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Review article

A review of thirty years of research on quinacridones. X-ray crystallography and crystal engineering

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Abstract

The various stages of the development of quinacridones are described progressing from the bonding hypothesis in the molecular lattice (1969), through light-microscopy examinations, to the study of the morphology of certain crystal faces (habit) and their representation by means of lego blocks (1972). Intermediate work was concerned with Cromophtal Red A3B, the molecular lattice of which was represented using Stuart–Briegleb space-filling models, and the bridging intermolecular H-bonds and $\pi\ldots\pi$ bonds were studied (1984). The long-range order (Bravais lattice) and the space group of 2,9-dimethylquinacridone were determined and a certain analogy to smectic liquid crystals was proposed (1985). Moreover, close-packing of molecules in the lattice was minimised and compared with the reflection intensities of the experimentally obtained powder diagrams. The positions of the molecules were determined independently of this. The finishing treatment by technological methods was described crystallographically (1987). Other work was concerned with the structure of beta-quinacridone (1983), alpha-quinacridone (1996) and a study on the structure and hue of all quinacridones known at that time (1997). The central theme of this 30 year work has been to provide a better comprehension of the bonding character of extended organic mesomeric molecules ($\pi\ldots\pi$ bond) in stacks with NH and CO groups capable of forming intermolecular H-bonds. The π-σ correlation in the crystal lattice was proposed for certain important organic molecules, and this is capable of inducing both light absorption and insolubility at the same time. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Quinacridones; Organic pigments; Colloids; Crystal structure; H-bonds/$\pi\ldots\pi$-bonds; π–σ Correlation; Crystal engineering

Preface

This review has been written because of the potential interest that the scientific community might have in approximately 30 years of studies on the crystal structures of quinacridone pigments. Contributions to this topic are diverse, and include both correct and false assumptions. Some have been restricting in their statements, others more forward-looking. It is interesting to gather together the individual results and evaluate them.

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The fox, it is said, knows many things,

The hedgehog, however, knows something of importance. (Free translation of a German saying.)

1. Introduction

An early review on the quinacridones is that of Labana [1]. Among other things, it deals with the first syntheses, the nomenclature, patents, and a large number of quinacridone compounds. Within the framework of the present review, emphasis is placed on the few quinacridones of industrial interest. These involve almost exclusively linear trans-quinacridone, which has become of great importance.

Quinacridone pigments were introduced into technical usage by DuPont in 1958[1] [2,3]. These proved to be an instant success due to their stability to light, weather and temperature (up to 400°C), and also due to their insolubility. This was unusual for such a small molecule with a molar mass of just 312 (see Fig. 1a). Quinacridone, however, is not stable and decomposes rapidly in a $Ca(OH)_2$ suspension in the presence of daylight. This would indicate that there must be strong intermolecular interactions in the molecular lattice which have a stabilizing effect; intermolecular hydrogen bonds being the most obvious candidate. A further indication of the role of the H-bonds is the substitution of both H atoms on the ring nitrogen atom to give *N*,*N*′-dimethylquinacridone: however, the 5,12-disubstituted derivatives are weakly coloured and are soluble in alcohol and pyridine [1]. The bridging H-bonds are apparently deeply incorporated in the characteristics of the crystal.

The existence of three polymorphic phases (modifications) is quite remarkable. In practice, only gamma-quinacridone (crimson) and beta-quinacridone (red-violet) play any important role. Alpha-quinacridone appears to be less stable. X-ray powder diffraction diagrams played an important role as a characterisation method in the granting of the patent, which was quite a novelty at that time, and invoked new characterisation processes.

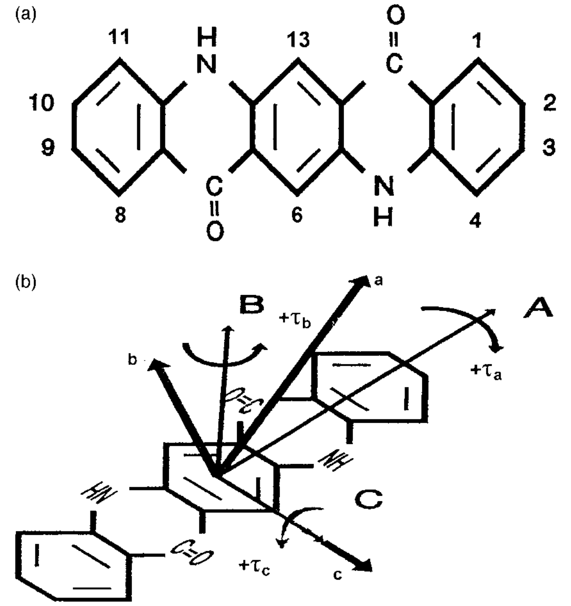

Fig. 1. (a) Planar molecule of linear trans-quinacridone. (b) Molecular A-, B- and C-axes of a quinacridone (right handed system); *a*-,*b*-, *c*-axes of its Bravais unit cell with rotating angles for orientational change.

An overview of inorganic and organic pigment classes, and knowledge of the divisions into organic and inorganic chemistry, immediately draws parallels to Fe_2O_3, Cr_2O_3, TiO_2 or carbon black when considering the extreme insolubility and the hue of quinacridone. There is no red Fe_2O_3 molecule or black C atom!

Light absorption and scattering are lattice properties of the pigment particles. It should be mentioned, however, that individual molecules of phthalocyanines are blue.

Carbon black finds universal use as a pigment, in particular due to its excellent stability, but in many cases it is also a necessary filler (e.g. for car tyres). The crystal lattice of carbon black is very similar to that of graphite. In the case of quinacridone, as in the case of graphite, the basic approach had to be concerned with evaluation of crystal faces (crystal planes) that were responsible for the pigment properties, i.e. for insolubility, light absorption, and stability.

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[1] This review uses the Labana nomenclature [1]: the 2,9-positions are substituted in certain quinacridones. The 2,3,9,10-positions lie on the outside regions of the molecule and play an important role for the van der Waals contacts. See also footnote 2.

It is perhaps useful to mention here a typical procedure for solid-state chemistry. Crystals are compared in relation to their similarities or certain systematic changes in the atomic bonding situation in the lattice. It is thus possible to find a plausible explanation, for example, for the cleavage, lubrication, and swelling properties, and even for interstitial compounds of a layered lattice with strong bonding between the atoms/ions within the layer and simultaneous low interaction between the layers (graphite, talcum, bentonite). Chemically similar crystals do not necessarily, therefore, have to have similar crystallographic parameters (unit cell or space group). I therefore applied the inorganic concept of the layered lattice (typical crystal faces) to quinacridone lattices. In doing this I was not only concerned with the mechanical properties, but also with light absorption and scattering.

In order to focus our train of thought, it is useful to consider a single quinacridone molecule with NH and CO groups on both sides of it, and which is capable of forming stacks based on aromatic six-membered rings. A Stuart–Briegleb space-filling model of the single molecule shows it to have the form of a brick. How do the bricks arrange themselves to form a wall? To ask the same question scientifically: how do the quinacridone molecules crystallize?

The assumption that the form was flat was initially evident, and (as was later shown) also correct, but it was not at all obvious. The reason for this was an article written by Koyama et al. [4], which assumed that quinacridone molecules were bent at the NH and CO groups and then ran through the lattice in a stair-like fashion. The original paper refers to a "spiral staircase". The assumption of planar quinacridone molecules to build up quinacridone lattices was thus rather adventurous, even if it was chemically stringent (see Fig. 1a). What persuaded me to question the Koyama structure was that strong interactions in the crystal lattice indicated resonance between the building blocks (individual molecules). This resonance, is more strongly pronounced in the case of planar organic molecules than in the case of bent molecules.

At that time, the usual impression that chemists and technologists had of pigments was dominated by those that were first dissolved and then processed; textiles were the major concern. It was not considered that all pigments remained as finely divided, insoluble powders in their various media. The difference between soluble and insoluble is of prime importance, however, and further characterises the technology of the dye and pigment industries. Only a few specialists in organic pigments recognized this question.

2. The role of quinacridones in the development of crystal engineering

It was unclear just how, in detail, intermolecular bonds form a lattice. This was even more problematic in that intermolecular bonds do not develop a constant direction as do covalent bonds (see graphite/carbon black). The graphite lattice is simple, and that of quinacridone was considered to be probably complicated, and in any case, it was completely unknown. In a first publication with respect to this, the limitation of the individual existence of the molecule in the lattice was postulated and the totality of all the molecules was discussed. Emphasis was placed on the limiting ionic structures and a 180° hydrogen bond [5], and it was assumed that the resonance structures of quinacridone existed throughout the entire crystal, but only in one dimension as regards the H-bonds. The question of the intermolecular effect (strength) of NH and CO groups on extended aromatic mesomeric molecules appeared, to be of fundamental importance. The question could be asked: how do the intermolecular H-bonds behave when they are formed from molecules with extended delocalized π electrons? A question which had not been previously posed. It became the crucial core of all my research on quinacridones and is the central theme per se. The intermolecular interactions in quinacridone appeared to be important in order to interpret the specific light absorption/reflection in comparison with (black) carbon black. In polarized light the crystals were often readily seen to be bent; this was clearly an indication of lattice defects. A layering of the planar molecules could be hypothesised, but it could not be proven on the basis of Debye powder patterns.

