The Perchlorophenalenyl Radical, $C_{13}Cl_9$: A Modulated Structure with Nine Threefold-Symmetric Molecules in the Asymmetric Unit

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Synopsis: The strongly ruffled, odd-alternant radical $C_{13}Cl_9$ stacks along crystallographic threefold axes, but the intrastack spacing is too large for the material to be a good conductor. The spacing is determined by interstack interactions, which are also responsible for the structural modulations.

Contents: PRECESSION projections for the first and second crystals showing layers hk5, hk6, and hk7 (2 pages).

Wilson plots (1) for reflections having different values of mod(l,6), and (2) for reflections having mod(l,6)=0 and different values of mod(-h+k-l,3) (2 pages)

SHELXL97 input/output file from the final least squares cycle.

Tables of crystallographic information generated in Chester.

Description of the quantum-mechanical calculations (5 pages).

PRECESSION projections hk$n$, n = 0, 1, 2, and 3 for a crystal of the "other" phase (2 pages)

Electronic and Molecular Structure of $C_{13}H_9$ (PLY) and $C_{13}Cl_9$ (PCPLY)

We have carried out *ab initio* density functional theory calculations, at the B3LYP/6-31G** level, on PCPLY ($C_{13}Cl_9$) and its parent radical, PLY ($C_{13}H_9$). Geometry optimizations were performed within D_{3h} symmetry constraints on PLY, its cation and anion; frequency calculations confirmed that these were true minima. In the case of PCPLY, where the X-ray results clearly signal a puckering of the molecule away from D_{3h}, geometry optimizations on all three oxidation states were performed in D_3 as well as in D_{3h} symmetry (Table 1).

Table 1. B3LYP/6-31G**Optimized Distances (Å)

		C 1-C2	C 3-C4	C 4-C5	C 1-R	C 2-R
D_{3h}						
	PLY+	1.394	1.417	1.422	1.086	1.084
	PLY	1.392	1.418	1.431	1.086	1.086
	PLY-	1.392	1.422	1.444	1.088	1.091
	Delta	-0.002	0.005	0.021	0.002	0.007
D_{3h}						
	P	1.	1.	1.	1.	1.

PCPLY+	1.402	1.439	1.454	1.718	1.729
PCPLY	1.398	1.436	1.461	1.742	1.742
PCPLY-	1.392	1.434	1.471	1.765	1.759
Delta	-0.010	-0.005	0.017	0.047	0.030

D_3

PCPLY+	1.404	1.433	1.438	1.716	1.724
PCPLY	1.402	1.425	1.439	1.734	1.732
X-Ray	(1.393)	(1.425)	(1.437)	(1.716)	(1.722)
PCPLY-	1.394	1.426	1.446	1.760	1.760
Delta	-0.009	-0.008	0.008	0.045	0.036

Delta = the difference in bond distances between the cation and anion

Total energies and energy differences, as a function of oxidation state, are shown in Table 2. While the distortion of PCPLY away from D_{3h}, measured in terms of the pitch angle τ, is relatively constant (near 8°) for all oxidation states, the stabilization energy occasioned by puckering changes with the charge on the ring. The anion is most stabilized by the distortion,

while the cation is least stabilized. These trends can be attributed to the introduction of s-orbital character into the π-system as the distortion progresses - it is the curved carbon effect.[1] As a result, both the IP and EA of PCPLY increase with ring puckering. Insofar as the changes are approximately the same, the overall value of the disproportionation energy (IP-EA) remains relatively constant.

Table 2. Computed total energies (Hartrees), IP, EA and ΔH_{disp} values (eV) for PLY and PCPLY.

	PLY (D_{3h})	PCPLY (D_{3h})	PCPLY (D_3)
R in $C_{13}R_9$	H	Cl	Cl
Cation	-500.6015695	-4636.8030039 (6.1[a])	-4636.8126578 (8.1[b])
Radical	-500.8247881	-4637.0521541 (10.1[a])	-4637.0683083 (8.5[b])
Anion	-500.8557502	-4637.1476201 (15.2[a])	-4637.1717728 (8.4[b])
IP	6.07	6.78	6.95
EA	0.84	2.68	2.81
IP - EA	5.23	4.18	4.14

The computed ionization potential (IP) and electron affinity (EA) values parallel the results of the electrochemical measurements on PLY and PCPLY; the latter is harder to oxidize, and much easier to reduce.[2,3]. Indeed the gas phase data for PCPLY rank it as a pseudo halogen. This conclusion is not surprising given the combined inductive and conjugative influence of nine chlorines on the PCPLY periphery. However, the change in IP-EA is much larger than the corresponding change in the E_{cell} value. Indeed a shift in IP-EA of near 1 eV would, on the basis of our experience with CSN radicals, should lead to a more substantial decrease in E_{cell} between PLY and PCPLY.

