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Rietveld refinement of a wrong crystal structure

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Rietveld refinements are generally used to confirm crystal structures solved from powder diffraction data. If the Rietveld refinement converges with low R values and with a smooth difference curve, and the structure looks chemically sensible, the resulting structure is generally considered to be close to the correct crystal structure. Here we present a counter example: The Rietveld refinement of the X-ray powder pattern of γ-quinacridone with the crystal structure of β-quinacridone gives quite a smooth difference curve; the resulting crystal structure looks reasonable in terms of molecular conformation, molecular packing and intermolecular hydrogen bonds. However, neither the lattice parameters, the molecular packing nor the conformation of the molecules show any similarity with the actual structure, which was determined from single-crystal data. This example shows that a successful Rietveld refinement is not always final proof of the correctness of a crystal structure; in special cases the resulting crystal structure may still be wrong.

1. Introduction

Crystal-structure solution from powder data is a challenging task, which requires a sophisticated approach. If the powder pattern is of limited quality, the structural model resulting from a structure solution step may be ambiguous or even questionable. Rietveld refinement is then used to determine the correctness of the crystal structure solved.

It should be stressed that the Rietveld method is *not* a method for crystal-structure solution; a reasonable starting model, which should be close to the real structure, is needed, because the convergence range of the Rietveld refinement is quite small.

The result of the Rietveld refinement is believed to be acceptable, if:

(i) the R values are small,
(ii) the difference plot is smooth, and
(iii) the structure looks chemically sensible.

1.1. When is an R value small?

There are several kinds of R values, each one more or less systematically smaller than the others, and each more or less attractive for publication. In, for example, *GSAS* (Larson & Von Dreele, 2004) the R values in the refinement are termed R_{wp} and R_p, but the R values with and without subtracted background have the same names. *GSAS* calculates R_p values with background correction by

$$R_p = \frac{\sum \frac{|I_o - I_c| \cdot |I_o - I_b|}{I_o}}{\sum |I_o - I_b|} \quad (1)$$

and without background subtraction by

$$R_p = \frac{\sum |I_o - I_c|}{\sum I_o}, \quad (2)$$

where I_o, I_c and I_b represent the observed, calculated and background intensities, respectively. Equation (2) gives a lower R value than (1). Since *GSAS* does not differentiate between R values, the lower value can be confidently chosen.

Hence, one cannot rely only on the R values of a refinement. A closer look at the difference curve is necessary.

1.2. What is a smooth difference curve?

The shape of the difference curve is determined mainly by:

(i) the quality of the peak-profile description (peak shapes, peak widths, peak asymmetry *etc.*),

(ii) the quality of the structural model, and

(iii) the presence of impurity lines.

Peak profiles can be difficult to describe, especially when the selected (or available) profile functions only allow for a limited number of parameters to be refined. For example, in *GSAS* it may be almost impossible to reach an acceptable fit if the peaks – mainly in the low 2θ region – are highly asymmetric, since *GSAS* has a limited number of suitable profile functions for those cases.

In addition, if the sample contains some impurities (another polymorph, starting material *etc.*) one has to deal with additional reflections that may overlap with the reflections of interest. If the other crystal phases cannot be identified, the only way to try a refinement is to exclude the corresponding regions in the powder pattern, which may result in loss of information.

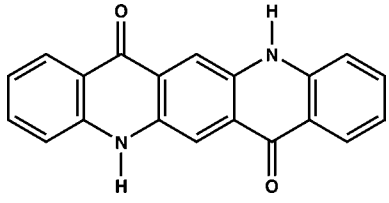

Figure 1
Molecular formula of quinacridone.

