

The quinacridones: structure and colour: a study by powder diffraction

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The known structure of 21 industrial gamma-quinacridone pigments served as a basis for the measurement of powder patterns with and without fluorophlogopite by a Bragg–Brentano diffractometer. Calibration and cell refinement were used to determine the cell parameters and to fit the profiles of the intensities. The unit cells vary systematically and the importance of the short b -axis is revealed. Averaging of all data leads to idealized unit cells. The corresponding criss-cross angles, τ_c , of the 21 pigments vary in a systematic way. It is possible to determine the relative frequency of the positions of the molecules inside the unit cell. The criss-cross angle of gamma-quinacridone increases from $2 \times 26.0^\circ$ (hydrogen-bond: 0.266–0.268 nm) to $2 \times 28.0^\circ$ (hydrogen-bond: 0.268–0.274 nm). The pigments are understood and described as physical mixtures of crystallographically similar structures. The colour of these pigments is one of the most important industrial properties. It varies from reddish purple to yellowish purple apparently depending on the structure. The difference between the gamma- and gamma'-form is described. Alpha-quinacridone is a special form of gamma-quinacridone and fits perfectly in the system of the latter. Evaluating the criss-cross angle of all known quinacridones, it is possible to classify their structure and colour, which are attributed to the cooperative effect of hydrogen-bonds and double bonds in the lattice (π - σ -correlation).

1. Introduction

Comparison of the X-ray powder patterns of various pigments of gamma-quinacridone using the known unit cell (single crystal), shows that the position and intensity of peaks differ systematically. In particular, the innermost, highest peak (100) varies in position and intensity. We can use these characteristics to standardize the product range of gamma-quinacridone pigments. Having calculated alpha-quinacridone in a previous paper [1, 2], we can use the same software to study gamma-quinacridone. The programs previously described [1, 2] are used again.

2. The product range of gamma-quinacridone characterized by X-ray powder patterns

2.1. Powder patterns and their evaluation

It is reasonable to examine by X-rays, the present day, production line, using samples of 1964, 1972 and 1985, as a basis for the evaluation of the measurements. To obtain as exact results as possible, powder patterns were scanned with and without standard reference material (National Bureau of Standards, fluorophlogopite, SRM 675), and evaluated with a calibration program (JADE +) followed by cell refinement

(MICRO-CELLREF and POWDMULT). (For further details see [1].)

The graphic program WinSTAT 3.1, was used to determine linear correction terms (polynomial least squares curve fit), the slope averages out the unit-cell parameters of the product range (a , b , c and β).

The correction terms are used to make linear regression fits, which allow "idealized pigments" of gamma-quinacridone to be analysed with a special program (BIND). This program calculates the size and orientation of the asymmetric unit, in particular the positions of each single molecule and the length of NHO bonds. A statistical evaluation leads to information about the differences of the product range. In addition, the short b -axis is revealed, i.e. b is the fibre axis in the stack. It would seem that b has an influence on colour.

Knowledge of the basic patents on quinacridones is assumed. The additional patent of Deuschel *et al.* is important [3]. It describes the production of the so-called gamma' form, a yellowish red pigment. It is characterized by three medium large lines at the diffracting angles (2θ) of 13.1° , 13.3° and 13.7° . Whitaker [4] described both the gamma and gamma' form, by their diffraction patterns. Jaffe argues for two polytypes of gamma-quinacridone [5]: "the newer form

being a yellow-shade red as a relatively large particle size pigment”.

Paulus *et al.* were the first to describe [6] the crystal structures of eight quinacridones, but without atomic coordinates, and not deposited at the Cambridge crystallographic Data Centre. In 1994, Potts *et al.* [7] analysed the crystal structure of gamma-quinacridone and indicated atomic coordinates. They reduced the differences of gamma, and gamma' form to morphology and particle size [7]. Filho and Oliveira tried to determine the unit cells of several quinacridones [8]. No further papers can be quoted on this problem.

WinSTAT 3.1 generates a first degree least squares fit for all data, see Fig. 1. This shows the straight line plot of the experimental innermost first peak (100) for the populations of 21 industrial pigments in relation to the *a*-axis of gamma-quinacridone. Ten pigments have been refluxed for 8 h with dimethylformamide (DMFA), to obtain better-crystallized samples. Fig. 1 also shows the four single crystals [5, 6, 7, 9] so far known and the ten pigments treated with DMFA. Fig. 2 shows the relationship between $d_{(100)}$, *b* and β .

