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On quinacridones and their supramolecular mesomerism within the crystal lattice☆

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Abstract

After making a comparison between inorganic pigments and quinacridone, several experimental results ensuing from 30 years of research are presented. Following this, the bridging hydrogen bond and crystal engineering are treated with some definitions, the pigment finishing is touched upon and the $\pi\ldots\sigma$ correlation is introduced. This is regarded as mesomerism between two non-covalent bond types, namely charge transfer and H bonds. It is compared with the lattice of the carbon blacks and thus used to explain the excellent stability of the quinacridones. In conclusion, Desiraju's supramolecular synthons serve in the interpretation of the somewhat abstract $\pi\ldots\sigma$ correlation. Quinacridone crystals are made up solely of $\pi\ldots\pi$ charge transfer bonds and bridging hydrogen bonds i.e. they contain both of these non-covalent bonding types in compact form. This means that each and every quinacridone molecule is in itself a source of supramolecular mesomerism which encompasses the entire crystal lattice. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Quinacridone pigments; H-bonds; $\pi\ldots\pi$ Charge transfer; Supramolecular synthons; Mesomerism within the lattice

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1. From inorganic pigments to quinacridone

Inorganic pigments such as chromium oxide, iron oxide, titanium oxide or carbon black are high performance pigments: insoluble, stable, and capable of absorbing and reflecting visible light. They also combine hiding power with colour strength (tinting strength) and are therefore of value to the pigment industry.

The crystal structures of the four key compounds mentioned above are well known. Their optical behaviour as pigments is well described by the Mie theory, e.g. Völz [1]. According to this, they absorb as entire entities in the form of dipoles or multipoles. Titanium dioxide is not a "white" single molecule, nor is carbon black a "black" C atom. The lattice of titanium dioxide consists of sphere-like [TiO_6] octahedra and carbon black is made up of a trigonal pattern of C atoms arranged on the tips of a set of planar, regular hexagons, as shown in Fig. 1. The well-known plane of graphite can be considered as being the mother substance of carbon black. This consideration in itself points towards lattices and not individual molecules. The pigment chemist has in effect little to do with dyestuffs, but plenty to do with crystals.

Quinacridones have been the subject of investigation in Krefeld since 1969. Unlike inorganic

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compounds, quinacridone molecules are extremely anisotropic, each one being a rigid, planar building block. In contrast to inorganic pigments, quinacridones form recognisable individual molecules. We know today that the molecules are connected via bridging hydrogen bonds and $\pi\ldots\pi$ charge transfer bonds. To put this in a modern way of speaking: quinacridone molecules recognise themselves in the lattice. There are more similarities between quinacridone and inorganic pigments with regard to the properties of crystal structure, insolubility, and stability than there are with organic dyes (each molecule is soluble in water, or can be made water-soluble for dyeing). It should be said at this point, however, that insolubility and stability to temperature and solvents are fundamental chemical properties. Many thousand applications under practice conditions have proven this to be the case and these are unrelenting controls.

Do quinacridone pigments absorb and scatter light as complete particles? This question leads to still further questions regarding the properties of the quinacridone crystals.

2. Some experiments on quinacridones

There is little point in speculating, it is better to carry out some experiments. Some results—that have been obtained over a period of many years—are presented here.

2.1. 2,9-Dichloroquinacridone

It proved possible to grow crystals (twins) that could be readily inspected with an ordinary microscope (see Fig. 2). The twinning plane is easily identified. Fig. 2 is an original photo from 1971. The question we posed ourselves was what is the position of the molecules in the twin? A model with rigid, planar building blocks made up the starting point (Fig. 3). Fig. 4 shows the planar molecule and the numbering system. We know today that this form is indeed correct, but from 1969 to 1971, and even somewhat later, it was just speculation. The centre of inversion in the middle of the third hexagonal ring is important. The molecules arrange themselves making use of bridging hydrogen bonds and $\pi\ldots\pi$ bonds. Both types of bond have to be *within* the crystal sheet (slice), whereas van der Waals bonds (note the 2,3,9,10 positions ≅ hydrophobic, Fig. 4) have to be *outside* the sheet (slice). These sheets (slices) are only connected by van der Waals forces and they are parallel to the crystal plates. This view is rather apparent,