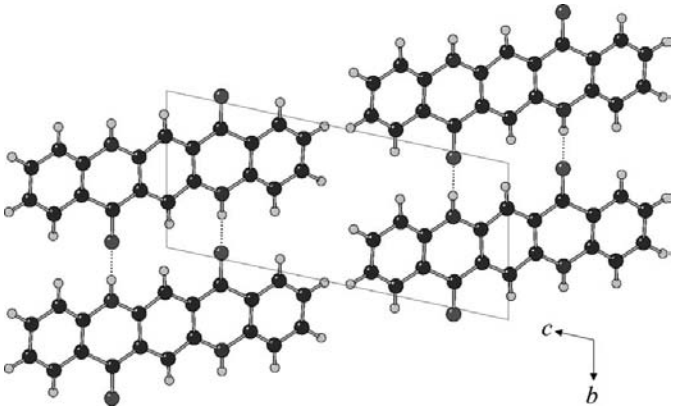

Figure 2
Crystal structure of α^{I}-quinacridone, view direction [100].

1.3. When is a structure chemically sensible?

When a refinement was successfully performed, the resulting structure should be chemically reasonable. Useful criteria applied to accurate crystal structures of organic compounds are molecular geometry and hydrogen-bond patterns – provided, of course, that the substance is able to form hydrogen bonds. Intramolecular distances and angles as well as intermolecular distances have to be analysed. There are no universal rules for checking if the structure is chemically sensible – it has to be checked by the structural chemist, for example, with the help of databases, *e.g.* the Cambridge Structural Database (CSD; Allen, 2002).

1.4. Pitfalls in single-crystal refinements

In single-crystal refinements there are also pitfalls, despite the higher information content of the single-crystal data set. Several cases are known of the wrong assignment of atom types, *e.g.* $[CuF_4]^-[ClF_6]^+$ rather than $[Cu(H_2O)_4]^{2+}[SiF_6]^{2-}$ (von Schnering & Vu, 1983), and wrong unit cells and space groups (*e.g.* Marsh & Sparks, 2001; Marsh *et al.*, 2002).

The present paper shows a nice example of a wrong unit cell, a wrong space group and consequently a wrong crystal structure, solved and refined from powder diffraction data, giving a sensible result.

2. The compound: quinacridone (Pigment Violet 19)

Quinacridone (Pigment Violet 19, Fig. 1) is the most important pigment for reddish-violet shades. It is used in automotive finishes, weatherfast emulsion paints, plastics and high-grade printing inks (Herbst & Hunger, 2004). Quinacridone crystallizes in four different modifications (α^{I}, α^{II}, β and γ), of which the β and γ phases are most commonly used in industry (Paulus *et al.*, 2007).

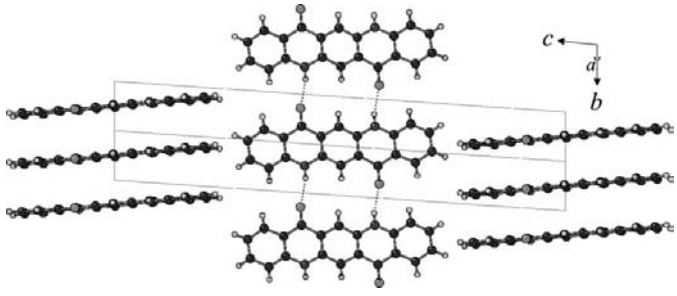

Figure 3
Crystal structure of β-quinacridone, view direction $[1\bar{1}0]$.

Table 1
Crystal data for the correct structures of α^{I}-, β- and γ-quinacridones.

Crystal phase	α^{I}	β	γ
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Z	1	2	2
Site symmetry	$\bar{1}$	$\bar{1}$	$\bar{1}$
a (Å)	3.802 (2)	5.692 (1)	13.697 (9)
b (Å)	6.612 (3)	3.975 (1)	3.881 (3)
c (Å)	14.485 (6)	30.02 (4)	13.402 (1)
α (°)	100.68 (8)	90.0	90.0
β (°)	94.40 (6)	96.76 (6)	100.44 (1)
γ (°)	102.11 (5)	90.0	90.0
V (Å^3)	346.7 (1)	674.5 (9)	700.6 (7)
ρ (g cm^{-3})	1.50	1.54	1.48

2.1. Description of the correct crystal structures

The crystal structures of β and γ quinacridone were determined from single-crystal data (Potts *et al.*, 1994; Mizuguchi *et al.*, 2002; Nishimura *et al.*, 2006; Paulus *et al.*, 2007).