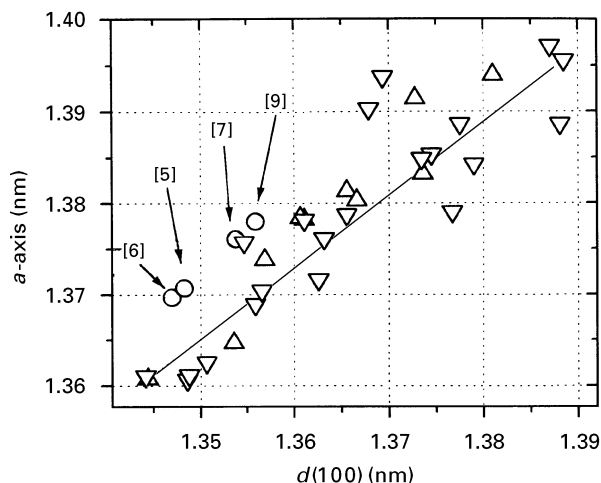


Figure 1 Relationship between the innermost (100) peak and the *a*-axis in (∇) 21 industrial pigments (Δ), for DMFA-treated pigments and (\circ) single crystals.

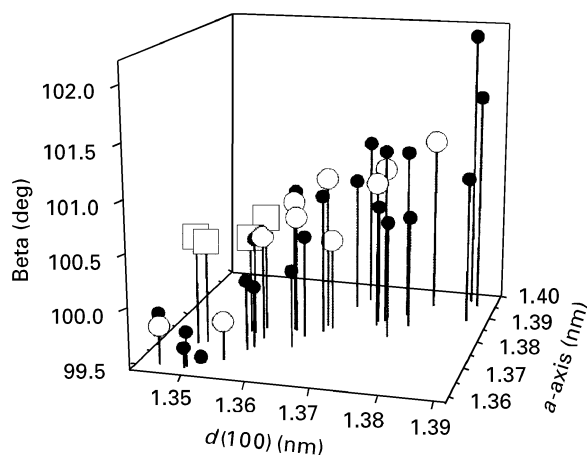


Figure 2 Relationship between $d_{(100)}$, *a* and β in (\bullet) 21 industrial pigments, (\circ) DMFA-treated pigments and (\square) single crystals.

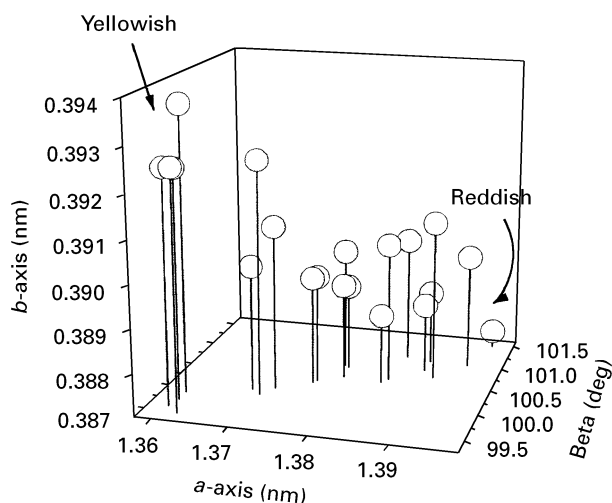


Figure 3 Relationship between *a*, β and *c*-axis in 21 industrial pigments.

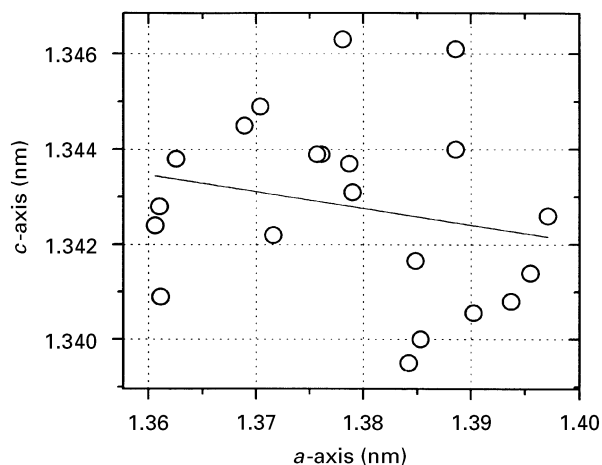


Figure 4 Relationship between *a*- and *c*-axes in 21 industrial pigments.

