

**Experiment title:**

Ab initio structure determination of Alkali-Pentamethyl-cyclopentadienide compounds by powder diffraction

Experiment**number:**

CH-189

Beamline:

BM16

Date of experiment:

from: 23-Nov-96 to: 04-Dec-96

Date of report:

1 g-Mar-97

Shifts:

12

Local contact(s):

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*Received at ESRF:***7 AVR. 1997****Names and affiliations of applicants** (* indicates experimental&s):* Robert E. Dinnebier ¹* Falk Olbrich ²* Markus Wunschel ¹¹ Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany² Institute of Inorganic Chemistry, University of Hamburg, D-20 146 **Hamburg, Germany****Report:**

The structures of all Alkali-Cyclopentadienides (Alkali-Cp's) have recently been solved *ab initio* by high resolution powder diffraction at a Synchrotron source [1,2,3]. During this run, we measured the powder pattern of the corresponding Alkali-Pentamethyl-cyclopentadienides (Alkali-Cp*) in order to solve their structures.

Data collection was carried out for LiCp*, RbCp* and CsCp* at room temperature using 0.84979 Å from double monochromator and 9 parallel Ge (111) analyzers. None of the structures could be solved unambiguously so far. The most probable lattices and space groups are $a = 14.7696(1)$ Å, $c = 3.82195(4)$ Å in $R3$ with $Z=3$ for LiCp* , $a = 75422(1)$ Å, $c = 19.1890(3)$ Å in $P4_1$ with $Z=4$ for RbCp*, and $a = 7.5384(2)$ Å, $c = 19.9646(4)$ Å in $P4_1$ with $Z=4$ for CsCp*. Application of the extinction rules, however, leads to much higher symmetry than allowed by molecular symmetry. There is strong evidence that in contrast to the Alkaline-Cp's the Alkaline-Cp*'s are heavily disordered.

In case of LiCp* this could be modeled by simulating three different orientations of the Cp* ring using the three fold axis of R3 symmetry [Fig. 2]

For the Rietveld refinements, the Cp*-rings were treated as rigid bodies. None of the hydrogens could be included in the model, since the orientation of the CH₃ groups is unpredictable. The actual Rietveld refinement of LiCp* yields to R-p = 6.45 %, R-wp = 9.45 %, and R-F = 18.18 % [Fig. 1].

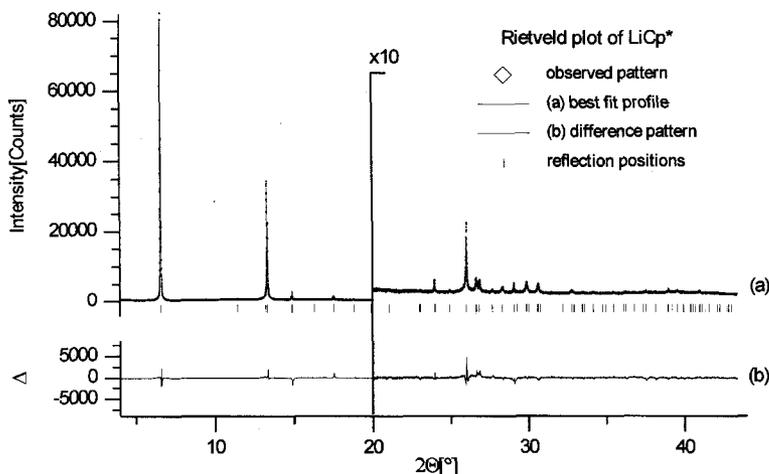


Fig 1:
Actual Rietveld plot of LiCp* using R3 symmetry. The pattern at higher angle (>20° 2θ) is enlarged by a factor of 10.

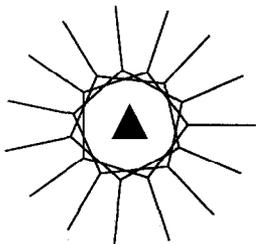


Fig. 2:
Model of disorder for LiCp*. The three-fold axis in R3 is incompatible to molecular symmetry.

References:

- [1] R. E. Dinnebier, F. Olbrich, P. W. Stephens & S. van Smaalen (1997), Acta Cryst B53, 153-158.
- [2] R. E. Dinnebier, U. Behrens, F. Olbrich (1997), Organometallics, in press.
- [3] R. E. Dinnebier, F. Olbrich, G. Bendele (1997), Acta Cryst C (53), in press.