

Application of a new similarity index for the crystal structure determination and cluster analysis of powder diagrams

D.W.M. Hofmann, L.N. Kuleshova, and F. Hofmann

DGK
Erlangen
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FlexCryst

Main features of FlexCryst

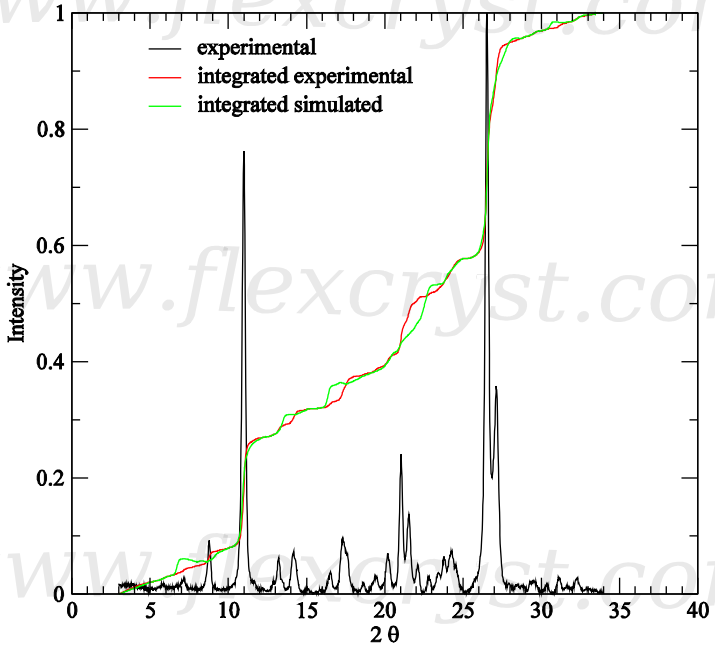
- program bases on classical mechanics
- very quick
- molecules are rigid
- energy function contains only short range interaction
- parameters optimized by data mining on the CSD
- structures are clustered and only unique structures are printed
- automatic structure refinement
- Interactive interface with visualization

Similarity Index

For comparison we use the area between the integrated and normalized powder

similarity index:

$$s_{\mathrm{int}} = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{\sum_{j=1}^{i} I_j^{calc}}{\sum_{j=1}^{n} I_j^{calc}} - \frac{\sum_{j=1}^{i} I_j^{count}}{\sum_{j=1}^{n} I_j^{count}}\right|$$



Comparison between experimental and integrated simulated and experimental powder diagrams for pigment PY111 for the predicted structure of rank 1, similarity index s = 0.41%.
(correct solution has been found on rank 3)

D.W.M.Hofmann and L.N.Kuleshova, J. Appl. Cryst. (2005) 38, 861.
D.W.M.Hofmann and L.N.Kuleshova,Crystallography Reports. (2006). 51. 452

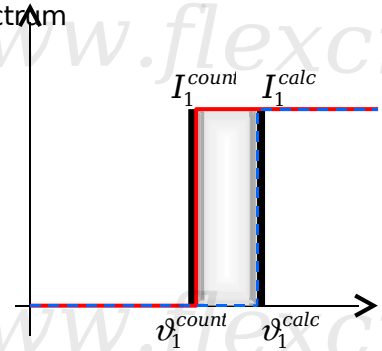
Advantages of the new similarity index

Similar powder diagrams are recognized, even if peaks are shifted.	The similarity index is calculated quickly because the evaluation works pointwise.	During refinement interchanged peaks can be reordered correctly.

Norm based indices of the difference spectra can be calculated quickly, but do not recognize shifts:

$$s_{l-norm} = \left\| \left| I^{count} - I^{calc} \right|^{l} \right\|$$

- l=1 Rietveld index
- l=2 sum of the squared difference spectrum



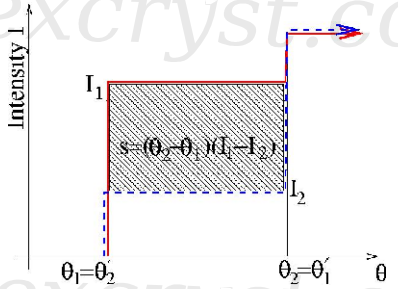
$$s_{\text{int}} = \left| \vartheta_1^{count} - \vartheta_1^{calc} \right| \left(I_1^{count} + I_1^{calc} \right) / 2$$