The parameters vary from lower to higher values along the body diagonal. Fig. 3 shows a similar relationship of *a*, *b* and β , and at the same time the yellowish ($b = 0.394$ nm) and reddish ($b = 0.388$ nm) forms of gamma-quinacridone are labelled. Contrary to the above-mentioned values, *c* displays considerable scatter around a constant value (≈ 1.343 nm), see Fig. 4. The first-degree least-squares fits of all 21 pigments lead to three idealized unit cells, see Table. I.

The following approximation [1, 2]

$$\cos\tau_c = d_{(100)}/1.523 \quad (1)$$

allows the τ_c -angles mentioned in Table I to be calculated. For the meaning and importance of τ_c , see ([1, 2]; Fig. 2b). Considering the hues of gamma-quinacridone pigments, some of which are reproduced in manufactures' pattern cards, raises the question of a correlation between hue* and criss-cross angle.

* Strictly speaking, the title of this paper should read "The Quinacridones: Structure and Hues". "Hue" is a psychological colour term and exactly defined (see Table II, DIN 5033 (14) Bunton (Farbton) and Judd and Wyszecki [11]).

TABLE I Three idealized gamma pigments, evaluated by Fig. 1 (least-square fit)

Idealized pigment	a (nm)	b (nm)	c (nm)	β (deg)	$d_{(100)}$ (nm)	τ_c (deg), Eq. 1
Id 1	1.3831	0.3889	1.3431	101.75	1.3735	≈ 26.0
Id 2	1.3698	0.3913	1.3431	100.09	1.3572	≈ 27.0
Id 3	1.3559	0.3939	1.3431	99.39	1.3402	≈ 28.4

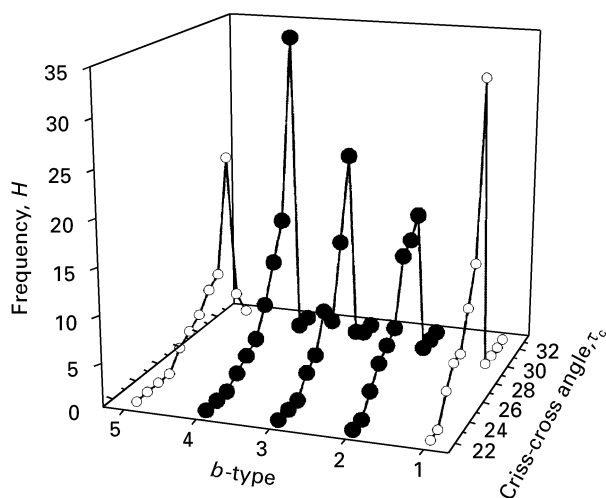


Figure 5 Relationship between criss-cross angle τ_c , and frequency, H . b -type; 1, 0.3860; 2, 0.3889; 3, 0.3913; 4, 0.3939; 5, 0.3960.

2.2. Gamma-quinacridone calculations with the geometric model

Starting by the known single molecule of gamma-quinacridone [5–7] it is mathematically possible to place the molecule in the unit-cell of Id1 to Id3 and to rotate the axes of molecule τ_a , τ_b and τ_c . These calculations are made with the program BIND [1, 2]. Keeping reasonably narrow the limits of parameters for length (0.268–0.284 nm) and angle (140° – 180°) of the hydrogen-bond, τ_a (-16° to $+16^\circ$), τ_b (-16° to $+16^\circ$), τ_c (22° – 32°) and the thickness of the planar molecule (0.3370–0.3385 nm \equiv the minimum intermolecular C ... C distances) and the corresponding width of pace (parameter in BIND), the output offers only a few (useful) solutions, which can be easily compiled. Fig. 5 reproduces the frequency curves (frequency distribution of $H =$ number of solutions of BIND for a distinct τ_c) for τ_c and five selected b axes:

- (i) all angles τ_c show lower frequencies with smaller angles, the maxima suddenly drop;
- (ii) larger b -axes create larger τ_c angles;
- (iii) there are no angles above $\tau_c = 31^\circ$;
- (iv) Colouristically speaking, smaller τ_c angles are associated with reddish and bluish gamma-quinacridone pigments and larger τ_c angles with yellowish pigments.

The shape of the frequency curves H in Fig. 5 is influenced by four of the above-mentioned factors, i.e. by the chosen limits of angle NHO, length NHO, τ_a and τ_b .

3. All quinacridone pigments at a glance – the correlation between structure and colour (hue)

It is interesting to arrange all known quinacridone pigments by their criss-cross angle (τ_c) and colour. We have used the structures of Paulus *et al.*, [6] Lincke and Finzel [1, 2] and this paper, see Table II.