2.1. *A look at various pigments*

This “bricks in a wall” picture was transferred to typical organic pigment classes and spoke in general of ionic-covalent bonds in a molecular lattice. Indeed, the proposal made Ref. 6 (p. 773) for the tetrachloroisoindolinone lattice does have a certain appeal [7]. The shape of an individual molecule only fits with the next one in the *trans*-position, etc. Fig. 12a shows the arrangement of individual tetrachloroisoindolinone molecules to give a large molecule. In principle, this was to some extent the anticipation of a supramolecule. The intermolecular hydrogen bonds form an infinite chain within the lattice. To my knowledge, the crystal structure of tetrachloroisoindolinone has not yet been described in the literature, but it is known [8].

2.2. *2.9-Dichloroquinacridone*[2]

Our research studies had no access to an X-ray generator and camera, or even appropriate software, at that time [see Section 2.7 (beta-quinacridone) and Fig. 9], so the morphology of the existing crystals was, therefore, studied using a microscope. It, thus, proved possible to state more precisely the picture of the “brick wall” for the first time on 2.9-dichloroquinacridone[3]. Two modifications were differentiated, viz., twin formation and polysynthetic twin formation were also detected due to the tendency of the crystals to undergo mechanical twin gliding. Models of the crystals using Lego blocks indicated that the molecules were positioned “end-over”, i.e. the 2,3,9,10-positions pointed outwards (van der Waals contacts), and intermolecular H-bonds (and $\pi...\pi$ bonds) pointed inwards (see Figs. 2 and 3). Fig. 2 shows an idealized twin (with twinning plane), and Fig. 3 represents the continuous transition (light grey) in the twin boundary (with twinning zone), which is much more probable. Even in Fig. 3, the transition area is still just an approximation. The twin boundary in Fig. 3 already has some amorphous character. In the twin and polysynthetic twin glides, the H-bonds remain intact, and thus an initial quantitative step had been achieved. The picture of the “brick in a wall” seemed to fit [9]. In the context of current knowledge, this proposal was very close to the truth [see Sections 2.6 and 2.7, [46], echelon grating].

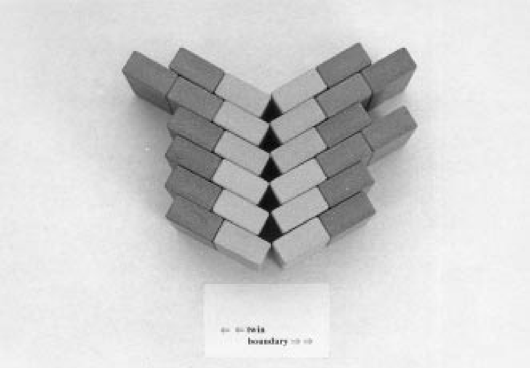

Fig. 2. Clinographic view of the F-face of 2,9-dichloroquinacridone. Idealized twin (model), showing the twin plane (light grey).

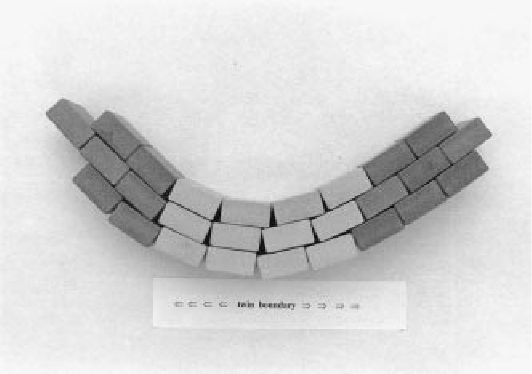

Fig. 3. Approach to the real twin of Fig. 2. Twin boundary: light grey. The real crystal consists of few hundred or thousand molecules within the boundary.

2.3. *Gamma-quinacridone*

> We don’t know anything, we are only guessing. (Topic of an interview conducted by Franz Kreuzer with Sir Karl. R. Popper (London) 1984, broadcast by the German TV channel 3 SAT.)

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[2] Presentation made to the Fachgruppe Anstrichstoffe und Pigmente in the GDCh in Rottach-Egern (Bavaria) on 30 April 1971.

[3] The paper [9] uses the older (German) nomenclature for quinacridone from Liebermann. He also called it chinacridone (Liebermann H. Ann. 1935; 518: 245).

In the meantime, Ohmasa and Süsse had proven the planarity of N,N′-dimethylquinacridone [10,11]. It was cited that "The main result is, that the molecule of N,N′(*trans*)-dimethylquinacridone is found to be planar, while the molecule of gamma-quinacridone is supposed to be bent. This may prove to be an important fact for interpreting the absorption spectra". However, pleasing the planarity of the molecule being studied might have been, even here, the bent form of gamma-quinacridone was not questioned at all. Thus, making a start with planar molecules (in the case of all quinacridone molecules) was not at all obvious, but in fact rather questionable. Zavodnik et al., in an independent study in 1981 also confirmed the planar form of N,N′-dimethylquinacridone [11], and concluded that, with respect to gamma-quinacridone: "the conclusions in the work cited (author's comment: [4]) require additional confirmation".

Particular use was made of the light microscope in order to visually inspect the many crystals [13]. As a matter of principle, it can be said that the leaf-like shape is favoured by crystal growth via sublimation. The crystal form, however, cannot be recognized and the crystals often have defects, i.e. they are real (imperfect) crystals. This is revealed particularly well by rotation and Weissenberg photographs. The F-face is very closely related to the leaf-like shape. The term F-face was conceived by Hartman and Perdok [12], and has been carried over to quinacridone. The F-face is formed when at least two PBC (periodic bond chain) vectors act within a crystal face, and this makes it morphologically conspicuous. This seemed to fit in well with the quinacridones. As a supplement to earlier publicized pictures of gamma-quinacridone (see Figs. 7 and 8 in [13]), a crystal with even more defects is shown in Fig. 4.

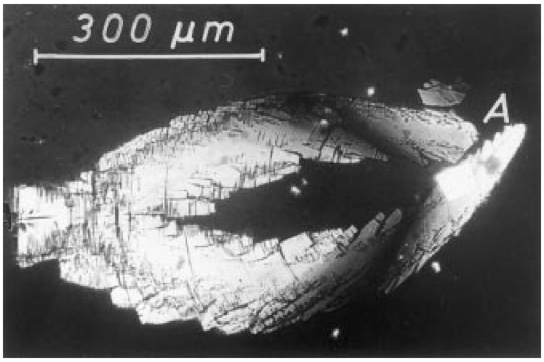

Fig. 4. Real crystal of gamma-quinacridone observed with polarized light. The crystal takes on the shape of a crayfish claw, caused by curved crystal planes.

The positions of the analyzer and the polarizer are also visible as broad black stripes. The crystal surfaces of gamma-quinacridone have a strong tendency to bend. The so-called fibre diagram was then published [14], from which the identity-period (repeat period) of 0.390 nm is immediately accessible. Fibre diagrams can be readily recognized from the X-ray rotation photograph and they are quite typical for the crystal. In Ref. 14, a relationship was established between the fibre diagram (see Fig. 11 in Ref. 14) and the stacking distance between the flat molecules (see Fig. 1 in Ref. 14). In addition, the angle of tilt of the molecules to the stacking axis was described (30.6°) and the leaf-like structure characterized (see Fig. 12 in Ref. 14). The interpretation of the perpendicular arrangement of the reflections was made by Schiebold. He called them type 2 layer lines. At that time I was not aware of the fundamental work carried out by Astbury and Street, in which characteristic rotation photographs of wool and hair were described with other type 2 layer lines [15]. The F-faces were classified as "herringbone" type, and the bifurcated H-bond is causally related with this. The F-faces had already been described as double-stitched, i.e. as "crystal walls" of charge transfer forces and H-bonds. This was indeed accurate. In addition to the "herringbone" lattice, Ref. 14 also disclosed the "zigzag" version. The criss-cross angle (instead of the herringbone structure), which was later found by Paulus et al., was not recognized, however, and, thus, the goal was narrowly missed (see Section 3 and [46]). It is still unclear, even with our current knowledge, why a herringbone lattice has not as yet been found in quinacridone crystals (see Sections 2.8.1 and 2.8.2). In Ref. 14, the van der Waals forces were once again assigned to the 2,3,9,10-positions and used as limiters for the F-faces; this was correct thus far.