Spin Densities and ESR Hyperfine Coupling Constants

PLY is an odd-alternant hydrocarbon; at the HMO level its non-bonding SOMO is nodal at all but the C01 positions. The computed spin densities for PLY (Table 2) and PCPLY (Table 3) at the B3LYP/6-31G** level) mirror these basic one-electron ideas, although both the C02 and C04 carbons are associated with a substantial negative spin density. The calculated hyperfine coupling constants for PLY are in reasonable agreement with the experimental values.[4]

In the case of PCPLY there is very little spin leakage to the exocyclic chlorines, and the of loss in ring planarity (from D$_{3h}$ to D$_3$) are minimal; the changes in spin densities accompanying ring puckering are small. Interestingly, spin leakage to chlorine decreases with puckering. Computed coupling constants are also provided in Table 2; the calculated a$_{Cl}$ values are small, regardless of geometry (D$_{3h}$ or D$_3$).

Table 3 Computed (B3LYP/6-31G**) spin densities and hyperfine coupling constants for PLY.

Position	C01/ C03	C02	C04	C05

D$_{3h}$

Spin density on C	0.308163	-0.149484	-0.135648	0.072246
Spin density on H	-0.013536	0.005128		
a(^{13}C) gauss	13.50894	-8.86341	-8.63495	4.23224
a(^{1}H) gauss	-7.198(6.30)[a]	2.671(1.82)[a]		

[a]Experimental values from ref 4.

Table 4 Computed B3LYP/6-31G** spin densities and hyperfine coupling constants for PCPLY.

Position	C01/C03	C02	C04	C05
D_{3h}				
Spin density on C	0.258131	0.127405	0.126526	0.07351
Spin density on Cl	0.026911	0.007324		
$a(^{13}C)$ gauss	13.8222	9.14431	8.67683	4.37525
$a(^{35}Cl)$ gauss	1.03929	0.41747		
D_3				
Spin density on C	0.262723	0.129879	0.135101	0.083778
Spin density on Cl	0.024102	0.003264		
$a(^{13}C)$ gauss	14.16471	9.15712	9.22015	18.68488
$a(^{35}Cl)$ gauss	0.797(0.6)[a]	0.021(<0.5)[a]		

[a]Experimental values from ref 5.

Experimental Section

***Ab Initio* Calculations** All calculations were run on Pentium workstations using the B3LYP DFT method and a 6-31G** basis set, as contained in the Gaussian 98W suite of programs.[1] The geometries of the PLY anion, radical and cation were fully optimized in D_{3h} symmetry; frequency calculations confirmed that the geometries were true minima.   Optimization of the PCPLY anion, radical and cation were performed within both D_{3h} and D_3 symmetry constraints. The puckering of the PCPLY framework away from D_{3h} symmetry is defined in terms of the pitch angle of the blades of the PCPLY propeller.

