

Application of Rietveld Refinement Combined with Force Field Energy Minimization to Structure Investigation of Cyclo-tris(2,6-pyridyl formamidine)

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Abstract

The structure refinement of X-ray powder data using the Rietveld method often results in false minima, i.e. not necessarily the energetically favored result. By introducing force fields as a new type of constraint into the recently developed BGMN program, a fully featured X-ray Rietveld system was created. With the model of bonding and nonbonding interactions, it was finally possible to refine the crystal structure of an aromatic trimer. By means of simple powder diffraction measurements, a set of structural data was obtained which was fitted mathematically to a structural model containing the geometry optimization by *ab initio* calculations, the indexing of diffraction pattern, the search of reasonable space group and the structure refinement under force field constraints.

As an example, it was found that cyclo-tris(2,6-pyridyl formamidine) crystallizes in a monoclinic unit cell with $a = 28.17 \text{ \AA}$, $b = 14.68 \text{ \AA}$, $c = 4.43 \text{ \AA}$, $\beta = 90.04 \text{ deg}$. The symmetry was determined as $P2_1/c$, unique axis b , cell choice 3, $Z = 4$. The expected threefold symmetry of the cyclic compound was slightly disturbed. The best approximation was obtained when water molecules were packed additionally into the unit cell.

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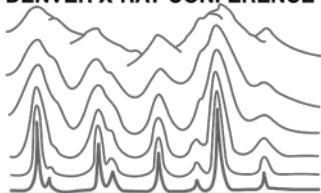
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1 Introduction

Structure modeling of crystallizable organic macromolecules based on X-ray powder data is a very complicated matter because of the limited number of observed peaks in the diffraction diagram. In the case of polymers, especially, no single crystals are available to carry out a classical single crystal analysis. Therefore a maximum of additional information must be included in modeling procedures.

For the first time a combination of the widely used Rietveld refinement with bonding information (chain model) as well as energy interactions (empirical force field¹) was carried out. That means first of all that all atoms must constitute the chosen compound, and second no one atom is allowed to overlap with neighbouring ones because of their repulsion energies.

In the following, by means of a typical example, the schedule of modeling and its results will be presented. A well justified proposal of the structure of the trimer cyclo-tris(2,6-pyridyl formamidine) including all atom respective coordinates could be obtained.

2 Experimental Procedure

X-ray powder diffraction was performed by using CuK_α radiation with the X-ray diffractometer HZG 4/A-2 (SEIFERT-FPM GmbH, Freiberg, Germany), equipped with an energy-dispersive detector EDR 288 (Röntec GmbH, Berlin, Germany). Transmission and reflection measurements were carried out in an angular range $2\theta = 3 \dots 50$ deg with $\Delta 2\theta = 0.05$ deg and $t = 125$ s.

Powder diffraction patterns of virgin samples as thin specimens because of the low absorption coefficient were measured with a primary vertical Soller collimator 0.5/25 and a primary horizontal beam divergence of 1.4 deg to achieve a high resolution in reflection technique as well as a small thickness convolution of measuring data in both techniques. In order to minimize the influence of texture due to preferred orientation, the sample powder was diluted with cork powder.

Density determination were performed pycnometrically with a result of $\rho = (1.35 \pm 0.03) \text{ g} \cdot \text{cm}^3$.

3 Calculation Steps

The recently developed BGMN program² was used because its mathematical kernel has an improved

stability and convergence behaviour. The formula interpreter integrated therein allows the user to define the chain model (chemical structure) and an empirical force field (interactions) in a very simple way.

The combination containing both the classical Rietveld part as the difference between the calculated and the measured scattering curve and the force field energy weighted by a scaling factor

$$(1) \quad Q_{WP}^* = Q_{WP} + c_{Theory} * Q_{FF}$$

could be utilized as the optimization target providing the reliability factor R_{wp} .

3.1 Unit Cell Determination

First, the unconstrained automatic peak search and the fit were carried out with the EFLECH program³ which includes the same advanced peak model as BGMN. The resulting peak list serves as the input for an indexing program⁴. The result of this procedure was an orthogonal unit cell with the parameters $a = 26.7 \text{ \AA}$, $b = 14.2 \text{ \AA}$, $c = 4.39 \text{ \AA}$.