$$s_R = \left(I_1^{count} + I_1^{calc} \right)$$

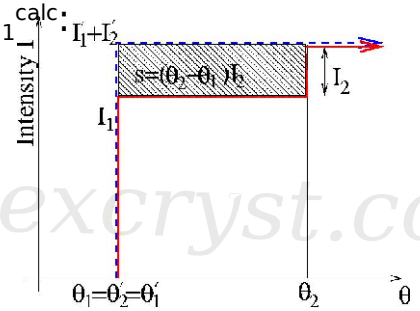
Folded indices recognize shifts by comparing environments of two spectra, but they are slow in evaluation.

$$s_{fold} = \left(I^{count} - I^{calc} \right)^T \mathbf{M} \left(I^{count} - I^{calc} \right)$$

Initial situation:



Intermediate situation, peak I_1^{count} matches now I_1^{calc}:



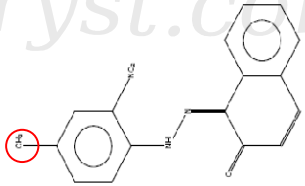
Applications

- Comparison of Powder Diagrams
- Clustering of Powder Diagrams
- Structure Determination of isostructural Crystals
- Comparison of Crystal Structures
- Clustering of Crystals Structures
- Structure Determination from Powder Diagrams

Structure Determination from isostructural Crystals

Pigment Red 3

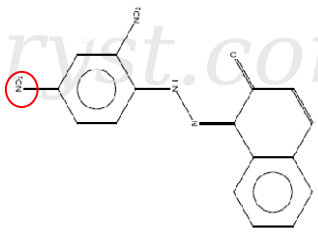
MNIPZN
Reference: A.Whitaker (1978) *Z.Kristallogr.,Kristallgeom.,Krystallphys.,Kristallchem.* ,**147,**99
Compound Name: 4-Methyl-2-nitrophenylazo-2-naphthol
Space Group: P21/a
Cell: a 16.316 ***b*** 12.860 ***c*** 6.960
Space Group No.: 14 ***(Å,°)*** a 90.00 b 102.00(50) g 90.00



The refinement works automatically, even if cell constants are different

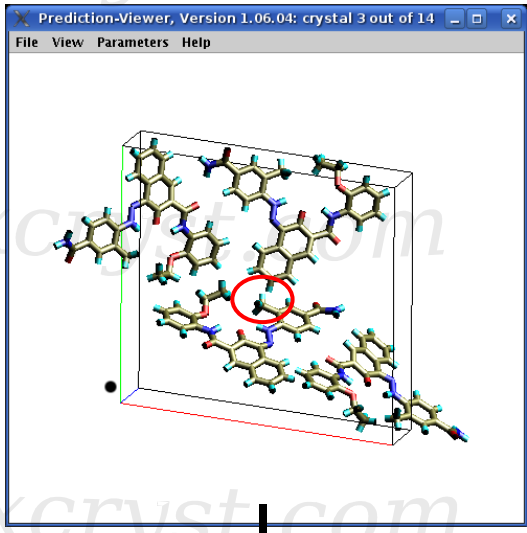
Pigment Orange 5

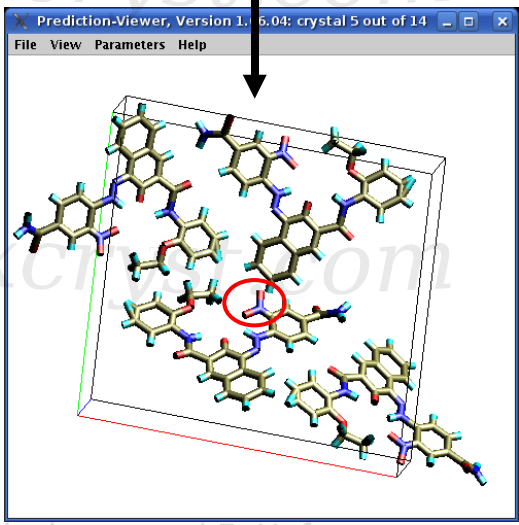
CICCUN
Reference: M.U.Schmidt, C.Buchsbaum, J.M.Schnorr, D.W.M.Hofmann, M.Ermrich (2007) *Z.Kristallogr.* ,**222,**30
Compound Name: 1-((2,4-Dinitrophenyl)azo)-2-naphthol
Space Group: P21/a
Cell: a 16.365 ***b*** 12.874 ***c*** 6.924
Space Group No.: 14 ***(Å,°)*** a 90.00 b 100.14(0) g 90.00