The new results available (alpha- and gamma-quinacridone [1, 2] enable us to specify the correlation: the smaller the criss-cross angle, the more bathochromic is the corresponding pigment (type 2). If the angle is zero, pigments become purplish blue or red–violet (type 1). This result is derived by comparison of data of organic structural chemistry. According to this paper, the gamma' form is characterized by a larger criss-cross angle (28.4°) than with the gamma-form (26.0°). In addition to the single crystal of gamma-quinacridone [5–7], it is possible that a second crystal structure type exists with a criss-cross angle larger than 26.0° and a b -axis of ≈ 0.394 nm, like Id 3 of Table I. Gamma-quinacridone not only produces yellowish and bluish varieties but also reddish ones [12]. X-ray powder patterns reveal τ_c quite well but not τ_a and τ_b . These two freedoms of rotation are probably responsible for additional colour varieties of gamma- and alpha-quinacridones.

This consideration of colour does not take into account any solid solutions of quinacridone pigments.

4. Calculation of colours of substances from theory

4.1. The Mie theory

The Mie theory is an efficient tool for calculating absorption and reflexion of pigments [13]. It uses non-structural parameters such as particle size, particle distribution, refraction index, n , and the scattering or absorption cross-section within the visible spectrum of the light. The Mie theory is based on Maxwell's theory and therefore is part of Newtonian physics. The Mie theory does not recognize electron orbitals! Nevertheless it is able to calculate the colour characteristics of organic pigment dyes quite well.

The Mie theory has its greatest success in the field of inorganic pigments. These are formed by rigid spheres of charged ions, exhibiting either one refraction index or two or three rather similar ones.

Organic pigment crystals consists of neutral (!) single molecules which, in the case of quinacridones, are rigid, flat and aromatic (thickness nearly 0.34 nm). Above all, they are two dimensional objects. These flat molecules of quinacridone form stacks and are

TABLE II Quinacridone pigments and some of their specifications

Quinacridone	Criss-cross angle (deg)	Type ^b	Hue ^c	Shift	Manufacturer	Reference
4.11-dichloro-qa	54.9	2	Reddish-orange	↓	—	[6]
Gamma ¹ -qa	28.4 ^a	2	Yellow-reddish purple	ba-	Ciba-Pigments	[1, 2, 4, 7]
Gamma-qa	26.0 ^a	2	Reddish purple	tho-	Hoechst, Ciba-Pigments, Bayer	[6]
Alpha-qa	20.0	2	Bluish purple?	↓	Bayer	[1, 2] ^d
2.9-dimethyl-qa	0, but steps of 8°	1	Purplish blue	chro-	Hoechst, Ciba-Pigments, Bayer, Sun	[6]
2.9 dichloro-qa	0, but steps of 4°	1	Purplish blue	↓	Sun	[6]
Beta-qa	0, but steps of 2°	1	Red-violet	mic	Hoechst, Ciba-Pigments, Bayer, Sun	[6]

^a From evaluation of 21 X-ray powder diffraction pattern.

^b See [6].

^c See CIE notation, Pigment Handbook, edited by T.C. Patton, part III, p. 242, Wiley & Sons, New York, 1973.

^d Atomic co-ordinates have been deposited at the Cambridge Crystallographic Centre and are now publically available.

hydrogen-bonded between the stacks, resulting in flat (F)-faces, [14, 15]. The F-faces can be designated as “hydrophobic” faces, which are bonded by van der Waals forces. Therefore, the refraction indexes of organic pigment crystals are very different and the crystals tend to be fibres or plates. Preparation of equally distributed pigment crystals in coatings, printing inks or plastics is not an academic problem. It is a problem of industrial application! Difficulties in the application of the Mie theory to organic pigments can probably be attributed to the unequal distribution of crystals in the organic matrix.

4.2. Structural theories

In the 1920s and 1930s, colour chemists – independently of and in parallel to the general organic chemists – developed mesomeric theories (inductive effects), particularly the absorption of light by single molecules. In the 1940s, organic dyes were accessible to quantum mechanics calculation that took into account important molecular parameters such as structural formula, auxochromes and chromophores, chemical elements, distribution of double and single bonds, the shape of the molecule, molecular weight, etc.