References

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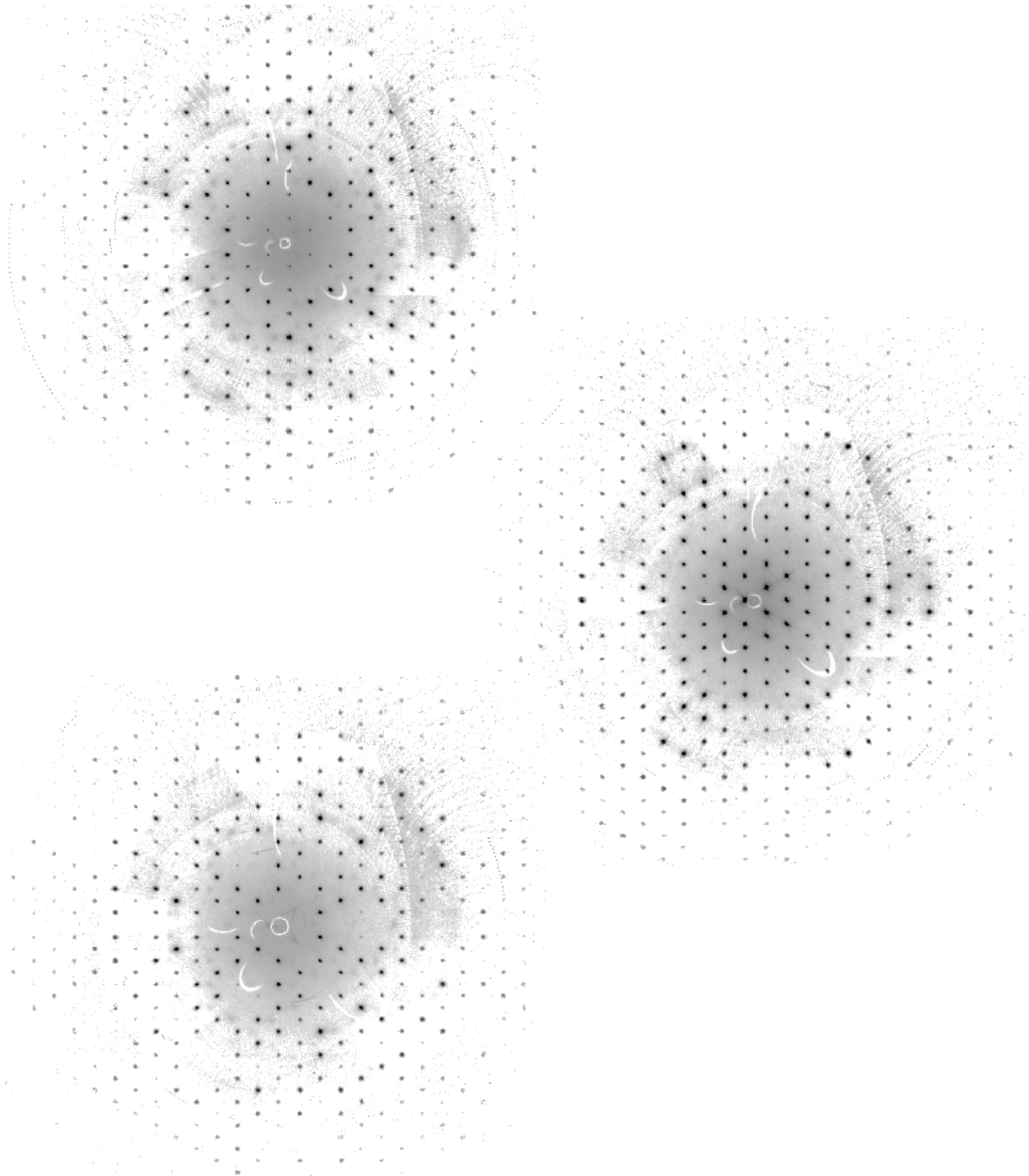