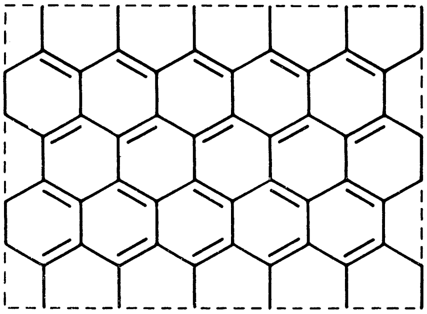

Fig. 1. Layer of graphite (002).

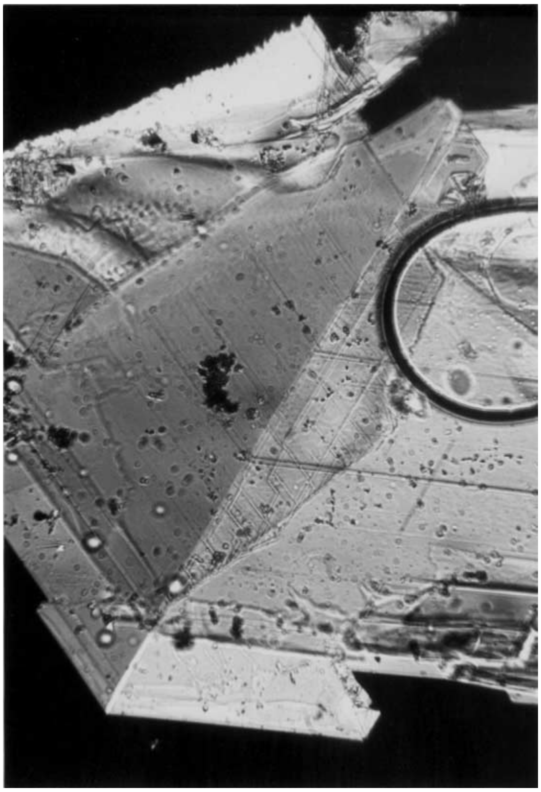

Fig. 2. Microscopic view of a twin of 2.9-dichloroquinacridone.

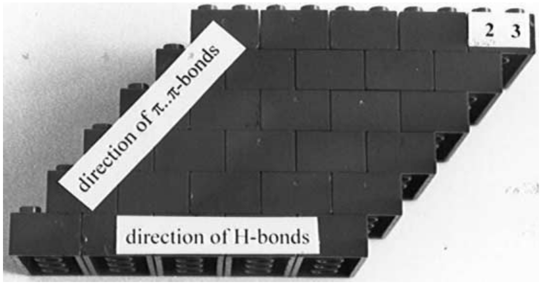

Fig. 3. Reproduction of "bricks in a brick wall" by Lego®.

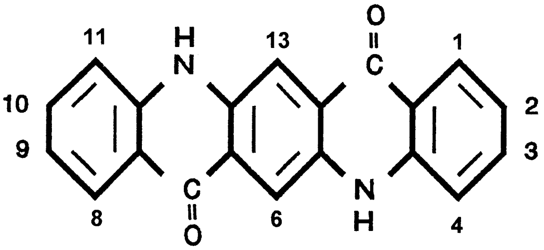

Fig. 4. Planar molecule and numbering system.

being based on the minimisation of energy (Fig. 3). The 2,3- positions point outwards and are readily recognised. The crystal is thus of the type "bricks in a brick wall". This type is very modern and is also found elsewhere Paulus et al. [2], Mizuguchi et al. [3], Mizuguchi [4].

Kitaigorodskii's fundamental law was taken into account in Fig. 3: "A crystal of an organic compound can be considered as a system of very closely packed layers... This rule should be considered as a generalisation from all existing experimental data; it can with complete justice be taken as the fundamental law of organic chemical crystallography", Kitaigorodskii [5].