4-((4-(Aminocarbonyl)-2-(methyl)phenyl)azo)-N-(2-ethoxyphenyl)-3-hydroxynaphthalene-2-carboxamide

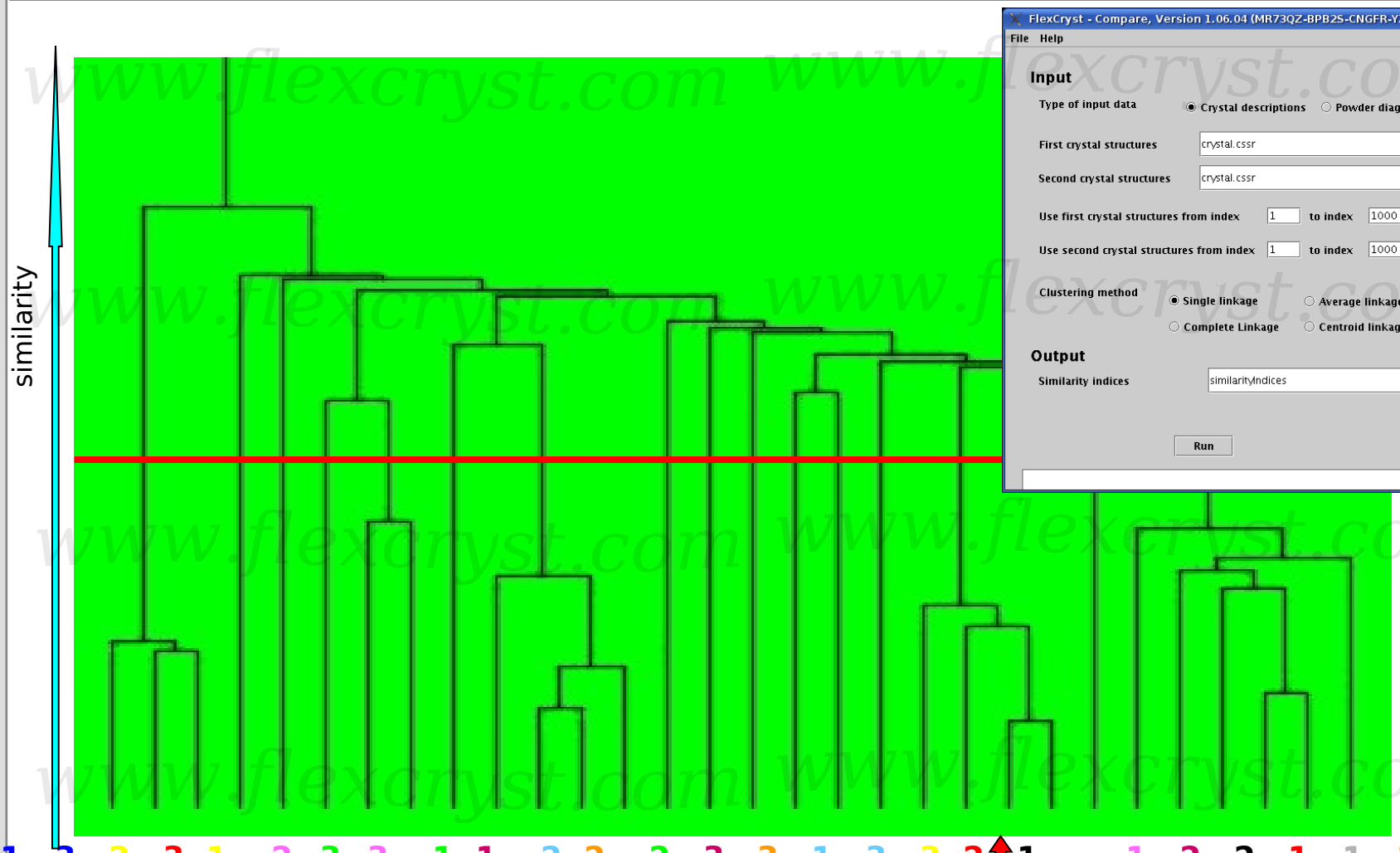
D.W.M.Hofmann and L.N.Kuleshova
Journal of Applied Crystallography (2005) 38, 861-866.