The following statements are then made in the reference: "The rustic method of using space-filling models in seeking the positions of important atoms... finds its justification in the defect.... which is connected in the make up of the crystal." and "It would admittedly be desirable if the stacking hypothesis presented here could be verified by the precise structural characterization of gamma-quinacridone...". Koyama's "spiral staircase" arrangement [4] had still not been refuted. The continuation of this Section 2.3 is to be found in Section 2.6.1, but the following factors should be noted with respect to the development of the elucidation of the crystal structure of gamma-quinacridone at this point viz., after Paulus [46] had presented the crystal structure of eight quinacridone molecules, Jaffe also partially made known the structure of gamma-quinacridone as found by DuPont [47]. Potts reported the complete structural characterisation of the compound [48]. The reason for holding back this important crystal structure was the technological consequence of doing so. Industrial companies use the results by their very nature of research to improve their own products and to develop patent specifications. The question as to the difference of the two polytypes gamma_{I}- and gamma_{II}-quinacridone, as interpreted morphologically by Potts [48], still remains unanswered today. The present author attributed the difference to variations in the position of the molecules in the crystal lattice [50].

2.4. Cromophtal Red A3B (4,4′-diamino-1,1′-dianthraquinonyl) [17]

The lattice was characterised by Koyama et al. [4,16]. Space-filling models made from moltoprene foam provided a vivid illustration of the F-faces already mentioned (see [12], PBC vectors). It was in the characterisation of Cromophtal Red A3R that I first made a statement on a *common* interaction of two intermolecular bonding forces.

The subsection was titled: "The role of molecular walls along (002) as the flat-face (F-face) and their significance for pigments". One has to have built the crystal as a space-filling model in order to understand the formulation "molecular walls". Only those parts of the molecule with van der Waals interactions point towards the outside. It was only noted that "It is presumed that the chemical bonds, portrayed by the two P B C vectors, represent one unit, i.e. are coupled". This is a very cautious statement [17]. The study of the internal twin formation as observed and reported by Ito in 2,4,6-trinitrotoluene [18] is also of significance. This was also observed in crystals of Cromophtal Red A3R using rotational and Weissenberg photographs. Polymorphism and twinning is apparently common among organic pigments. The impression that pigments, and in particular the quinacridones, are partially crystalline colloids and not at all "single crystals", was thus strengthened. It was the single crystals, however, that opened up the understanding for real crystals (see for example Fig. 4 in Section 2.3 and Fig. 7 in Section 2.7.

The $\pi...\pi$ exchange forces existing in the lattice at any one time were expressly considered in Ref. [17] in 1984. Chemists have always been concerned with the stability of the free NH_2 group in such a single molecule, since this gives information about the effect of intermolecular H-bonding forces and $\pi...\pi$ bonds in the lattice. Physicists and crystallographers do not appear to have been so involved in this criterion.

2.5. 4,11-Dichloroquinacridone

> Nevertheless, the method of attempting reductions is most fruitful, not only because we learn a great deal by its partial successes, by partial reductions, but also because we learn from our partial failures, from the new problems which our failures reveal. Open problems are almost as interesting as their solutions; indeed they would be just as interesting but for the fact that almost every solution opens up in its turn a whole new world of open problems. (Karl R. Popper from *The Open Universe* and *Alles Leben ist Problemlösen*.)

> No work done in the service of investigations is ever lost, not even when carried out under false assumptions. (Karl R. Popper from *Alles Leben ist Problemlösen*[4].)

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[4] It is gratefully acknowledged that the quotations from Karl R. Popper's *Alles Leben ist Problemlösen* were made possible by permission of the Estate of Sir Karl Popper, South Croydon, Surrey, England.

This pigment is scarlet red in colour and thus important in practice, but it does not have the same kind of stability normally associated with the quinacridones. Since we had no X-ray crystallographic facilities (single crystals) at this time, we attempted to determine the lattice structure using the known method of space-filling models [19]. The still incomplete work of Chung was a help in this, as it at least contained the Bravais lattice and the space group [20]. The fundamental work of Kitaigorodskii on the statistics of the space groups and the theory of the conservation of the inversion centre were also known. It states that if a molecule contains an inversion centre (e.g. as in quinacridone), this fuses with an inversion centre in the lattice [21–23]. At this point a further line of work should be mentioned, on the build up of crystal lattices from molecules, namely that of von Stackelberg [24,25]. This work can be described as being at least simultaneous with that of Kitaigorodskii, possibly even preceding it, although in the light of modern "crystal engineering" (see Section 4) it has probably been forgotten.

In spite of its successes, my initial work ended unsatisfactorily. From today's viewpoint, the following was correct: the assumption that the molecules were flat, their stacking along the axis ($c = 0.7423$ nm), and the fusion of the inversion centre of the molecules with that of the Bravais lattice and the space group Pbca. The flat molecules also lay quite correctly on (041) and the 2,3,9,10- positions were aligned parallel to the (001) face. After a presentation at Hoechst (Frankfurt), on this lattice, the single crystals grown were passed on to Paulus for either verification or refutation of the proposal. Paulus succeeded in elucidating the first quinacridone lattice and my sole mistake became obvious. In the last step a (forbidden) acyclic permutation (= exchange) of the Bravais axes was assumed. Hydrogen bonds were thus avoided, although they were readily recognizable in the model when the Bravais axes were assigned correctly. I did not want to believe in the presence of H-bonds in order to interpret the great jump to the scarlet hue. Moreover, the connection between the hue and the structure of quinacridones was not known at this time (see Section 3 and Table 4). Such is the fate of trial and error! Nonetheless, I now knew from Paulus' structural characterization that the molecules were flat, stacked, and formed a typical criss-cross lattice, a possibility which had not been previously considered. The angle between the two molecular stacks connected by H-bonds was found to be $2\times62.5^\circ$, and as such the stacks are strongly twisted in opposing senses. Other quinacridones also form the criss-cross type. For this reason, Paulus et al. later characterized the criss-cross lattice in general as type 2, but this is anticipating future developments (see Section 3 and [46]). The proposal made by Koyama [4] was not so far from the truth. The "spiral staircase" arrangement of bent molecules only had to be applied to flat molecules and the criss-cross angle would have been recognized. The crystallographers lacked the ability to apply the inductive resonance theory to the individual molecules of a pigment dye.

If you take the first 49 of 50 steps, then you are admittedly close to your goal, but you still have not quite reached it! I later used the computer program "POWDER", which permits the calculation of reflection intensities and transforms these into a pattern trace which can be directly compared to the experimentally determined powder diagram (overlay). The mistake would have been avoidable with this program.

It is thus established: the molecules are connected once again via H-bonds and at the same time via $\pi\ldots\pi$ exchange forces. The question remains is "why are they orange in colour?" What was going on in the crystal faces parallel to (001) in which the intermolecular bonds were located?

2.6. 2,9-Dimethylquinacridone

2.6.1. Qualitative model[5]

After this, work started on 2,9-dimethylquinacridone. The crystals had certain morphological similarities to those of 2,9-dichloroquinacridone, but they were not suitable for a statistical evaluation of the angle on the twinning planes. Here too, the F-faces were developed preferentially, i.e. the

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[5] Presentation made at the 17th Congress FATIPEC in Lugano, Switzerland, on 27 September 1984.

crystals had a leaf-like form. The long-distance order (Bravais lattice), the character of the molecular stacking (fibre diagram), and the connection pattern to give leaf-like structures (type 2 layer lines) were recognized with the help of the rotation camera (Fig. 5) using crystals that had as uniform an appearance as possible. The corresponding results were recorded [26].

Kitaigorodskii's close-packing theory proved to be useful here too [21–23]. In addition, two papers from Hoppe indicated the pattern of the semi-quantitative evaluation of certain reflections. Hoppe had been able to determine the angle of tilt of the molecular planes relative to the stacking axis on dye molecules which formed stacks at room temperature [27,28]. He was able to determine the reciprocal coordinates ξ and ζ from the Bernal chart, the quotient of which gives the tilt. The colloid theme was important, and all the more so as it was concerned with dyes (from the pseudo isocyanine group). It should perhaps be mentioned that these pseudo isocyanines are of considerable industrial importance as sensitizers for photographic films. The stacking of the molecules seems to play a significant role. In [26], the X-ray photographs showed once again the character of a real crystal, just as did previously those of the cultivated crystals of 2,9-dimethylquinacridone. The unit cell, with $a = 0.389$ nm, $b = 0.645$ nm and $c = 1.608$ nm, was so small that only one quinacridone molecule could fit in, and as usual, "end-over".

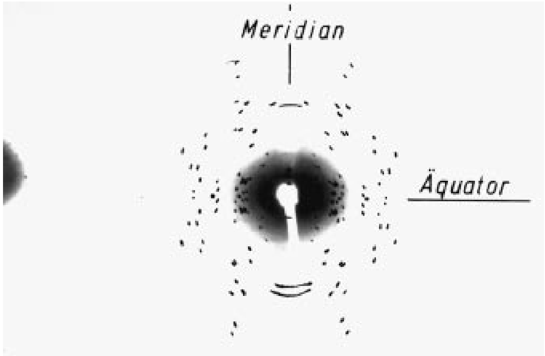

Fig. 5. Rotating-crystal photograph of 2,9-dimethylquinacridone. Axis of rotation perpendicular to the F-face. Notice the spots vertical to the equator. These are "Schiebold's type 2 layer lines", "Schichtlinien II.Art".