Physicists have calculated the colour of existing single dye molecules and predicted the colour of ones not yet synthesized. But they have not been able to predict the colour of many pigment dye molecules because they not only have to consider single molecules but also lattice rearrangement of planar molecules in stacks, hydrogen-bonds (number, position) and other factors. Crystallographic concepts such as unit cell, number of molecules/unit cell, specific gravity, asymmetric units, atom positions, herringbone structure, 0.4 nm structure [16], fluorescence of light and electron and proton conductivity are not taken into account. Therefore, the investigator is limited to empirical or semi-empirical concepts like criss-cross

angle (type 2 structure), steps between parallel molecules in neighbouring stacks (type 1 structure), area of contact of π electrons within the molecular piles, inclination of molecular plane to the pile axis, length, angle and number of hydrogen bonds etc., freedom of rotation of molecules in the lattice.

As in the early period of dyestuff theory, the pigment colour chemists unintentionally creates quantum-mechanical concepts in order to describe qualities (and hue). Crystal structure and theory are the only ones that can provide information about differences in colour (hue) if pigments of the same type have the same particle size.

5. Discussion

A single crystal exhibits exactly the three dimensional order of molecules of a phase. However, it does not comprise all possible molecular positions in the lattice. In other words, materials science and pigment finish have their origin and end in the variety beyond the rigid laws of scientific crystallography. The variation in unit-cell dimensions is unusually large and forms the basis of all technological properties related to gamma-quinacridone pigments. Orientational disorder, movements of molecules during pigment finish or boiling with dimethylformamide, variation of unit-cell parameters (a, b, c, β) and the criss-cross angle, are different aspects of the same thing, i.e. the crystal structure of gamma-quinacridone. Similar conditions are likely to be valid for other quinacridone pigments like alpha-, beta-, 2.9.dimethyl- and 2.9-dichloroquinacridone. In the same way, production difficulties and the diversity of colours and hues are attributed to the orientational freedom of the molecules.

Only the poster lecture of Paulus [6] in Moscow mentioned the role of structure and colour of quinacridones. However, he made a connection based on the angle between the “axes of pile” and the “axes of molecule”.

Meanwhile a valid suggestion is made for the structure of alpha-quinacridone and this paper reveals subtle differences in gamma-quinacridones. It demonstrates the relationship between structure and colour (hue) in a better way, as is shown in Table II.

This paper intends to give empirical evidence of the role of the hydrogen bond as an auxochrome group within the lattice of organic pigments, especially the quinacridones. However, other modern pigment classes (DPP, irgazine, benzimidazolone) also exhibit this phenomenon.

The three quinacridone pigments (alpha, beta and gamma) show the influence of the crystal structure on hue, without the effect of different substituents. The substituents (4.11-dichloro-, 2.9-dichloro- or 2.9-dimethyl-) seem to force the whole molecule to take up different positions inside the crystal, building H-bonds and piles well tolerated by close dense packing. The influence of the substituents seems to be confined to the asymmetric unit, specific gravity and inclination of molecular piles. Dyes behave virtually as single molecules, while pigment dyes act as crystals in a well-distributed powder form.

It is interesting to examine the function of hydrogen bonds both as (hue-generating and determining) auxochromes and (mechanically operating) couplings between the molecular piles during the process of pigment finish. The structural theory is awaiting the calculation of the energy of multiple electron orbitals in the crystal of organic pigment dyes, especially quinacridones, by Hartree-Fock. Only Hartree-Fock calculations can determine whether the π - π forces within the piles and the hydrogen bonds between them produce the hue alone (separately) or together, i.e. by mesomeric forces. We suppose, however, that these calculations would be difficult. Quinacridones are an example of extremely conjugated systems in the crystal lattice. Infinite chains are built up alternately by aromatic molecules and intermolecular hydrogen bonds. This is the whole point. In the lattice, millions of π -electrons alternate with millions of hydrogen bonds. These lattices are an example of the extreme phenomenon of the cooperative effect (π - σ -correlation), known with hydrogen bonds. Therefore, we expect that hydrogen bonds will not only be auxochrome groups but also conductors of electrons and protons in the lattice of pigment dyes, such as the quinacridones. This characteristic leads us to suppose that some quinacridones are catalysts for chemical reactions.

6. Conclusion

Figs 1 and 2 show further details. The four single-crystal structure analyses represent the field of science (exact crystallography). On the other hand, the 21

pigments represent the large part of the industrial market with its technical requirements.

This paper is not meant to solve the everyday problems of processing industries (printing inks, automotive coatings, plastics). These questions are better handled by the technical developing experts in the manufacturing industries mentioned in Table II. Converting quinacridone pigments by boiling with dimethylformamide is a method used by the solid-state chemists to obtain homogeneous crystals for scientific purposes.

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