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SUPPORTING INFORMATION

Title: Charge Density of Intra- and Intermolecular Halogen Contacts
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Supporting Information to the Article

Charge Density of Intra- and Intermolecular Halogen Contacts

by Ruimin Wang, Thomas S. Dols, Christian W. Lehmann, and Ulli Englert

Preparation and Crystallization of **10**

2 mmol (272 mg) $ZnCl_2$ and 4mmol (368 mg) of 4-aminopyridine were dissolved in 30 mL of methanol and stirred at room temperature for 30 min. The solution was left at room temperature for evaporation; colourless crystals formed after several hours.

Crystallization of **11**

500 mg of triphenylchloromethane (commercial, Aldrich) were dissolved in 50 mL of dry (dest from Na) hexane under N_2 at reflux temperature. The solution was slowly cooled to 4 °C; colourless crystals formed over night.

Crystallographic studies:

X-ray data collection

Intensity data for **10** were collected at 100 K on a Bruker D8 goniometer equipped with an APEX CCD detector using Mo *Kα* radiation (λ = 0.71073 Å). The radiation source was an INCOATEC I-*μ*S microsource equipped with multilayer optics. An Oxford Cryosystems 700 controller was used to ensure temperature stability during data collection. Information concerning data completeness has been compiled in Table S1.

Intensity data for **11** were collected at 100 K on a Bruker AXS Kappa Mach3 goniometer with an Apex-II CCD detector. X-rays were generated by a rotating anode (Bruker AXS FR 591) equipped with Montel mirror optics using Mo-Kα radiation (λ = 0.71073 Å). An Oxford Cryosystems 700 controller was used to ensure temperature stability during data collection. Information concerning data completeness has been compiled in Table S2.

For both data sets the SAINT software [1] was used for integration. Absorption corrections based on multiple observations were performed with the SADABS software.[2] Crystal data are summarized in Table S3.

Spherical-atom refinement and multipole refinement

The structures were solved with direct methods and the independent atom refinement was performed by full-matrix least squares on F^2.[3] Anisotropic displacement parameters were assigned to non-H atoms; H-atoms were included as

riding in idealized geometry.

The multipolar refinement was based on the independent atom model as starting geometry. It was carried out on F^2 according to the Hansen & Coppens formalism for aspherical atomic density expansion[4] as implemented in *XD*2006.[5]

For **10**, the VM databank was adopted for the refinement. For the metal center, the 12 electrons of $3d^{10}4s^2$ were regarded to populate the valence shell with the initial valence state of +2. Multipole coefficients up to hexadecapoles were refined for non-H atoms. For H atoms, positions were constrained to C-H bond distances of 1.083 Å and monopoles and bond-oriented dipoles were considered in the multipolar refinements. Contraction parameters κ were refined for all atom types; κ' for Cl and Zn were fixed to 1.0 and refined for the remaining atom types.

For **11**, the CR databank was used. Multipole coefficients up to hexadecapoles were refined for the Cl atoms and up to octapoles for C atoms. H atoms were freely refined, and monopoles and bond-oriented dipoles were considered in the multipolar refinements. In the 15 phenyl rings, all ipso-C, ortho-C, meta-C and para-C atoms were assigned the same multipole occupancies. Contraction parameters κ were refined for all atom types; κ' for Cl was fixed to 1.0 and refined for the remaining atom types.

In all refinements the multipoles were introduced stepwise until the full multipolar expansion was reached. Convergence results have been compiled in Table S3.

Table S1: Data completeness for **10**

```
================================================================================
Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)
================================================================================
Theta sin(th)/Lambda Complete  Expected Measured  Missing
--------------------------------------------------------------------------------
 20.82     0.500     0.999          671      670        1
 23.01     0.550     0.999          885      884        1
 25.24     0.600     0.999         1140     1139        1
 27.51     0.650     0.999         1466     1465        1
 29.84     0.700     0.999         1818     1817        1
 32.21     0.750     1.000         2233     2232        1
 34.65     0.800     1.000         2725     2724        1
 37.17     0.850     1.000         3255     3254        1
 39.77     0.900     1.000         3858     3857        1
 42.47     0.950     1.000         4556     4555        1
 45.29     1.000     1.000         5296     5295        1
 48.27     1.050     1.000         6139     6138        1
 51.43     1.100     1.000         7062     7061        1
 54.82     1.150     1.000         8062     8061        1
 57.79     1.190     1.000         8938     8937        1

================================================================================
Summary of Reflection Data in FCF - Note: Friedel Pairs Averaged
================================================================================
Total # of Reflections in FCF.   8937  (Hmax = 20, Kmax = 23, Lmax = 35) Obs
Number above Rep. Theta(Max) .      1
Actual   Theta(Max) (Deg.) ... 57.790  (Hmax = 20, Kmax = 23, Lmax = 35) Exp
Reported Theta(Max) (Deg.) ... 57.790  (Hmax = 20, Kmax = 23, Lmax = 35) Rep
Actual   Theta(Min) (Deg.) ...  3.148
Reported Theta(Min) (Deg.) ...  3.150

Unique (Expected) .............   8937
Unique (in FCF) ...............   8937
Observed [I .gt. 2 Sig(I)] ...    6683
Less-Thans ....................   2254
Negative Intensities ..........    255
Negative Intensities < - 2 SIG      0

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

Space Group Extinctions .......    288
```