Other publications on morphology and X-ray diffractometry were considered in [26], including that of McLachlan, which relates the laminarity of a network plane with its structure factor in the form of $F^2(hkl)$ [29–31]. It is even possible to describe the F-face in terms of McLachlan's rather abstract language. Papers written by both Buerger and Wells also bear an interesting relationship to morphology [30–31]. As Buerger commented: "It might be pointed out here that an interesting relation exists between form development,..., and the powder photograph of a crystal. The order of importance of the crystal faces is exactly that of the order of appearance of the corresponding lines on the powder photograph (proceeding from $\theta = 0$ to $\theta = 90°$), provided that no orders of a line other than the first are considered". This draws one's attention to the innermost reflection in the powder photographs of quinacridones, which usually lies between 1.35 and 1.6 nm. It was just this reflection that was attributed to the F-faces within the framework of my studies. In connection with this, "Crystal Form and Structure" written by Schneer also deserves a mention, as it can be regarded as a veritable treasure trove for morphological considerations [32].

After this, smectic liquid crystals were studied. Researchers in this area had to be satisfied with far less X-ray reflections than those involved with pigments such as quinacridone. A substantial collection of relevant literature can be found in Ref. [26]. Care should be taken to avoid a possible misunderstanding, however: Quinacridones are not liquid crystals. But it was considerations of this that proved decisive, providing the answer to the question of how to deal with lattice defects in molecular crystals. Smectic crystals arrange their long, stretched organic molecules in a parallel manner, much like matches in a matchbox. The "end-over" picture thus appears here, too. The complicated twisting movements of the so-called smectics are described elsewhere, as are the many different variations of their arrangements. It was of importance to show here that the arrangement of long, stretched molecules in this "end-over" sense is reasonable, and it had already been carefully studied on liquid crystals, in particular using X-rays. The details make up a large special field in themselves, and at least part of the studies are given in Ref. [26].

Crystallographers love the single crystal. With modern methods it can provide fast and unequivocal results. Everyone connected with pigment chemistry, however, knows that industrial tasks lie beyond any ideal molecular arrangements. This work on 2,9-dimethylquinacridone in particular made it very clear that *Pigments are colloids, not small single crystals.* Today, after the elucidation of the lattice by Paulus et al. [46], it can be said that — to make use of a German hunting expression — my paper [26] was like shooting an "11", i.e. I only missed hitting the target by the narrowest of margins. This is also true to some extent of the work on 2,9-dichloroquinacridone, in which I came somewhat closer to the truth [9].

The meticulous literature work was a substitute for the lack of partners for scientific discussion. From 1984 on, I contacted experts on liquid crystal research at the Physical Chemistry Institute of the University of Halle-Wittenberg in order to learn more in this field. This proved to be of great help later on in connection with alpha-quinacridone (see Section 2.8.1).

2.6.2. Quantitative calculations[6]

After all the difficulties with 4,11-dichloroquinacridone, it was imperative that the information contained in the intensities of the powder diagrams be processed. This led to a cooperation with J. Moebes, a physicist and mathematically well-versed computer programmer who worked at the FH Niederrhein in Krefeld. Our first step was to activate Williams' close-packing program "PACK5" [33,34]. This minimized the repulsion energy of the asymmetrical unit in the lattice. In order to do this, the 2.9-dimethylquinacridone molecule was set with its inversion centre in the middle of a Cartesian coordination system parallel to the plane of the paper (see Fig. 1b, extended to take in both CH_3 groups in the 2.9-position). The A axis runs parallel to the length of the molecule, the C axis perpendicular to it. The positive sense of rotation was also laid as a basis, so that the rotation axes τ_a, τ_b and τ_c resulted. It proved possible to determine the molecular sites with minimum energy. A similar thing was now done for the X-ray intensities of the powder diagram. The residual value $R(\%)$ is the deviation between the structure amplitudes found from experiment and those calculated from the lattice model in accordance with Eq. (1):

$$R(\%) = (\Sigma \| F_{\mathrm{obs}}| - |F_{\mathrm{cal}} \|) / \Sigma |F_{\mathrm{obs}}| \qquad (1)$$

If with the aid of a computer program, the molecule in the lattice is turned and varied systematically, and the structure amplitudes in each position are calculated, constant comparison with the experimentally determined amplitudes enables the positions of lowest R value according to Eq. (1) to be located. This minimum value gives a clear indication of a reasonable position for the molecule in the lattice. The environment in which the minimum is located is also of interest (see Fig. 6) [34]. Using Hamiltonian statistics, the position of the molecule thus found was used in order to answer the question as to whether the molecules in the lattice formed bifurcated or simple H-bonds [35,36]. The answer was that simple H-bonds existed; the test rejected the possibility of bifurcated H-bonds.

In order to check the quality of the proposed lattice, Table 1 shows a comparison of the lattice parameters obtained from the model with those from the exact solution [46].

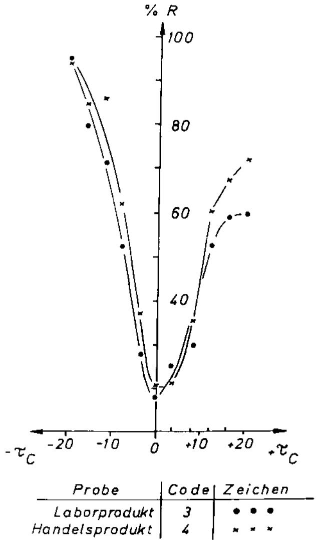

Fig. 6. Minimization of R-value with 2,9-dimethylquinacridone with respect to τ_c.

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[6] The author wishes to thank Professor Dr. P. Zugenmaier, TU Clausthal-Zellerfeld, for valuable discussions.

The deviations in Table 1 may be a result of genuine differences in the build up of both crystals, and not at all just "measurement error" (see Section 3). Due to their flat and rigid molecular form, there is a tendency for quinacridone molecules to display orientational disorder.

Furthermore, it became clear that the technical process of the pigment finish (aftertreatment) led to high mechanical shearing of the crystallized raw material. The flat and rigid molecules thus slide over one another and form more or less ordered crystalline regions, often streaked with twinning and polysynthetic twinning, orientational disorder, and particularly rotational disorder. Coarse grain zones, small-angle grain boundaries and edge dislocations also make up part of this.

2.7. *Beta-quinacridone*

Crystals of this phase became accessible and as usual, they too were highly disordered; as could be clearly seen from rotational and Weissenberg photographs. Attempts to prepare single crystals only proved successful later on, but extremely lamellar and very thin crystals became accessible by growing them from beta-quinacridone powder in boiling xylene. Fig. 7 shows just such a crystal in polarized light. It has the typically chequered pattern and is thus precisely built. The results of subsequent experiments were never publicized, which is why they are described here. If several of these crystals are placed in layers on a glass slide, a preparation of extreme texture is obtained. In the Bragg-Brentano camera this preparation leads to excellent results measured in terms of reflection, showing reflections of up to 12 orders of the type (00L), i.e. the basal reflections and only these. The correct measurement of the reflection intensities was made possible by cold cathode tubes (see Table 2). This method no longer finds use today.

In these crystals the molecules had to lie end-over. A further confirmation for this assumption was provided by photographs of selected crystals with the transmission flat plate camera (see Fig. 8). Two lattices axes with $a = 0.403$ nm and $b = 0.565$ nm were determined from these. The angle γ was near to or exactly 90°. These are values which correspond to "end-over" molecular dimensions for quinacridone. The molecules are apparently stacked along the crystallographic a axis, the crystallographic b axis reflecting the breadth of the molecule at the pyridone rings. At this point, it was even for us to be able to make attempts at solving the lattice structure by building

Table 1
Lattice parameters of 2,9-dimethylquinacridone

Parameter	Lincke [26,34] (nm)/deg.	Paulus et al. [46] (nm)/deg.
a	0.389 (2)	0.3901 (1)
b	0.645 (3)	0.6407 (1)
c	1.068 (6)	1.5817 (1)
α	91.6 (5)	93.44 (1)
β	92.1 (5)	91.59 (1)
γ	99.4 (1.5)	100.78 (1)
Z	1	1
SG	P-1	P-1
$\rho_{\text{rö}}$	1.42	1.459

Fig. 7. Crystal of beta-quinacridone grown in boiling xylene, observed under polarized light.