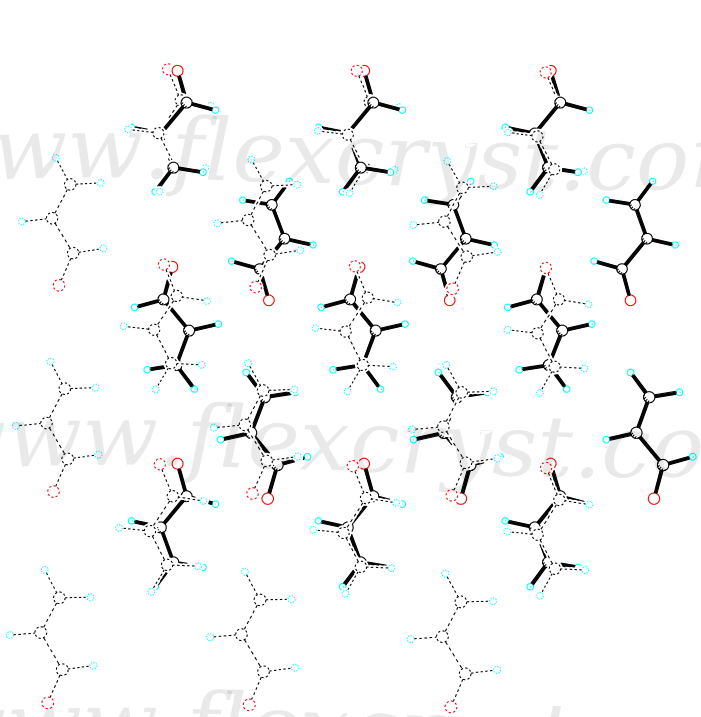
Pigment Red 170 and its Derivates
M.U. Schmidt, D.W.M.Hofmann, C. Buchsbaum, and H.J.Metz,
Angewandte Chemie Int. Ed. (2006) 45, 1313-1317.

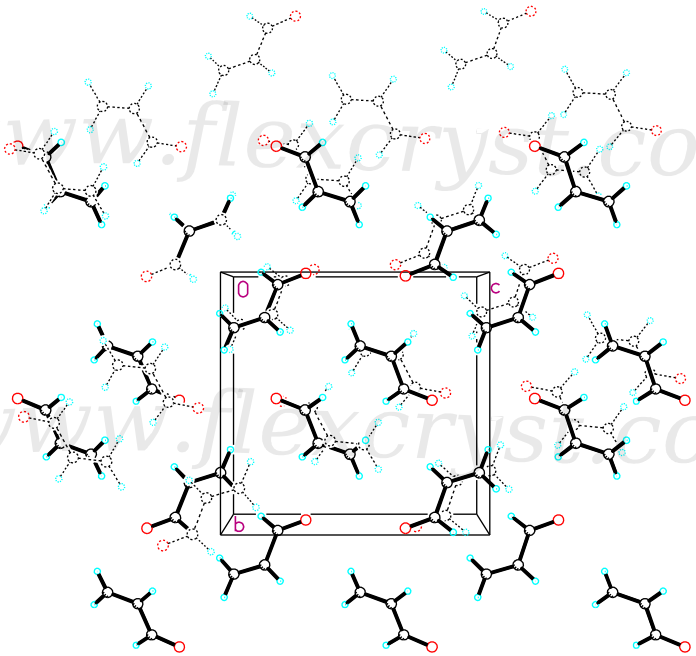
Clustering of Crystal structures (CSP 2007, molecule XII)



similarity in different spacegroups $P2_1$ and $P2_12_12_1$

The limit for the clustering is chosen from the most similar powder diagrams between different crystal structures, in general between centrosymmetric and non-centrosymmetric space groups