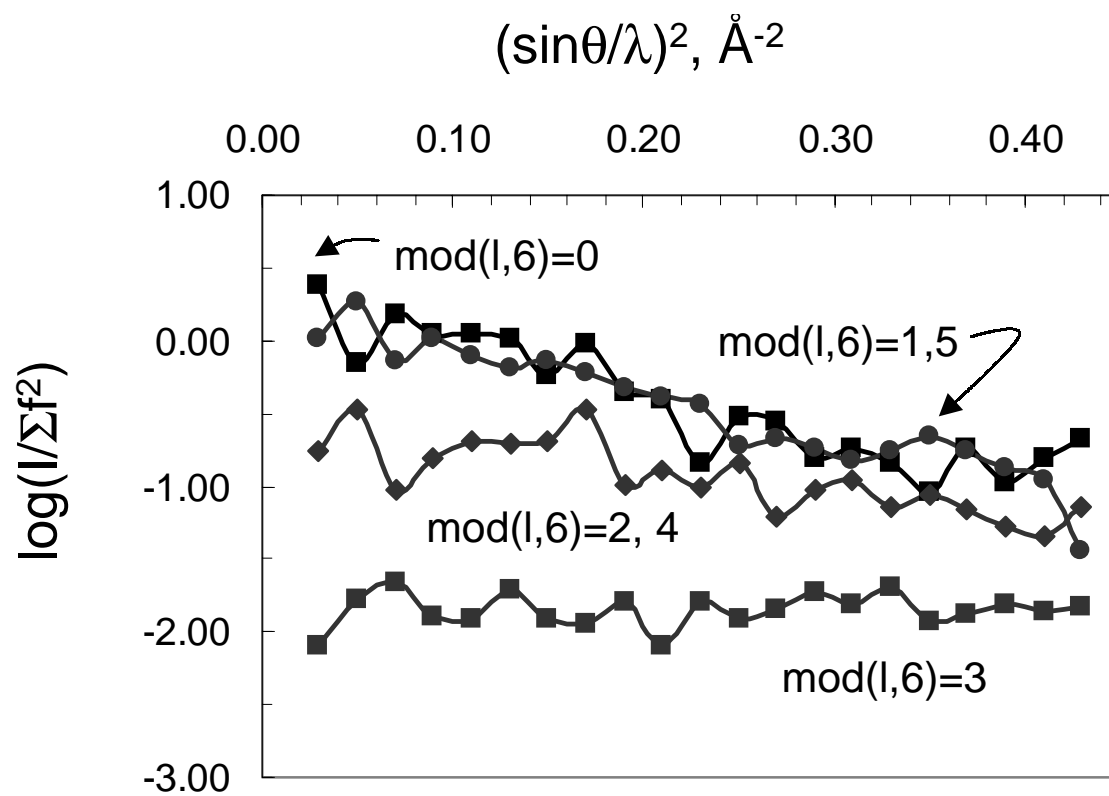
K99081 (first crystal)
hkn, n=5 (top), 6 (middle), and 7 (bottom)
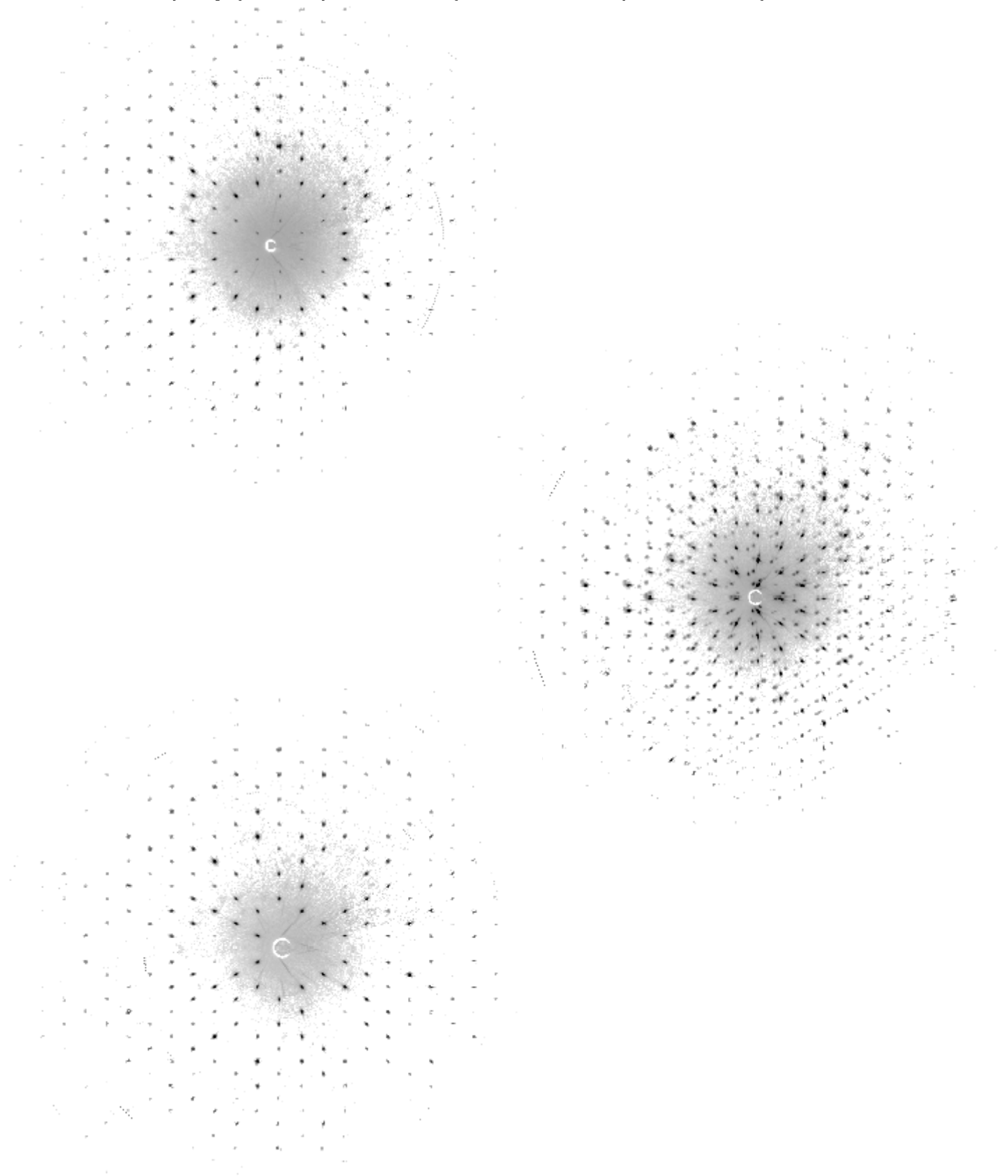