In the α^{I}, β and γ phases the quinacridone molecule is planar. Each molecule forms four hydrogen bonds to neighbouring molecules; in the α^{I} and β phases two neighbouring molecules are connected by two hydrogen bonds each, resulting in molecular chains (Figs. 2 and 3). In the α^{I} phase the chains are parallel with small steps between the molecules, while in the β phase the molecular chains show two different orientations in the crystal structure. In the γ phase the molecules form hydrogen bonds to *four* neighbouring molecules, so that a criss-cross arrangement of molecules is achieved (Fig. 4).

Crystallographic details for α^{I}, β and γ quinacridones are listed in Table 1.

3. Refinement of the wrong crystal structure

By chance we realised that the powder diagram of the γ phase can be explained by a slightly modified structure of the β phase. Even worse: although lattice parameters and molecular packings are totally different, the Rietveld refinement converges with acceptable R values. Both the crystal structure as well as the molecular structure are chemically reasonable and sensible.

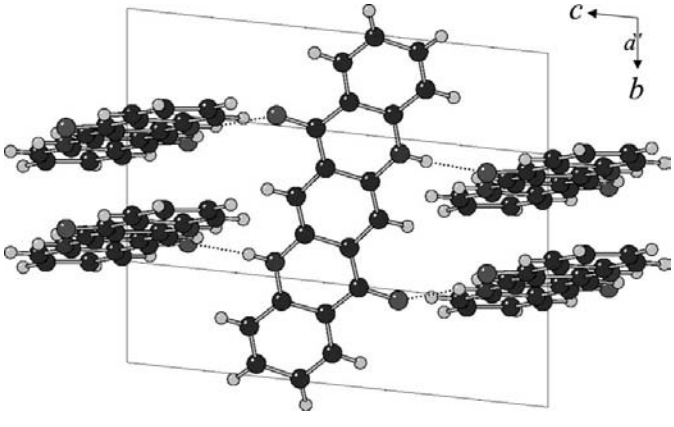

Figure 4
Crystal structure of γ-quinacridone, view direction [2$\bar{5}$0].

3.1. Data collection

The powder diagrams of the β and γ quinacridones (Fig. 5) were recorded in transmission mode in the 2θ range 3–35° on a STOE Stadi-P diffractometer with a curved Ge(111) monochromator; Cu $K\alpha_1$ radiation was used. It has to be stressed that the limited quality of the powder data is caused by the quality of the powder (small domain sizes), not by the diffractometer.

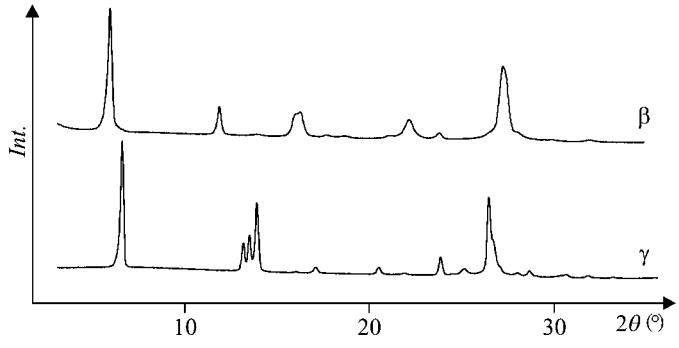

Figure 5
Powder diagrams of the β and γ phases of quinacridone.