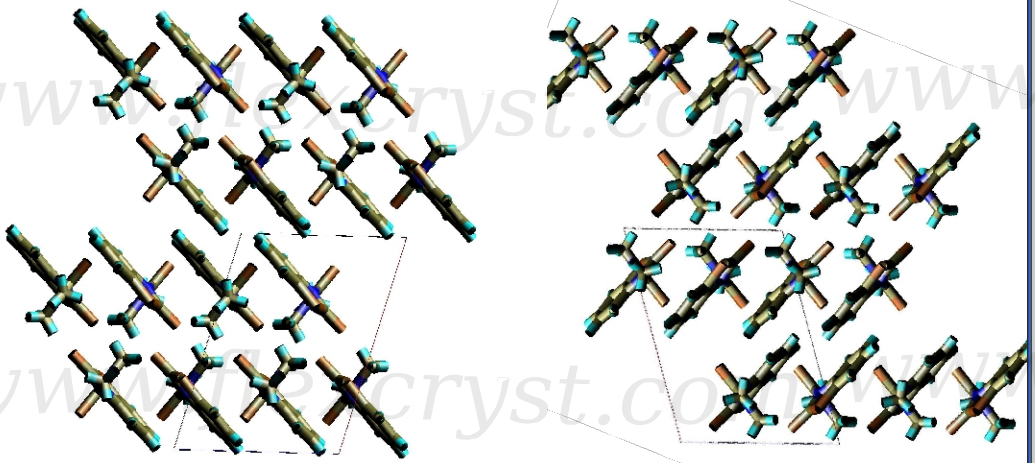


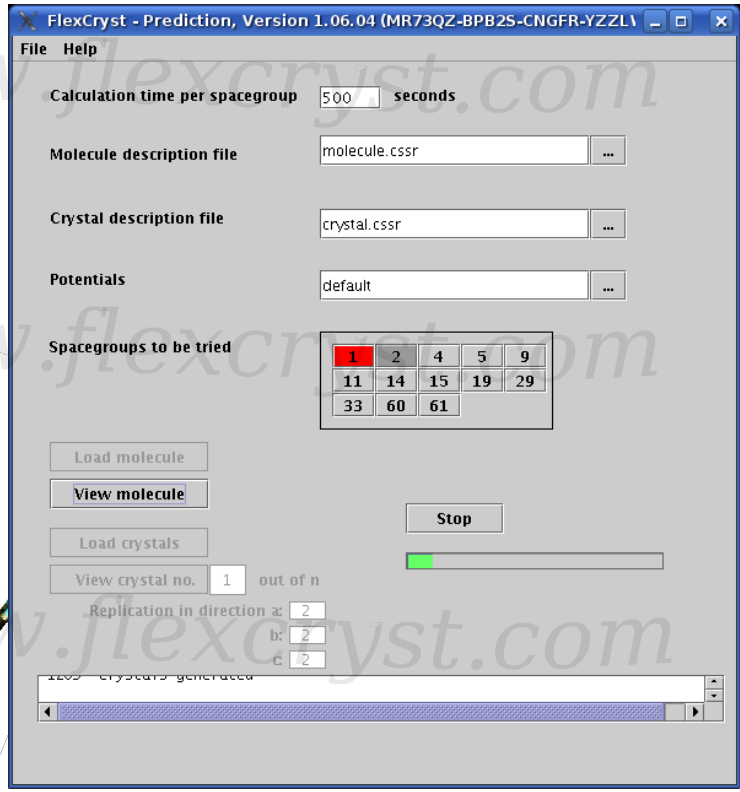
CSP 2007, molecule XII, Calculation in space group Pbca, rank 245, powder similarity 0.006, inertia superposition 0.961