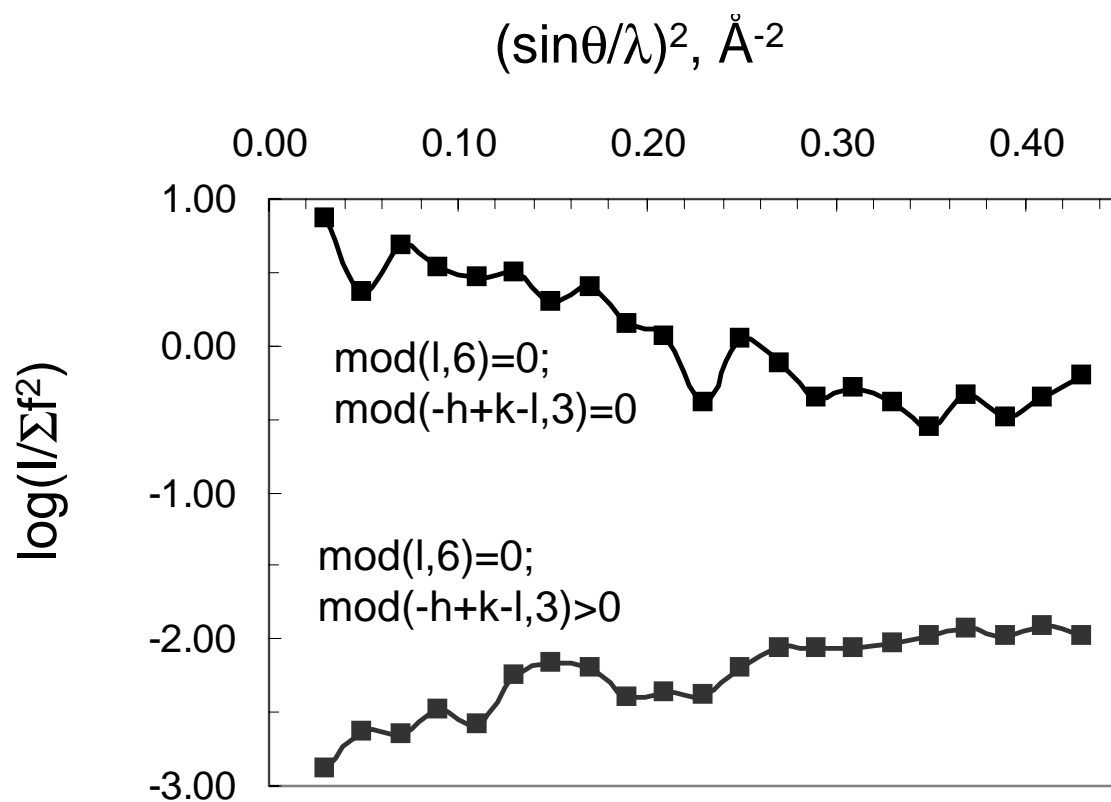
K99092 (second crystal)
hkn, n=5 (top), 6 (middle), and 7 (bottom

