S1. Final Difference Fourier map from neutron diffraction experiment in the Zn(2)-Zn(1)-C(1) plane. Contour values at $0.1 \text{ e } \text{\AA}^{-3}$.

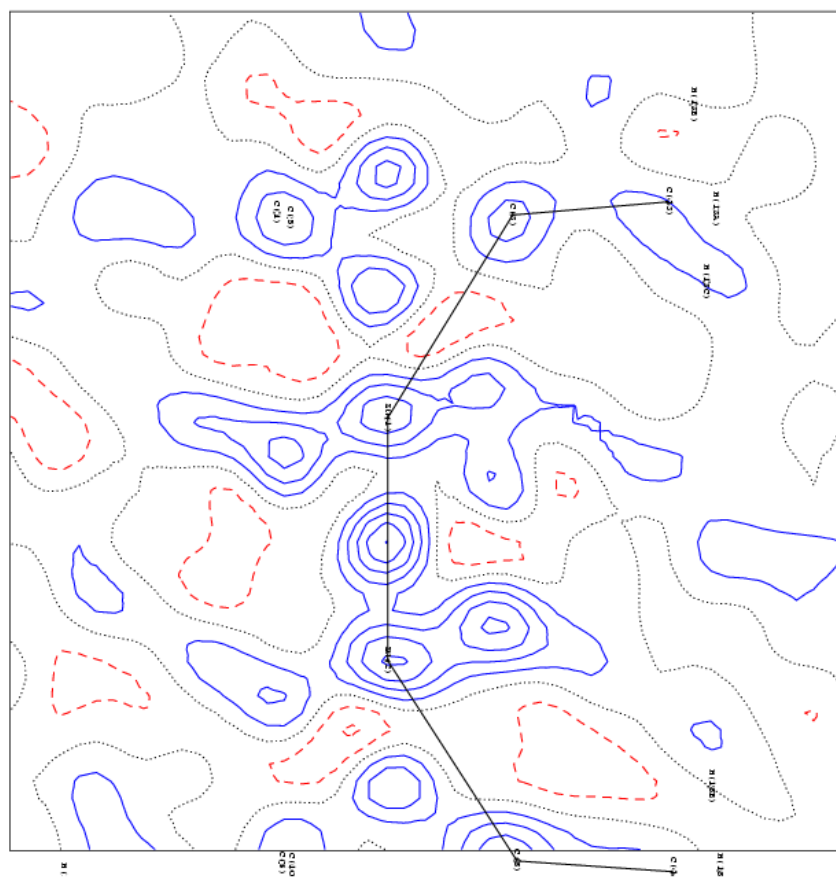


Figure S2. Final Difference Fourier map from X-ray synchrotron radiation experiment in the Zn(2)-Zn(1)-C(1) plane. Contour values at $0.1 \text{ e } \text{\AA}^{-3}$. Positive values plotted as solid blue lines, negative values as dashed red lines, and zero value as dotted black lines.