If the left part of the Lego® crystal is held firmly and the right part is hit in an upward movement, the "molecules" would then slide on their planes one over the other, without cleavage of the bridging hydrogen bonds. The twin is thus complete (Fig. 5). The model represents the twin, and in particular the twinning plane. Mechanical twin formation was often observed, but in spite of this, it is neither an unequivocal proof of the planar form, nor of the rigidity of the individual molecule, nor of the arrangement of the hydrogen bonds or π...π bonds in the crystal. Nevertheless, it is possible to explain the twin shown in Fig. 1, Lincke [6], Lincke [7]. The trail of evidence is perhaps somewhat weak, but it does make up a part of the puzzle.

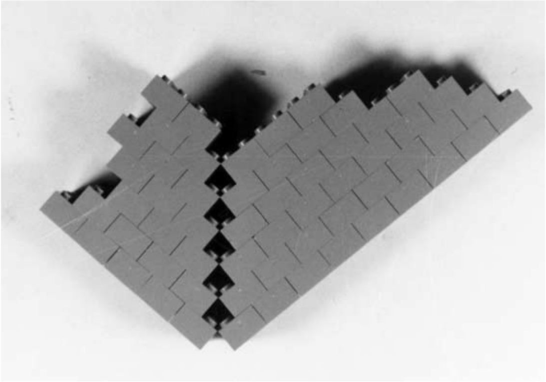

Fig. 5. Reproduction of twins of 2.9-dichloroquinacridones by Lego®-blocks.

2.2. 2,9-Dimethylquinacridone

The crystal structure is based on many diffraction experiments and calculations. The unit cell of the real crystal was determined by X-ray diffraction, Lincke [8], and by calculation of close dense packing, Lincke and Moebes [9]. Table 1 shows a comparison of the lattice parameters obtained from model with those from the exact solution, 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" [8] and Paulus et al. [2]. The morphological behaviour was interpreted, compared with smectic crystals (liquid crystals), experiments with rotating-crystal and Weissenberg methods were carried out and close-packing structures were calculated (minimum repulsive lattice energy considerations [10][1]). A structure was then proposed for 2,9-dimethylquinacridone. Therefore, considerably more facts went into this proposal than was the case for 2,9-dichloroquinacridone, see Lincke [8,9] too. The molecules are tilted towards (001) (Fig. 6). This crystal face incorporates all the 2,3,9,10-positions, i.e. the van der Waals bonds. The rigid planar

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[1] Energy repulsion minimizations are not unambiguous.

Table 1
Lattice parameter of 2.9-dimethylquinacridone

Parameter	Lincke [9,10] [Ang.]/deg.	Paulus et al. [2] [Ang.]/deg.
a	3.89 (2)	3.901 (1)
b	6.45 (3)	6.407 (1)
c	16.08 (6)	15.817 (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
ρrö	1.42	1.459

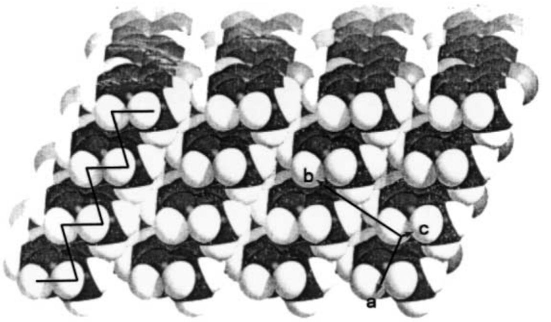


Fig. 6. Crystal structure of 2.9-dimethylquinacridone. View on (001).

molecules lie close to the (−112) face. As a result, Fig. 6 shows molecules from neighbouring stacks (piles) in this plane without showing the steps. A staircase is drawn from bottom left to top right and indicates the lateral displacement of the molecules within a stack. We know today the exact structure as determined by Paulus, Hoechst, from which the step-like arrangement of the molecules in (−112) follows (height of the steps between neigbouring stacks 0.876 Ang.) Paulus et al. [2]. The publications Lincke [8] and Lincke and Moebes [9] were close to the truth (height of the steps between neighbouring stacks 0.0 Ang.), and one could say, to make use of a German hunting expression, that they were like "shooting an 11" i.e. they only missed hitting the target by the narrowest of margins. The structure is indeed one of the typical "bricks in a brick wall" type. For more details see also Lincke [7] and beta-quinacridone, Section 2.5 of this publication.