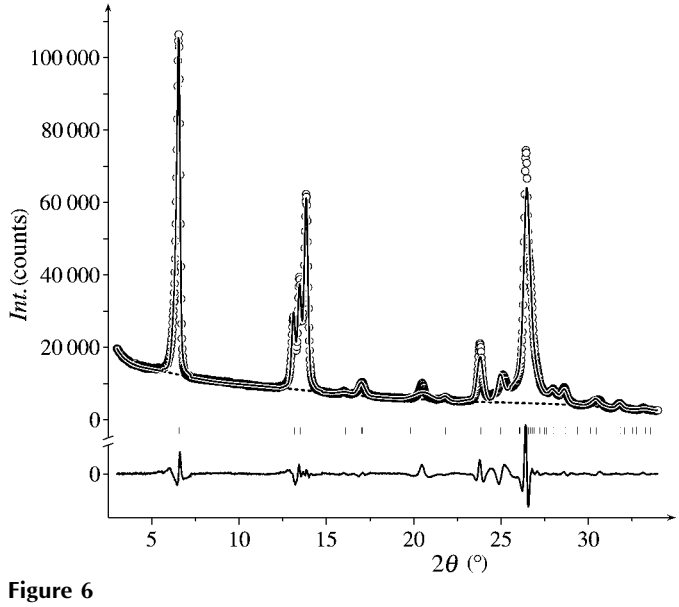

Figure 6
Le Bail fit of γ-quinacridone with the wrong unit cell; small circles: experimental data; thin line: simulated pattern; dotted line: background; tickmarks indicate possible reflection positions, the difference plot is at the bottom.

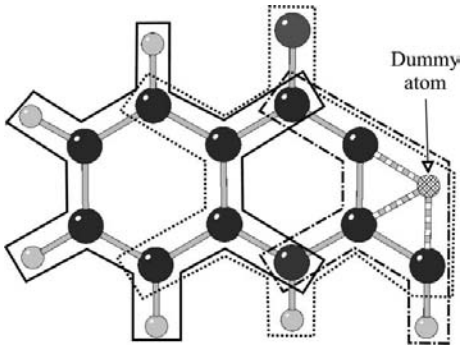

Figure 7
Planar group restraints used in the refinement; each group is outlined differently.

3.2. Le Bail fit

Starting from the crystal structure of the β phase, the cell parameters were manually adjusted in order to explain the reflection positions in the powder diagram of the γ phase.

The Le Bail fit was carried out with *GSAS* (Larson & Von Dreele, 2004; Toby, 2001) and converged with $R_{wp} = 0.0702$, $R_p = 0.0452$, red. $\chi^2 = 54.56$ and $a = 6.665$ (1), $b = 3.881$ (3), $c = 27.369$ (3) Å, $\beta = 100.68$ (2)°, $V = 695.7$ (1) Å^3.

The Le Bail fit is shown in Fig. 6; because of the low quality of the powder data this result is acceptable.

If if was not known that the unit cell was wrong, the remaining differences might have been attributed to an inadequate description of the peak profiles.

3.3. Rietveld refinement

The crystal structure of the β phase was used as the starting model for the Rietveld refinement of the powder pattern of the γ phase, although the packing of the molecules is totally different. The crystal structure of β-quinacridone is in $P2_1/c$, $Z = 2$, with a molecule on $\overline{1}$. Half a molecule was set up, connected to a dummy atom which was placed on a crystallographic inversion centre.

The Rietveld refinement was performed with restraints for bond lengths, bond angles and planar groups (Fig. 7). The refinement was carried out carefully in order not to risk divergence. The weight of the restraints was reduced step by step (from 100 000 down to 400). Owing to the limited quality of the powder data it was not possible to remove the restraints completely. The refinement converged with $R_{wp} = 0.0847$, $R_p = 0.0522$, red. $\chi^2 = 98.79$ and $a = 6.666$ (1), $b = 3.868$ (1), $c = 27.386$ (5) Å, $\beta = 100.58$ (2)° and $V = 694.1$ (1)Å^3 (Fig. 8). Atomic coordinates are given in the supplementary material.[1]

The Rietveld refinement looks quite reasonable with respect to the limited data quality, except for the peaks at ~ 23.5 and ~ 26.5°. These two peaks in the difference curve might be explained by *e.g.* texture effects or preferred orientation, or maybe the sample contained impurities, such as by-products or other polymorphs. Quinacridone has four known polymorphs, thus the existence of a fifth polymorph would hardly be a surprise.