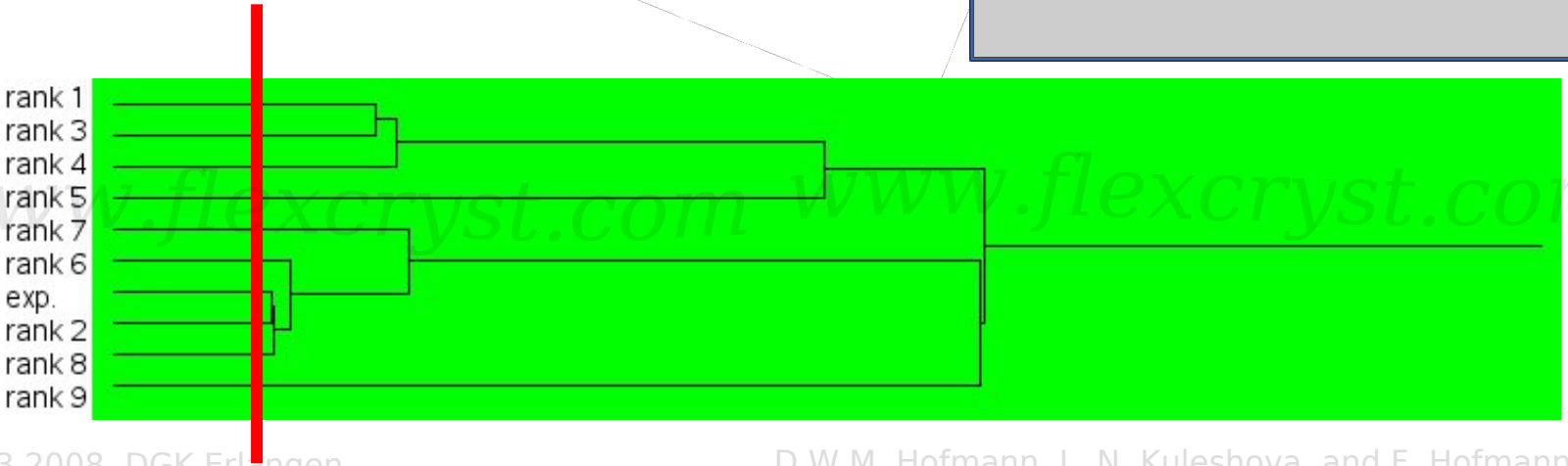
“Crystal Structure Prediction” for molecule XIV

graphics:
FlexCryst

calculation with correct conformation
rank 2 powder similarity 0.005
inertia superposition 0.961







Algorithm for the crystal structure determination

conformation generation (Materials Studio, intuitive)

↓

conformation optimization (DMOL3, Gaussian)

↓

crystal structures generation (FlexCryst)

↓

crystal structure minimization (FlexCryst)

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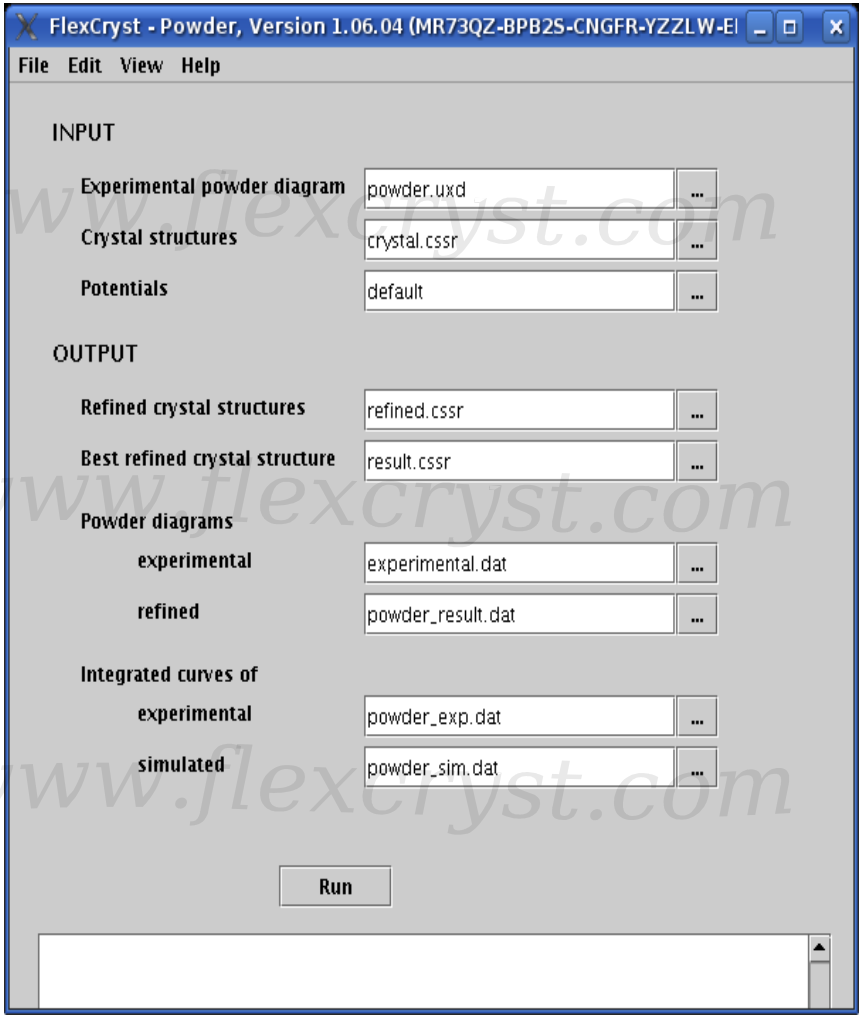
crystal structures clustering (FlexCryst)