$(\sin\theta/\lambda)^2$, Å^{-2}

log(I/Σf²)

mod(I,6)=0

mod(I,6)=1,5

mod(I,6)=2, 4

mod(I,6)=3

mod(I,6)=	Slope	Intercept
0	-3.3(3)	+0.32(8)
1, 5	-3.2(2)	+0.36(5)
2, 4	-1.6(3)	-0.57(8)
3	+0.1(2)	-1.88(6)

(First and last points omitted)

(sinθ/λ)², Å⁻²

$(\sin\theta/\lambda)^2$, Å^{-2}
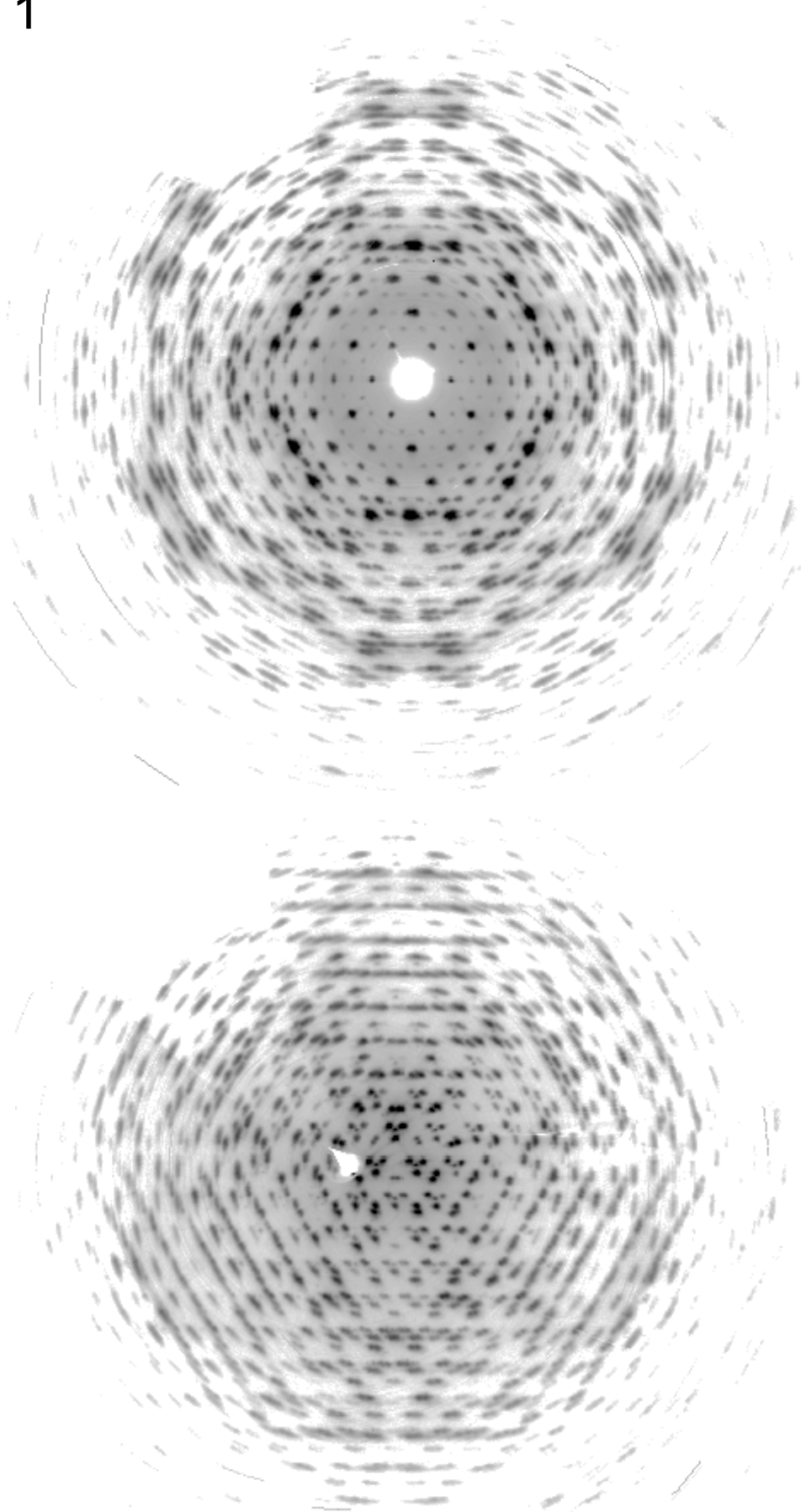
mod	Slope	Intercept
=0	-3.4(3)	+0.81(8)
>0	+2.1(2)	-2.73(6)

(First and last points omitted)

K99072 (another phase?)
hkn, n=0, 1

K99072 (another phase?)
hkn, n=2,3