However, taking into account the quality of the powder data, the problems in peak-profile description and the possible presence of another phase, as well as the hydrogen-bond pattern, the structure looks quite reasonable (Figs. 9 and 10). The 'S' shape of the molecule may be true. In fact, the first single-crystal analysis of quinacridone reported the molecule to exhibit a strong 'S' shape, the outer benzene rings being bent by 40° against the central ring (Koyama *et al.*, 1966). Also, the first crystal structure determination of 2,9-dimethylquinacridone resulted in a strongly bent molecule (Fig. 11; Otaka, 1975).

All-in-all, the Rietveld refinement seemed to be reasonable and the structure looked sensible. However, the crystal

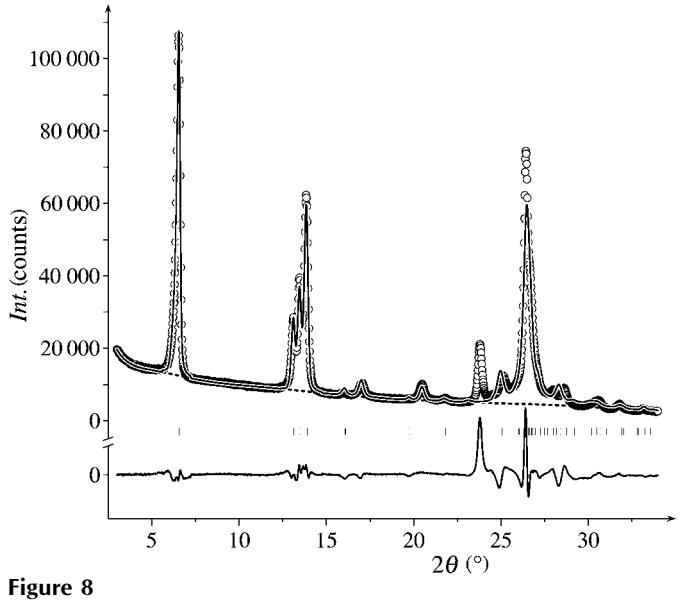

Figure 8
Rietveld refinement of the wrong crystal structure: Refinement of a modified β-quinacridone structure with γ powder diagram. Small circles: experimental data; thin line: simulated pattern; dashed line: background; tickmarks show possible reflection positions, difference plot at the bottom.

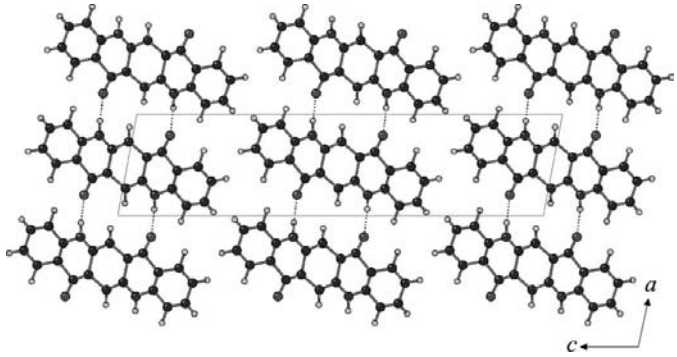

Figure 9
Wrong structure of γ-quinacridone, view direction [010].

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV5092). Services for accessing these data are described at the back of the journal.

Table 2
Crystal data for β, γ and wrong-γ quinacridones.

Crystal phase	β	Wrong-γ	γ
a (Å)	5.692 (1)	6.666 (1)	13.697 (9)
b (Å)	3.975 (1)	3.8680 (5)	3.881 (3)
c (Å)	30.02 (4)	27.386 (5)	13.402 (1)
β (°)	96.76 (6)	100.58 (6)	100.44 (1)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

structure is *completely wrong*! The lattice parameters are considerably wrong, the molecular conformation is wrong and the molecular packing is also wrong: the refined structure shows molecular chains, whereas in the correct structure the molecules form a criss-cross pattern (Fig. 12). The correct Rietveld refinement is shown in Fig. 13.