Next, the raw diffraction data were analyzed by the BGMN program in its unit cell constrained mode using the indexing results. The best reliability factor $R_{wp} = 3.5 \%$ could be obtained by generalizing the symmetry as monoclinic with $\beta = 90.04^\circ$. The resulting fit is shown in Fig. 1.

This result was verified by means of rotating crystal experiments using a trimer sample prepared as whisker ($\varnothing \approx 5 \text{ \mu m}$, length $\approx 1 \text{ mm}$, but no single crystal). It was found that the corresponding reflections in relation to an orthogonal cell did not show the same intensity in the sense of Laue symmetry. Thus, the orthorhombic crystal system had to be excluded and the monoclinic had to be assumed.

3.2. Space Group Determination

Symmetry operators of the monoclinic system are the following: primitive and body centering, glide planes and screw axis depending on the unique axis. The formula interpreter used allows corresponding reflection conditions using logical operators (Le Bail method). By a systematic search body centering translations could be excluded because their reliability factors were calculated as unacceptable high values. The glide plane **c** and the screw axis 2_1 could not be excluded.

Considering the experimentally determined density at least 4 trimer molecules were necessary to fill the unit cell. Testing the remaining space groups $P2/m$, $P2_1/m$, $P2/c$, $P2_1/c$, respectively, resulted in the $P2_1/c$ with the smallest reliability factor.