Table S2: Data completeness for **11**

```
================================================================================
Resolution & Completeness Statistics (Cumulative and Friedel Pairs Averaged)
================================================================================
Theta sin(th)/Lambda Complete  Expected Measured  Missing
--------------------------------------------------------------------------------
 20.82     0.500     1.000         7538     7536        2
 23.01     0.550     1.000        10057    10055        2
 25.24     0.600     1.000        13054    13052        2
 27.51     0.650     1.000        16610    16607        3
 29.84     0.700     1.000        20710    20707        3
 32.21     0.750     1.000        25481    25472        9
 34.65     0.800     0.998        30961    30905       56
 36.96     0.846     0.965        36611    35316     1295

Note: The Reported Completeness refers to the Actual H,K,L Index Range


================================================================================
Summary of Reflection Data in FCF - Note: Friedel Pairs Averaged
================================================================================
Total # of Reflections in FCF.  35316  (Hmax = 21, Kmax = 23, Lmax = 35) Obs
Number above Rep. Theta(Max) .      1
Actual   Theta(Max) (Deg.) ... 36.962  (Hmax = 21, Kmax = 23, Lmax = 35) Exp
Reported Theta(Max) (Deg.) ... 36.960  (Hmax = 21, Kmax = 23, Lmax = 35) Rep
Actual   Theta(Min) (Deg.) ...  1.513
Reported Theta(Min) (Deg.) ...  1.510

Unique (Expected) ............  36606
Unique (in FCF) ..............  35316
Observed [I .gt. 2 Sig(I)] ...  25917
Less-Thans ...................   9399
Negative Intensities .........   3886
Negative Intensities < - 2 SIG      0

Missing (Total) ..............   1295
Missing Below Th(Min) ........      1
Missing Th(Min) to STh/L=0.600      1
Missing STh/L=0.600 to Th(Max)   1293
Missing Very Strong Refl. ....      0
Beamstop Effected Reflections       0

Space Group Extinctions ......      0
```

Table S3. Crystal data, data collection parameters and convergence results for **10** and **11**.

	10	**11**
Crystal data		
Chemical formula	$C_{10}H_{12}Cl_2N_4Zn$	$C_{19}H_{15}Cl_2$
M_r	324.50	278.76
Crystal system	Monoclinic	Triclinic
Space group	*C*2/c	*P*-1
a, *b*, *c* (Å)	8.8228(2), 9.8007(2), 14.9616(2)	12.8750(18), 14.0425(19), 21.097(3)
α, β, γ (°)	90, 102.3660(6), 90	105.500(2), 99.335(2), 93.248(2)
V (Å^3)	1263.71(4)	3606.8(9)
Z	4	10
μ (mm^{-1})	2.25	0.25
Crystal size (mm)	0.30 × 0.10 × 0.10	0.34 × 0.24 × 0.21
Data collection		
T (K)	100	100
T_{min}, T_{max}	0.895, 0.943	0.920, 0.950
No. of measured, independent observed [$I > 2\sigma(I)$] reflection	72878, 8937, 6683	315715, 35316, 25918
R_{int}	0.029	0.050
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.19	0.85
Completeness to θ_{max}	1.000	0.965
IAM refinement		
$R[F^2 > 2\sigma(F^2)]$, *wR*(all F^2), *S*	0.028, 0.052, 0.90	0.041, 0.118, 1.09
No. of parameters	86	901
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, -0.53	0.53, -0.49
Multipole refinement		
No. of refls in refinement	6683	35316
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.015, 0.017, 1.248	0.027, 0.084, 1.408
No. of parameters	312	1482
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.211, -0.234	0.292, -0.191

References:

[1] SAINT, Version 6.45. Bruker AXS Inc., Madison, Wisconsin, USA, **2003**.

[2] SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

[3] Sheldrick, G. M. Acta Crystallogr. Sect A **2008**, 64, 112.

[4] Hansen, N. K. & Coppens, P. Acta Crystallogr. Sect A **1978**, 34, 909.

[5] Volkov, A., Macchi, P., Farrugia, L. J., Gatti, C., Mallison, P. R., Richter, T. & Koritsanszky, T. XD2006, University of New York at Buffalo, USA, **2006**.