4. Discussion

How can we explain that we obtain a suitable Rietveld fit although the structure is wrong?

4.1. Comparison of the unit cells

First the relationship between the unit cells of β, γ and wrong-γ quinacridone (Table 2) must be understood. The relationships are

$$a_{\text{wrong}-\gamma} = c_\gamma/2,$$
$$b_{\text{wrong}-\gamma} = b_\gamma,$$
$$c_{\text{wrong}-\gamma} = 2a_\gamma \text{ and}$$
$$\beta_{\text{wrong}-\gamma} = \beta_\gamma.$$

The unit cells of γ and wrong-γ have the same volume and $Z = 2$. The transformation matrix for both the transformations from γ to wrong-γ and back is

$$\begin{pmatrix} 0 & 0 & \frac{1}{2} \\ 0 & -1 & 0 \\ 2 & 0 & 0 \end{pmatrix}.$$

Owing to the performed cell transformation the indexing of the peaks of the powder diagram changes (Fig. 14).

4.2. Indexing

We tested if both unit cells could have been found by indexing. The program *TREOR*90 (Werner *et al.*, 1985) was used.

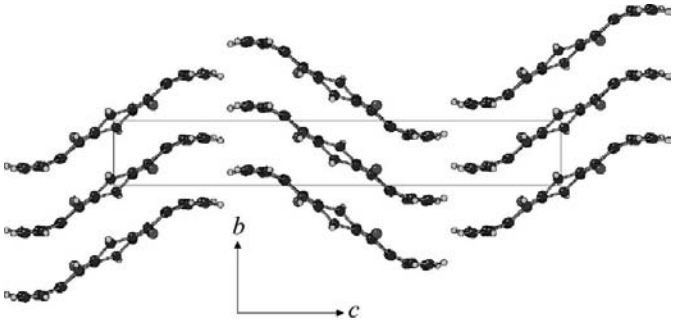

Figure 10
Wrong structure of γ-quinacridone, view direction [100].

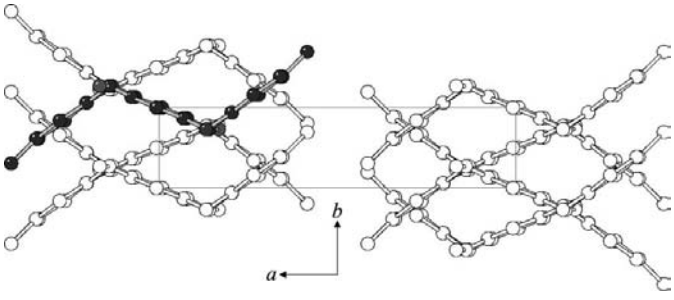

Figure 11
Wrong crystal structure of 2,9-dimethylquinacridone (single-crystal data), view direction [001].

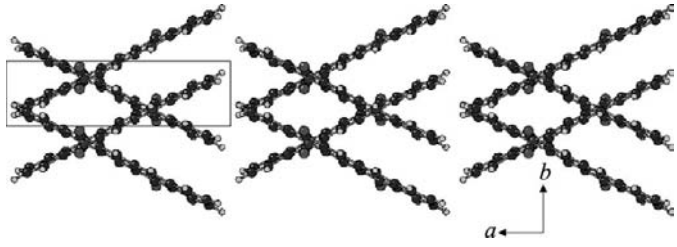

Figure 12
Correct structure of γ-quinacridone, view direction [001] (single-crystal data).