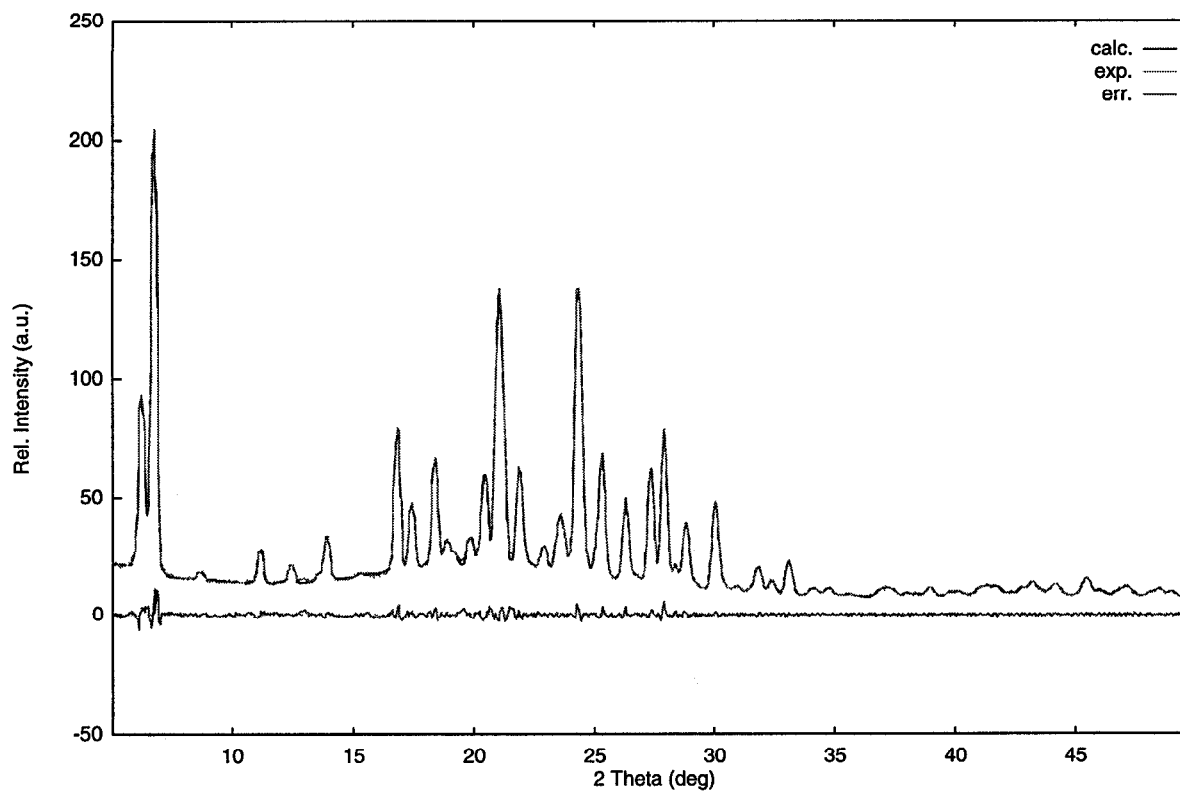


Figure 1: Approximation of the unit cell parameters of the trimer

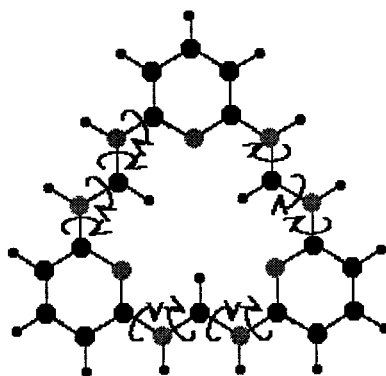


Figure 2: Molecular structure of the trimer

3.3 Cyclic Trimer Structure and Crystal Packing

The trimer molecule was assumed as the asymmetric unit described by internal coordinates (Fig. 2), i.e. bonding lengths, bonding angles and torsion angles, respectively defined by means of vector functions. The molecular structure was calculated using the quantum mechanical *ab initio* method⁵. The internal coordinates were converted into cartesian ones⁶ assuming a shift of the center of mass to the origin of the Cartesian system and the orientation of the flat molecule into the xy-plane^{6,7}. There are 6 global movement parameters: Twists with ρ_1, ρ_2, ρ_3 around the Cartesian axes and a displacement along the shift vector SP(x,y,z).

3.4. Empirical Force Field

The force field contains two parts, i.e. nonbonding interactions and penalty functions for additional bonding restrictions

$$(2) \quad Q_{FF} = Q_{nbd} + Q_{bd}.$$

Nonbonding terms like Lennard Jones potentials avoid overlapping of atoms:

$$(3) \quad Q_{nbd} = \sum_{ij} (A_{ij} * r_{ij}^{-12} + B_{ij} * r_{ij}^{-6}).$$

Penalties enable a correct chain continuation or the ring closures in this case:

$$(4) \quad Q_{bd} = \sum_b f_b (r_b - r_{b,eq})^2,$$

which play an important role to guarantee the cyclic structure of the molecule during the optimization procedure. The interaction parameters used were derived from IR spectroscopical investigations.

4 Structure Proposal

A two-step procedure has to be executed to find a sufficient approximation of the crystalline structure of the compound discussed here.

First, it was tried to achieve the fit using the trimer molecules alone. This model resulted in a bad approximation with $R_{wp} = 14.8\%$ and a too small theoretical density calculated at $\rho = (1.297 \pm 0.002) \text{ g}\cdot\text{cm}^3$.

Second, in order to rectify these misfits, one molecule of water per trimer molecule was added as suggested because of the basic character of the trimer (proton acceptor properties of this nitrogen-rich compound). Now, a $R_{wp} = 8.4\%$ and a theoretical density of $\rho = (1.361 \pm 0.002) \text{ g}\cdot\text{cm}^3$ were computed and a significant improvement of the fit of 8 reflections was obtained. The final result is shown in Fig. 3 and Table 1.

Besides the well-fitted scattering curve, a minimized interaction energy (< 0) was obtained, in which a negative value refers to a stable structure.