Table 2
Beta-quinacridone: spacings D, intensities, F-values and (HKL) of lamellar crystals

No. of peak	Range of angle (°)	Counts[a]/peak	Int. (obs) (%)	D (nm)	c-axis (nm)	F (obs)	H K L
1	5.5–7.5	1 344 826	100	1.473	2.946	2.292	0 0 2
2	11.0–13.0	656 806	48.8	0.7468	2.987	2.621	0 0 4
3	17.0–19.0	3697	0.27	0.4975	2.985	0.210	0 0 6
4	23.0–25.0	113 502	8.4	0.3734	2.987	1.359	0 0 8
5	29.6–31.6	61 702	4.6	0.2982	2.982	1.146	0 0 10
6	35.3–37.5	12 564	0.93	0.2487	2.984	0.575	0 0 12
7	41.5–43.5	8598	0.64	0.2134	2.987	0.528	0 0 14
8	48.0–50.0	3038	0.23	0.1866	2.986	0.347	0 0 16
9	54.5–56.5	3327	0.25	0.1659	2.987	0.394	0 0 18
10	75.5–77.5	22 088	1.64	0.1244	2.987	1.229	0 0 24
11	83.0–85.0	7185	0.53	0.1150	2.988	0.722	0 0 26
12	91.5–93.5	635	0.047	0.1067	2.987	0.217	0 0 28

[a] Background adjusted.

space-filling models (van der Waals radii), and in anticipation of the exact result of beta-quinacridone we can refer here to Fig. 10.

The next step was the study of the X-ray crystallographic literature for mineralogists on interstratified layer silicates (smectites). Mineralogists had carried out one-dimensional Fourier syntheses on these in order to more exactly determine their build up [37]. Amongst the very extensive literature on this subject, a paper by Sudo was recognized [38]. In this work a computer program, which had been developed by Moebes, was tested [39]. Fig. 9 resulted from the application of this program on beta-quinacridone (see Table 2). In the lower part the electron density (y axis) is plotted against distance in nm (x axis). Two symmetrical maxima and a clear minimum can be easily recognized at a distance of 1.52 nm. In the upper part, the quinacridone molecule is shown displaced parallel to this. The electron density maxima fit in

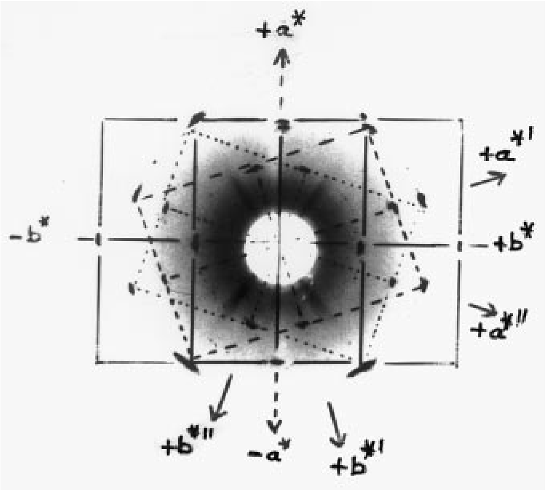

Fig. 8. Flat plate photograph of a crystal of beta-quinacridone. Note two reciprocal lattices $a^{*\prime}/b^{*\prime}$ (dashed line) and $a^{*\prime\prime}/b^{*\prime\prime}$ (dotted line) symmetrical (± 18°) to the reciprocal lattice a^*/b^*.

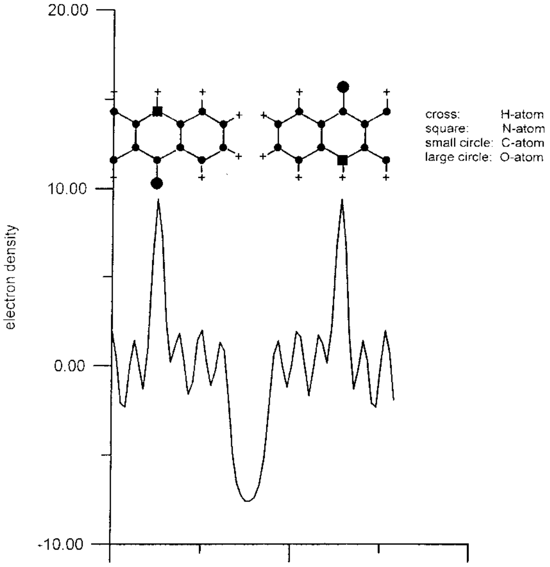

Fig. 9. Electron density of the (00L)-face, F-face, of beta-quinacridone (below) and two halves of molecules, fitted in perfect position (above).

with the heaviest atoms N and O and the minimum is attributed to the van der Waals contact between the molecules. All C atoms find their correct positions. Strictly speaking, we had inserted some additional mosaic pieces for the "end-over" position. In more general terms, the "end-over" position became more probable. It must also be said that the molecular geometry was determined independently of the Bragg distance of 1.52 nm. The only random thing about Fig. 9 is the fixing of the position parallel to the x axis [39].

There was one further observation to be made about Fig. 8. It can be seen that a second identical network exists, twisted at an angle of about 36°. This means that an identical molecular network must exist in crystals of beta-quinacridone in the direction of irradiation of the surfaces parallel to (00L). A further identical molecular network can be identified twisted at 72°. This can be interpreted by a study of the OD (order–disorder) structures termed by Dornberger-Schiff. In her summarizing portrayal of this complicated field, she defined imperfect identity operations [40,41]. It was possible to reconstruct the angle of 36° within the F-face with space-filling models (van der Waals radii) of the molecule. Fig. 10 shows the F-face tilted somewhat from the c axis, looking directly onto a/b. The a axis is the stacking axis and points upwards. The molecules are arranged on top of one another in a step-like fashion (Fig. 10, bottom left), within each molecule corresponding to a diagonal line to a/b as a direct contact between the π electrons and the H-bonds, and as the shortest distance from molecule to molecule as a π…π interaction.

Fig. 10. Clinographic edge-on-view perpendicular to the F-face of beta-quinacridone. The two stairs (left, grey) indicate the π–σ correlation of three adjacent molecules. a- and b-axes are marked. The photo shows the end-over position of quinacridone molecules represented by real space-filling models.

The geometry makes quite clear here what I referred to as π–σ correlation; σ electrons from intermolecular H-bonds and π electrons from aromatic molecules are brought together in close proximity throughout the entire crystal lattice. The "cooperative effect" can hardly be imagined in a more compact form. Fig. 11 shows the projection of the aromatic molecules onto the best plane and thus also the lateral displacement.

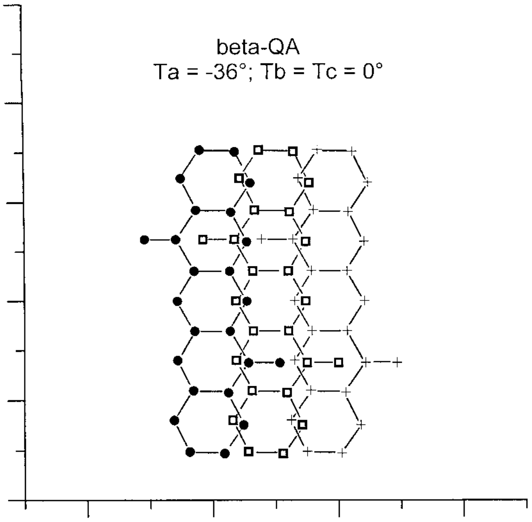

Fig. 11. Projection of three molecules on the least-squares plane in one stack of beta-quinacridone.

It is fitting to look back on the following statements made by Coulson in reference to molecules with conjugated double bonds (aromatics) [42]:

> The choice of the particular structures to be included has to be made on the basis of chemical intuition, or mathematical convenience. There are many cases in which the choice is by no means unequivocal as in benzene, particularly in view of the established fact that with larger and larger molecules the excited structure become progressively more important than the unexcited ones. It seems as if a definite limit is placed on the size of the molecule that may be dealt with conveniently. And even for small molecules the inclusion of ionic structures presents almost insuperable technical difficulties and:
>
> Moreover, we know by now that the tacit neglect of interaction between σ and π orbitals is certainly not correct, since energies of δ and π electrons are often nearly the same.

At the same time a further field was being elaborated with which disordered crystalline structures could be studied. The foundation for this field was laid by Bragg [43]. A film negative called a "mask" (2×3 mm) was irradiated with visible light and the resulting diffraction pattern behind this recorded on a light-sensitive film. These "masks" had to be prepared by hand and were in fact pen-and-ink drawings of possible atomic and molecular sites according to choice. The drawings were photographed and miniaturised to produce the finished masks. Every possible atomic position could thus be tested, including disordered lattice sections. The method was later considerably improved [44,45]. Initial trials at the Physical Chemistry Institute of the TH Clausthal-Zellerfeld were encouraging. The method more or less died out in spite of this due to the time involved in the preparation of the masks.

The results of the studies on beta-quinacridone were not published because just a short time after, single crystals became available. The dispatch to Paulus (Hoechst) resulted in the three-dimensional Fourier synthesis, also known as the crystal structure analysis, being very quickly available. Our partial results were confirmed and this structure analysis, together with 7 others, made up the subject of a poster presentation made by Paulus in Moscow. The molecules are found — once again — to lie "end-over" in the F-face and the molecular planes are tilted at about 36° to the stacking axis. In the poster presentation, Paulus designated the crystal structure of beta-quinacridone type 1 [46]. The molecules, connected via both H-bonds protruding from the sides, do actually lie in one and the same plane. The H-bonds lie within the crystal layer and are, from a chemical point of view, ideally bonded.