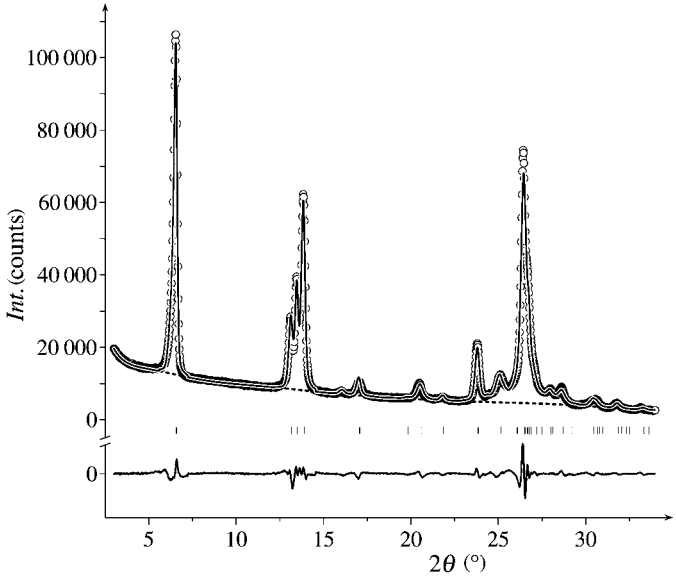

Figure 13
Rietveld plot of γ-quinacridone (correct structure); R_{wp} = 0.0447, R_p = 0.0319, red. χ^2 = 24.38. Small circles: experimental data; thin line: simulated pattern; dashed line: background; tickmarks show possible reflection positions; the difference plot is at the bottom.

Taking all 15 peaks into account, the correct unit cell was found among other possible solutions. Assuming that the peak at $\sim 23.5^\circ$ may be caused by phase impurities and thus removing it, both the correct as well as the incorrect unit cell are found. In both cases no line of the powder pattern remains unindexed. The M_{14} values for the correct and the wrong unit cell are 15 and 8, respectively.

Nevertheless, since there were only 15 clearly distinguishable peaks, the result of the indexing should always be regarded with caution.

4.3. Could we have seen that the structure was wrong?

If we had not had the single-crystal data of γ-quinacridone, would we have recognized that the crystal structure obtained from Rietveld refinement was wrong?

(i) From the Rietveld refinement: Maybe. But surely we had put some effort into additional crystallizations in order to try to obtain a sample of better crystallinity resulting in a better powder pattern. If we had measured the powder data of 10–20 different samples, we would have observed that the peak at 23.5° is always present and always has the same intensity, hence it cannot be caused by texture effects or phase impurities.

(ii) Concerning the reflection conditions: Since $b_{\text{wrong-}\beta} = b_\gamma$, the condition $0k0$, $k = 2n$, remains fulfilled. Since $c_{\text{wrong-}\gamma} = 2a_\gamma$, there are only even values for l, so the condition $h0l$, $l = 2n$, is also fulfilled.

Hence, the reflection conditions in the space group $P2_1/c$ are fulfilled both for wrong- and correct-γ. This means that the correct crystal structure cannot be identified either from the unit cell or from the space group.

(iii) Low-temperature X-ray powder diffraction would not help: the peaks would shift but the quality of the data would not improve: the peak at 23.5° would still be the only hint that the structure might not be correct.

(iv) Higher 2θ powder data would not help: at higher 2θ values peaks can be indexed in multiple ways, even with a wrong unit cell. Rietveld refinement can easily follow the low-intensity humps at $2\theta > 35^\circ$.

(v) Synchrotron measurements would not improve the data quality considerably, since the large peak widths are caused by the crystal quality, not by the diffractometer.

(vi) Quantum mechanical calculations show the individual molecule to be planar. However, the mean deviation from the molecular plane in our structure is only 0.23 ± 0.16 Å (the biggest distance from a C atom to the plane is 0.45 Å), which is within the accuracy of the Rietveld analysis. The same holds for the in-plane distortion of the six-membered rings: If the molecular structure is calculated on the 6-31G** level, our structure is reproduced with an average deviation of 0.31 ± 0.11 Å for the non-H atoms. This is acceptable with respect to the limited quality of the powder data.

(vii) Single crystal structures of substituted quinacridones show the quinacridone molecules to be planar, but most quinacridone single crystals are of poor quality. Even in the single-crystal structures the C atoms deviate from planarity and the six-membered rings are distorted.