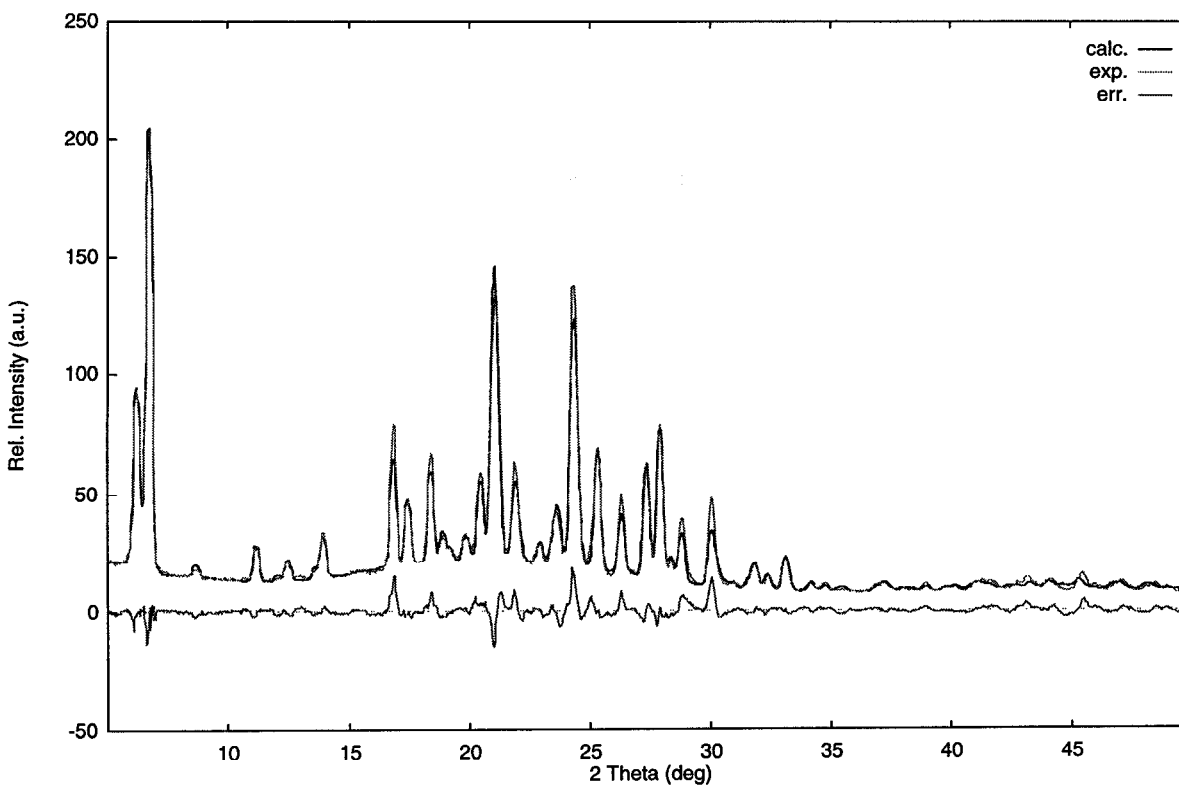


Figure 3: Approximation of the internal structure parameters of the trimer (including water)

In the solid state, the pyridyl rings are more or less tilted against the formamidine groups, a fact that results in violations of the threefold symmetry of the trimer ring. Therefore, it is assumed that hydrogen bonds on the one hand and sterical hindrances of the pyridyl hydrogens in *ortho* position on the other hand give rise to these alterations. The asymmetric structure is supported by solid-state ^{15}N NMR measurements which will be described in a further publication.

Monoclinic lattice Space Group: P2 ₁ /c (No. 14)	a (Å)	28.17(1)
	b (Å)	14.675(4)
	c (Å)	4.427(1)
	β (°)	90.04(2)
	V (Å ³)	1830(1)
	Z	4
Trimer molecule <i>Twist angles</i> <i>Shift vector SP</i>	ρ_2 (°) (b-axis)	24.6(6)
	ρ_1 (°) (a-axis)	39.5(8)
	ρ_3 (°) (c-axis)	-9.2(7)
	x (Å)	4.83(5)
	y (Å)	0.14(4)
	z (Å)	0.36(4)
Water molecule <i>Shift vector SP</i> <i>(Oxygen position)</i>	SP(x) (Å)	8.34(4)
	SP(y) (Å)	0.88(4)
	SP(z) (Å)	-0.35(6)

Table 1: Summary of the results of structure investigations.

5 Outlook

It has been shown that the crystal structure of cyclo-tris-(2,6-pyridyl formamidine) can be determined even if single crystal experiments in a classical manner are not possible. The problem was solved by Rietveld refinement taking into account spectroscopical and density data.

The newly developed BGMN program that offers the unique facility to combine classical Rietveld refinement with force field constraints is an essential prerequisite in such complicated situations. Results obtained in this manner have a high probability of being correct.

This program was also a useful working tool in order to investigate crystalline polymers in which structure determinations were rather difficult as in the situation described here. Corresponding results will be published.

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