2.8. *Alpha-quinacridone*

The structure of alpha-quinacridone was still unclear as yet; it was important though, being formed industrially as a raw material; both the commercial products, gamma- and beta-quinacridone, were formed from it via the previously mentioned pigment finishing process (see also Section 2.5.2). Moreover, it was significant that no substituents, e.g. in the 2,9-position, could cause any changes in the hue arising from the individual molecule.

Even over a period of $4\frac{1}{2}$ years, no useful single crystals could be grown. The crystals obtained were needle-like (300 μm and larger) with a cross-section of irregular pentagons, hexagons and heptagons within *one* crystal. The morphological findings of disordered crystal growth were confirmed by rotation photographs which showed a stacking distance of between 0.356 nm and 0.372 nm, meaning that they were also completely unusable.

2.8.1. *Alpha-quinacridone (criss-cross type 2)*

Numerous studies on the hues of alpha-quinacridone revealed that it was closely related to gamma-quinacridone. For this reason well-crystallized alpha-quinacridones were assigned to the criss-cross lattice and their crystallizations followed by means of X-ray powder diagrams (Fig. 12). For the purpose of calculating the powder diagram, the molecules were systematically rotated around the molecular axes A, B and C using a computer simulation (Fig. 1b). The atomic coordinates were

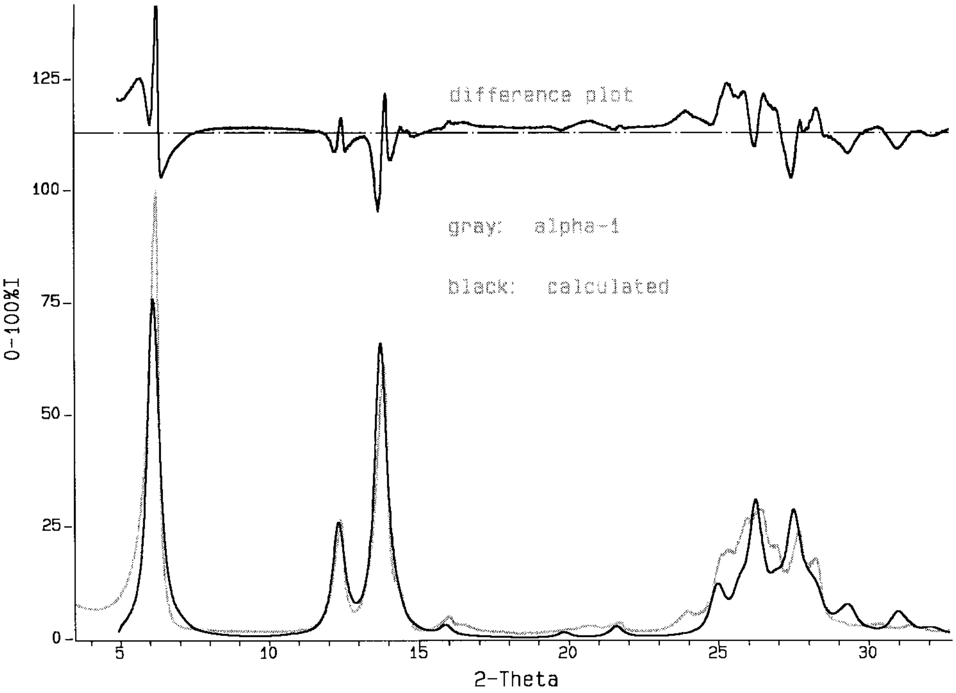

Fig. 12. Overlay and difference plot of experimental and calculated alpha-quinacridone.

determined for each position and the reflection intensities and the R value calculated. The procedure was very similar to that described in Section 2.6.2 [see also Eq. (1)]. Details are given in [49], which also shows the result of the minimization and the ensuing lattice proposal (see Figs. 4–6 in [49]). The alpha-quinacridone studied there still showed certain differences between the calculated and measured diagrams (Fig. 12).

2.8.2. Lattice defects

It is imaginable, therefore, that still further structures (phases) could play a role in the case of alpha-quinacridone, e.g. those of the "herringbone", "step", or "zigzag" type. This leads to a field which is closely connected with that of alpha-quinacridone, namely that of lattice defects.

On taking a closer look at Fig. 12, it becomes apparent that there are certain differences between the calculated diagram and that actually measured. These could be caused by defects in the crystal, for example by twinning by reflection or rotation [18]. Fig. 13 shows the herringbone and zigzag structures made up from building blocks (obtained from the Modellbaustein-Spiele GmbH, D-07407 Rudolstadt, Thueringen, Germany). Fig. 14 shows a simplified step-like lattice of beta-quinacridone (type 1) and Fig. 15 the criss-cross lattice of gamma- /alpha-quinacridone (type 2) which were discussed earlier. This is not limited to just the criss-cross and step phases, as it can also contain herringbone and zigzag phases without prejudicing the building principle of the F-face.

The scientist tends to think in terms of single crystals. The quinacridone pigments, however, are more closely related to partially crystalline colloids than to single crystals, and this is presumably valid for all industrial pigments. In the case of the quinacridones this is applicable firstly due to the particle size (0.1–0.6 μm), and secondly because of the ease with which the molecules within the stacks can slide over one another due to the influence of the H-bonds. In many cases these effects can be retained after the finishing process has been applied. It is much more probable that amorphous regions are thus formed, e.g. by the translation of twin boundaries due to the application of mechanical force.

3. Conclusions

A further piece of work on the quinacridones was concerned with gathering together all known structures of types 1 and 2, and classifying them according to their hue. Emphasis was placed in particular on the cooperative interaction between the π…π and σ electrons within the F-face [50].

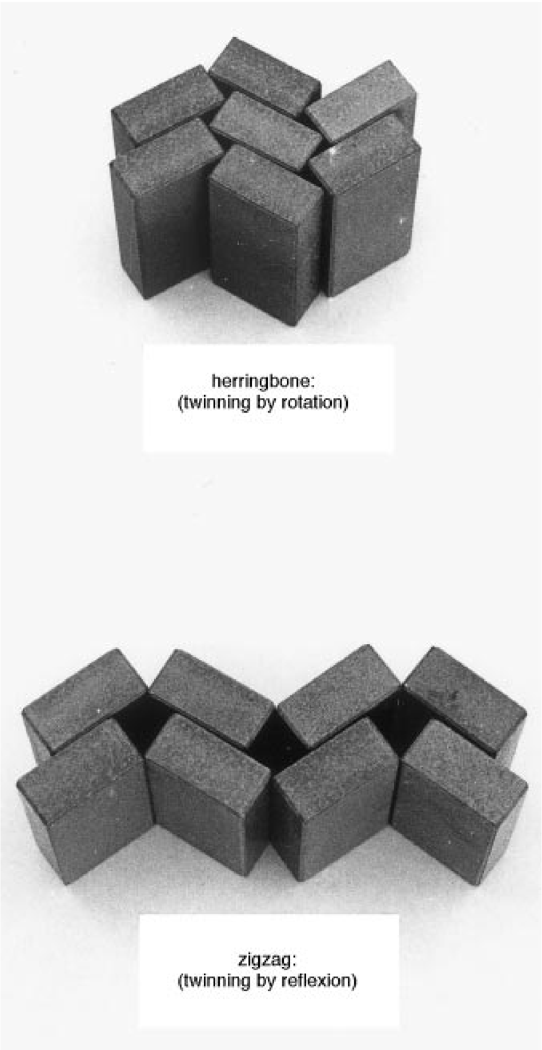

Fig. 13. Idealized models of herringbone and zigzag structures of quinacridone. Both structures are formed by symmetry operations, both are possible with double-tilted pieces and they fit together.

It is apparent that in the quinacridone lattice all the molecules are stacked, and the stacks themselves connected via H-bonds. The stacks and the H-bonds together form the F-faces. For this reason the projection of the different quinacridone molecules should — at least initially — be represented by their best plane (see Figs. 11, 16–18). Beta-quinacridone is shown in Fig. 11. The molecules are only displaced on the short "C" axis (transverse offset), whereby the π electrons of adjacent molecules lie directly above one another. At the same time, the NH and CO groups form intermolecular H-bonds of almost 180°. This is a quite different situation to that found in 4,11-dichloroquinacridone (Fig. 16). Here the molecules are only displaced along the long molecular axis "A" (longitudinal offset). This is achieved exclusively by the formation of a criss-cross angle of 2×62.5°. As regards their molecular offsets, gamma- and alpha-quinacridone lie between beta- and 4.11-dichloroquinacridone (see Figs. 17 and 18). It is conspicuous in Fig. 18 that the C atoms of the second molecule lie exactly in the middle of the C skeleton of the benzene ring of the previous molecule. They are said to lie in the dimples, i.e. alpha-quinacridone is a typical example of close-packing. The vector offsets of the second molecule with respect to the first are summarized in Table 3.