↓

scoring and sorting (FlexCryst)

↓

refinement (FlexCryst)

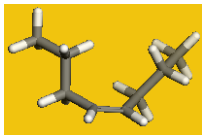


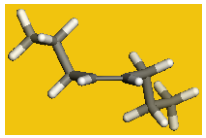
Crystal Structure Determination from Powder Diagram

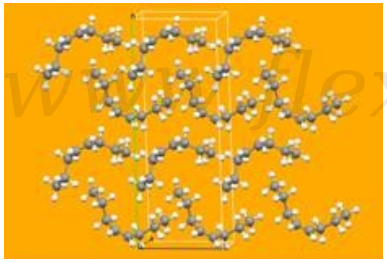
This index was used for the refinement of crystal structures to determine various crystal structures from powder diagrams

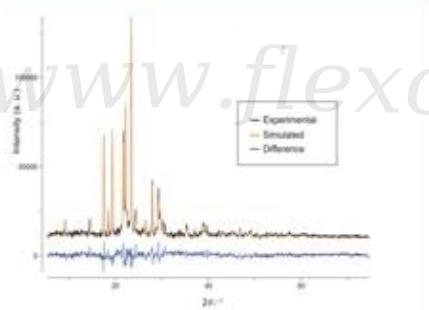
cis-4-octene

C. Schauerte, C. Buchsbaum, L. Fink, D. W. M. Hofmann, M.U. Schmidt, J. Knipping, and R. Boese
Acta Cryst. (2005). A61, C290

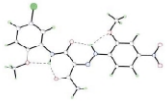


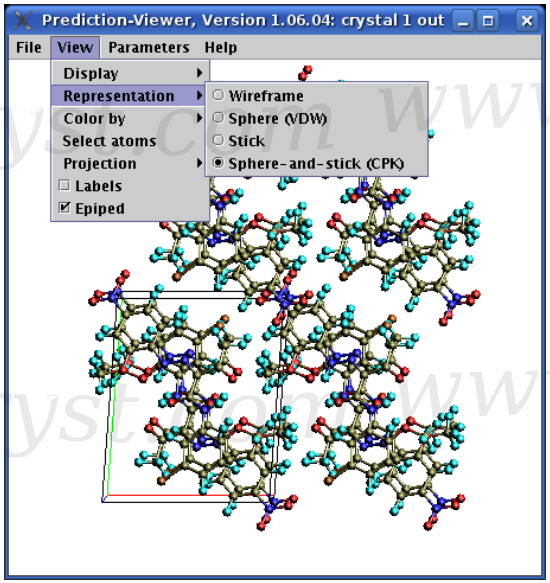


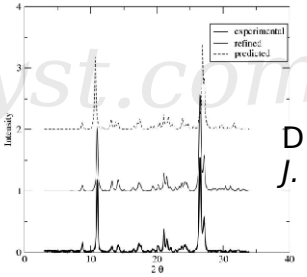




Pigment Yellow 11







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J. Appl. Cryst. (2005) 38, 861-866.

Pigment Red 181