(viii) In IR spectroscopy the most characteristic band is the ν(C═O) vibration at 1600–1700 cm^{-1}, which is significantly shifted if there is a C═O···H—N hydrogen bond. However, both our structure and the correct-γ structure exhibit C═O···H—N bonds. In each structure, the two C═O groups are crystallographically equivalent, thus there is no splitting of the vibration band. Only a very detailed analysis (*e.g.* of the 0–400 cm^{-1} region) might have shown that the crystal structure does not match the IR spectrum. The same holds for Raman spectroscopy.

(ix) Using electron diffraction on individual crystals (below 100 nm) we would have easily seen that the *a* axis needed to be doubled and the *c* axis halved. But who carries out electron diffraction, if the structure is solved?

(x) In neutron powder diffraction the simulated powder diagrams of the wrong and the correct structure show significant pattern differences (Fig. 15). However, the same question as for electron diffraction arises here: Who carries out neutron diffraction if the structure is solved?

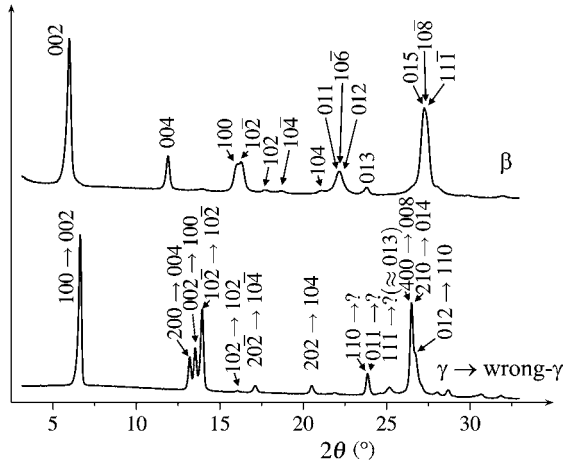

Figure 14
Comparison of the indexing of the powder diagrams of β, γ and wrong-γ quinacridone.

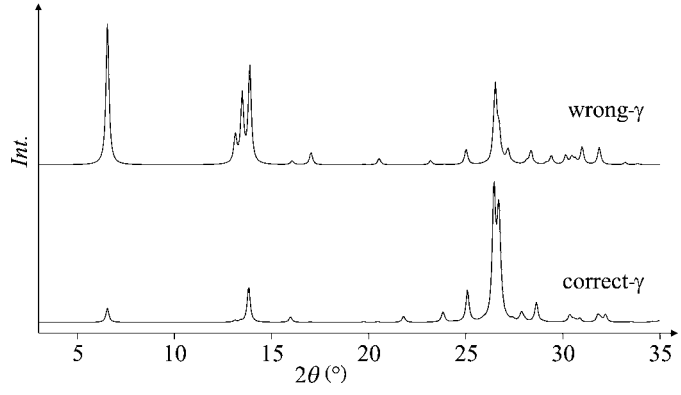

Figure 15
Simulated neutron diffraction patterns of (*a*) 'wrong-γ (top) and (*b*) correct-γ (bottom) at $\lambda_{\text{neutron}} = 1.54$ Å.

(xi) We may have suspected that the structure was wrong from the colour of the powder: quinacridones with chain structures such as α^{I}-quinacridone, β-quinacridone and 2,9-dimethylquinacridone tend to show more violet shades, whereas quinacridones with criss-cross structures like 4,11-dichloroquinacridone are red. On the other hand, the colour of γ-quinacridone is closer to 2,9-dimethylquinacridone than to 4,11-dichloroquinacridone, which would be an argument supporting the wrong structure.

Hence, it is only the misfit of a *single peak* (at 23.5°) which would have indicated that the structure might be wrong.

5. Conclusion

The present paper clearly shows that a Rietveld refinement might not be enough to prove the correctness of a crystal structure solution. It is always better to have additional data – which, however, might not necessarily help (see §4.3).

In ambiguous cases it might be helpful to synthesize a series of mixed crystals and derivatives, hoping that either the mixed crystals have a better crystallinity (for example, see Schmidt *et al.*, 2005) or that an isostructural compound of better crystallinity is found (Schmidt *et al.*, 2006*a*,*b*).

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