The prime concern is not so much the crystal structure of each individual quinacridone, but rather their classification in relation to all the others, with particular regard to the change in the

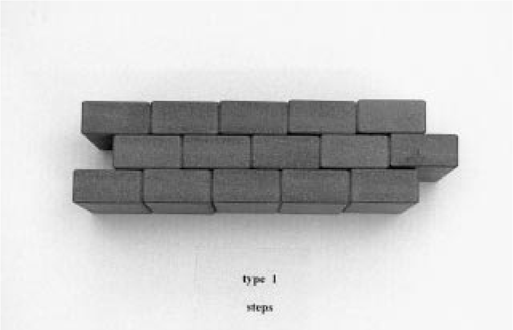

Fig. 14. Idealized lattice (model) of beta-quinacridone. Clinographic projection of the F-face. Lattice type: 1.

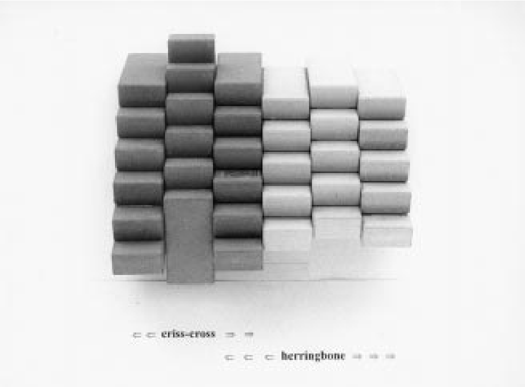

Fig. 15. Left hand (dark grey): idealized criss-cross structure of gamma-quinacridone. Lattice type: 2. Right hand (light grey): herringbone connected with criss-cross. Both structures indicate the same tilt τ_c, both go over to each other.

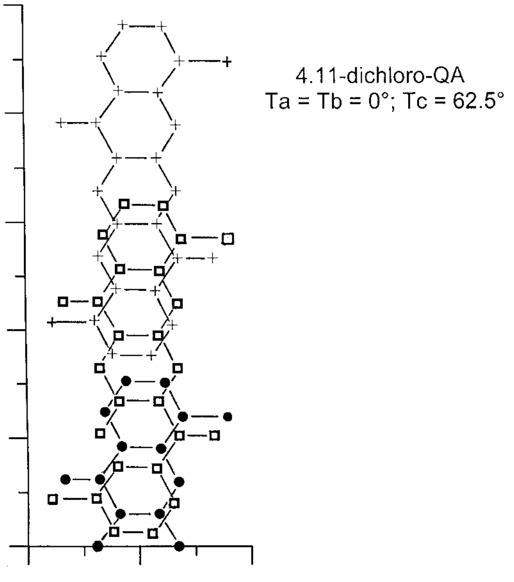

Fig. 16. Projection of three molecules on the least-squares plane in one stack of 4,11-dichloroquinacridone.

structure of the F-face. The tilt angle τ_c is of central importance in these considerations. The hue and the lattice characteristics were, therefore, compiled in [50], and because of their importance they are listed again in Table 4.

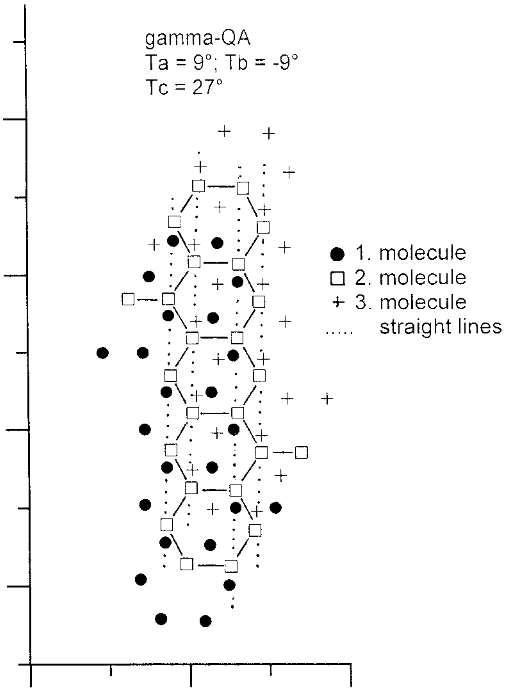

Fig. 17. Projection of three molecules on the least-squares plane in one stack of gamma-quinacridone.

4. Quinacridones and crystal engineering

4.1. General and special (pigments)

Crystal engineering is a modern expression for "... the understanding of intermolecular interactions in the context of crystal packing and in the utilisation of such understanding in the design of new solids with desired physical and chemical properties" (Desiraju, Ref. 51). There are some early examples of applied "crystal engineering" to be found in chemistry, e.g. wool, hair [15], perlon, nylon, kevlar, isotactic polypropylene, or the wide field of the biomesogens [52]. This latter paper in particular seems to have been quite unjustifiably the subject of only little regard.

In the field of pigments it is true to say that phthalocyanine blue, with its typical pigment finish, was an example of crystal engineering with industrial application dating back to 1935.

The small number of vat pigments, such as indanthrene blue and tetrachlorothioindigo, were also conditioned in the 1950s, i.e. they were tailor-made in

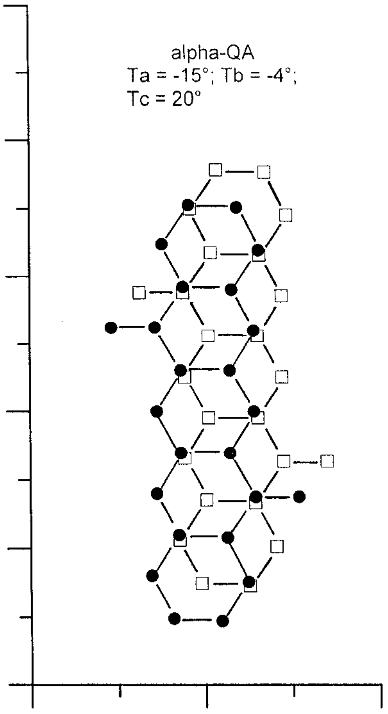

Fig. 18. Projection of three molecules on the least-squares plane in one stack of alpha-quinacridone.

Table 3
Displacement of the second molecule within the stacks of four quinacridones. Reference substance is the C-skeleton of benzene: length (0.28 nm) and width (0.24 nm)

Quinacridone	The second molecule is displaced in the direction of molecular axis A by the amount of (1 = 0.24 nm)	B (1 = 0.28 nm)	Hue
4.11-Dichloro	2.75	0	Scarlet
Gamma	0.70	0.28	Purple
Alpha	0.42	0.29	Purple (faint bluish)
Beta	0	0.84	Red violet

terms of particle size, distribution and shape. A short time later new pigment syntheses, such as those of the cromophtals [53,54], benzimidazolones [55,56], tetrachloroisoindolinones [7], the present group of the quinacridones, and the diketopyrrolopyrroles [57–60] became possible. Only little attention is paid to the subsequent pigment finish (conditioning) in the generally accessible literature, but it is an example of "crystal engineering" with relevance to practical application.

The pigment industry with all its difficulties in regard to tinting strength, hue and dispersibility blossomed, and indeed continues to blossom.

Quinacridone pigments, with their subtly built stacks and F-faces are extreme examples of crystal engineering. When quinacridones are edge-milled, their crystal structure is altered dramatically under the influence of shear forces and they lose the hue that was installed in the production process. This is of course highly undesirable. For this reason the pigment producer also has to take over this task: ready dispersibility as attained by the finishing process is made available and delivered to the user. The question as to the crystal structure and modification is thus very much in the foreground and particularly important in the case of the quinacridone pigments.

Before crystal engineering was recognized as an independent field in its own right and then systematically studied and developed, it had already been the subject of practically oriented specialists in a variety of industrial branches for decades. In this sense pigments represent a special field which was not especially recognized by chemists and engineers in the dye and textile industries. Even today, the chemist generally thinks in terms of individual molecules and indeed enjoys great success with dyes and other substances. Crystals belong in the field of mineralogy, or perhaps to the metals and building materials. This was the reason why pigments had such a difficult time in establishing themselves as an independent field.

Papers on crystal engineering started to become of interest around 1985, initially with statistical studies on $N{-}H\ldots O{=}C$ groups in crystals [61,62], then with resonance considerations on the intermolecular H-bond by Gilli et al. [63–65], and finally with the summarizing portrayals of Desiraju [51,66], Lehn [67], and Aakeröy [68,69] amongst others. Aakeröy made the statement "Since the early days of structural and solid-state chemistry, many chemists have (sometimes unbeknown to themselves!) been working in the field of crystal engineering". Science finally began to elaborate this fast-growing field in a systematic and fundamental manner around 1971, thus opening it to other applications. This process is by no means complete, but our researches demonstrates ultimately the relationship between "crystal engineering" and the pigment sector, thanks to indications that Desiraju made on papers written both by Gilli [63–65] and by himself [51,70]. As of this point it became important to take this new direction into consideration.

Desiraju's explanations on the 4-Å structures (0.4 nm structures in SI units) and their distinct separation from other structures are particularly impressive: "However, the presence of hetero atoms in a planar molecule enables a large number of such molecules to adopt this structure type" ([51] p. 160) and "Thus a large number of fused-ring quinones crystallise in this structure even though the parent hydrocarbons do not. Typical examples are pyranthron, violanthron and isoviolanthron" [51, p. 162].

Reference to the paper written by Krishnamohan et al., in which the interaction of π–π charge transfer with H-bonds in the crystal lattice were studied [71], was made by Desiraju [70]. The π–σ correlation is also referred to in this paper, albeit with other words: "The assumption of charge transfer through hydrogen bonding involves a new perception in studies of hydrogen bonding and $\pi \ldots \pi$ interactions", and "hydrogen bonds can act as channels for charge transfer" and "stacking interactions influence the nature of hydrogen bonding and vice versa". There was of course no reference made to organic pigments, nor to any of my previous works. Krishnamohan's paper [71] is perhaps the one most closely related to the fundamental theoretical idea of the π–σ correlation. The significant difference is that in quinacridone molecules both the donator (NH) and acceptor (CO) are united in a single molecule, whereas in [71] two different molecule types are referred to: donators and acceptors. When donators and acceptors are united within a single molecule through extended π electrons (as in quinacridone for example), it is then referred to as a chromophore. The transition to a pigment dye and to industry was thus complete. These represent their own synthon within the context of crystal engineering [66].

In the words of Aakeröy, pigment researchers were applying crystal engineering "unbeknown to themselves". One might add that crystal engineering has developed over a period of decades under the ever increasing pressure of quality improvement. If we also take the inorganic pigments into consideration, the first documented preparation of pigments becomes lost in the beginnings of the production of Chinese inks and the first paintings in the caves of prehistoric times (Altamira, Lascaux and others).

Substance purity has been an important concept for chemistry to date, and its pendant in crystal engineering is phase purity, not just in theory, but also in practice. This is in effect the search for new modifications, which has become of such importance in patent specifications.

Regardless of the scientific development and character of crystal engineering, the author of this article has taken the liberty of addressing the various questions at hand by drawing parallels to, and using examples from quinacridone pigments. The phenomenon of the interaction between intermolecular H-bonds and extended π electrons in mesomeric dye molecules has been described in this respect. The π–σ correlation effect was also mentioned, which in my opinion is responsible for the stability and the light absorption properties of the quinacridone pigments. It is quite possibly also effective in other pigments with intermolecular H-bridges.

> There have been some heroic attempts and a few minor advances, but rationalisation of crystal structure–hydrogen bonding patterns is still at the foot of the rainbow. [Cited from G.R. Desiraju ([51], p.115).]

4.2. A misleading conception

> Student to teacher: "I have a stupid question!"
>
> Teacher to student: "There are no stupid questions, just stupid answers. Go ahead and ask!"
>
> Student: "Why are there no coloured carbon blacks?"

Table 4
Structure and hue of quinacridones

Quinacridone	Criss-cross angle (°)	Type	Hue	Shift	Manufacturer
4.11-Dichloro	62.5	2	Scarlet	⇓	Ciba
Gamma$_\mathrm{I}$	28.4	2	Reddish-purple (Y)	⇓	Clariant, Ciba, Bayer
Gamma$_\mathrm{II}$	26.0	2	Reddish-purple (B)	⇓	Clariant, Ciba, Bayer
Alpha	20.0	2	Bluish purple	Bathochromic	Bayer, Sun
2.9-Dimethyl	0, but steps of 8°	1	Purplish-blue	⇓	Clariant, Bayer, Ciba
2.9-Dichloro	0, but steps of 4°	1	Purplish-blue	⇓	Sun
Beta	0, but stpes of 2°	1	Red-violet	⇓	Clariant, Ciba, Bayer, Sun

Answer: it depends on one's point of view, whether or not they exist. Even within the smallest graphite layer (002), the absorption of visible light is total or almost total. The architectural principle of this graphite layer thus always dictates complete absorption of light in the visible region.

Imagine now a graphite layer, however. Take some elongated molecules, and place these perpendicular (end-over) to the layer, each in the middle of the benzene rings. Now imagine the covalent aromatic C bonds to be removed and replace them with intermolecular $\pi\ldots\pi$ bonds and H-bonds. We now have coloured "carbon black" within the context of pigments. In the case of quinacridone, the graphite layer increases from 0.336 nm to 1.37–1.50 nm. The effective "resonance" within the molecular layer is drastically decreased with respect to graphite and leads to selective absorption of light and to decreased stability. Quinacridone takes up a leading position among the coloured organic pigments. It is an example of "molecule and architecture". The wide range of hues is synonymous with the question as to the fine structure of the flat-face i.e. just how the flat-faces are formed by the molecules.

Industry's pragmatic way of thinking created an excellent group of crimson pigments out of the quinacridones, and they were successfully marketed throughout the world.

5. Epilogue

An important point remains to be made here. Mathematicians and physicists differentiate between "sufficient" and "necessary" evidence. The evidential value of a good single crystal analysis is "sufficient", i.e. the statement is verified. The high evidential value is substantiated by the measurement and evaluation of several thousand X-ray reflections. The evidential value of a model is only "necessary", i.e. the individual parts are related to each other and to the whole in a reasonable manner. Every unknown, disregarded, or later-discovered fact can put the model in doubt, however. The advantage of working with models is that new facts are found constantly. This requires interdisciplinary thought, or the ability to look beyond one's own horizons. It is this constant procedure of "trial and error" which leads to new results. When working with models, one is never finished, simply because it only provides "necessary" evidence. The more individual facts can be taken into consideration, however, the more convincing the evidential value becomes.

It can also be said that working with models of crystal lattices is not a typical method used by industrial research and development departments. These tend to be directed at making the fastest possible decisions, because R&D is subject to certain constraints involving time, money, and personnel. Work on and with models is always a question of realisation. It is full of pitfalls and errors and demands a great deal of patience.

> In English and German "knowledge" means "certain" knowledge. But there is no such thing. What we have at best is conjectural knowledge: that is all we can have. Our best knowledge, by far our best, is scientific

> knowledge. Yet scientific knowledge too, is only conjectural knowledge. (Karl R. Popper from *Alles Leben ist Problemlösen*.)

6. Concluding remarks

The golden lustre of large quinacridone crystals immediately conjures thoughts of electrical conductivity. The bonding theory for solids, i.e. the band theory, states when applied to quinacridones, the σ electrons of the H-atoms in the H-bonds have a similar energy to the free π electrons of the planar heterocyclic quinacridone molecules. Both energies probably overlap, thus creating a semiconductor with a valence band and a conductance band in the crystal. The size of the energy gap between the two is determined by the orientation (position) of the π electrons in the adjacent stacks of molecules. If these are parallel (crystal type 1), then the gap is small. If they form a criss-cross angle (crystal type 2), then the gap will be larger.

In order that the organic semiconductor has pigment properties its crystal lattice has to be finished, i.e. the size of the coherent crystal regions for the X-rays have to be adjusted to the wavelength of visible light (i.e. reduced). The size of the coherent scattering crystal regions can be calculated from the Scherrer equation used in X-ray diffraction: $\mathbf{D} = K\lambda/\beta\cos\theta$ ($\mathbf{D}$ = particle size; β = line breadth; λ = wavelength; K = shape factor; θ = Bragg angle). Calculations made on powder diagrams show that for quinacridones the size varies between 50 and 70 nm (500–700 Å).

Due to the particle size reduction, the valence band becomes the HOMO and the conductance band the LUMO in the context of Hückel's molecular orbital theory. The particle size reduction and adjustment during finishing bears a certain resemblance to the transition of graphite (metallic conductor or semiconductor) to carbon black (pigment). The particle size reduction from graphite to carbon black is not attained in practice by milling, however, but rather by the combustion of, for example, anthracene oil (pyrolysis). In terms of solid-state chemistry, it is, however, a drastic reduction of the particle size which leads to the pigment properties of carbon black.

The band theory makes the connection between the light absorption properties and the particle size of quinacridone pigments. As such, the π–σ correlation is nothing other than the influencing of the energy gap in the energy diagram of the organic quinacridone semiconductors, and the influence of the energy diagram on the optical properties in the visible region. One can also say that the gap in the semiconductor quinacridone is the description made by solid-state physics of the π–σ correlation conceived by solid-state chemistry.

The first publication on HOMO–LUMO calculations made on pigments was written by Kazmaier and Hoffmann and dealt with perylenes [72]. These flat molecules are arranged along infinite π...π-stacks, so the problem was therefore a one-dimensional one (oscillating string). Quinacridones lattices, however, form infinite π...π-stacks and infinite chains of H-bonds and thus require rather complex two-dimensional HOMO–LUMO calculations (oscillating drumskin). These have not been carried out as yet.

Questions do remain to be answered of course, but it is up to the following generation to take an interest in addressing them.

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