Important results:

1. all molecules are planar,
2. all molecules are connected throughout the entire lattice by means of infinite $\pi\ldots\pi$ stacks and
3. infinite bridging hydrogen bonds,
4. the molecules of neighbouring stacks are almost coplanar, but do form small steps, however.

This type of structure was named 'type 1' by Paulus [2].

2.3. 4,11-Dichloroquinacridone

Single crystals were sent to E. Paulus, Hoechst. The structure is shown in Fig. 7, [2].

Important results:

1. all molecules are planar,
2. all molecules are connected throughout the entire lattice by means of infinite $\pi\ldots\pi$ stacks and
3. infinite bridging hydrogen bonds,
4. the angle between neighbouring stacks is 125.1°, twisted in opposing directions,
5. the points of intersection of the molecules in Fig. 7 are formed by the bridging hydrogen bonds (direction of view). The molecules form a longitudinal displacement within a particular stack (see also Fig. 8a). Paulus called this structure 'type 2', [2,7, 11]

2.4. Gamma-quinacridone

The single crystals obtained were of sufficient quality for a structural determination by Paulus [2]. The structure is similar to that of 4,11-dichloroquinacridone (Fig. 9), but the angle between two neighbouring stacks is only 59.1°, twisted in opposing directions (i.e. 'type 2'). The structure is also referred to as a criss-cross structure. Neighbouring molecules within a particular stack form a

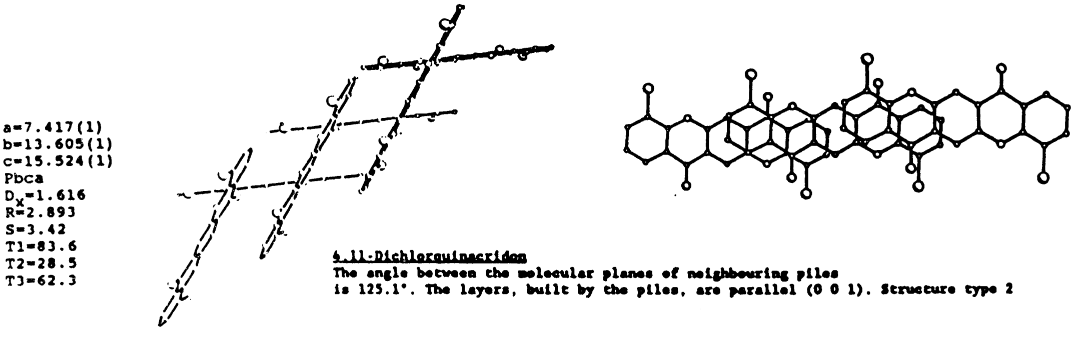


Fig. 7. Crystal structure of 4.11-dichloroquinacridone. Criss-cross angle 125.1° [2].

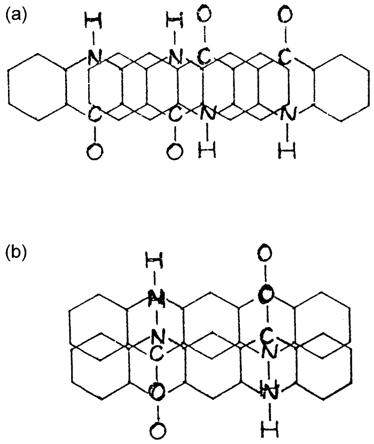


Fig. 8. Longitudinal (a) and lateral (b) displacement.

combined longitudinal and lateral displacement (Fig. 8b). More details can be found in [2,7].

2.5. Beta-quinacridone

Extremely laminar crystals were obtained which made up a typical chequered pattern (Fig. 10). When several of these were placed in layers on top of one another on a glass plate, they produced 12th order reflections of the type (00L) in a conventional X-ray powder diffraction experiment. Moebes and Lincke performed a one-dimensional Fourier synthesis [12]. Following the information from Fig. 11, it can be inferred that all the molecules in the crystal are aligned along their lengths. All atoms (positions and scattering power) show the correct electron density (see maxima and minima). Further observations on crystals of beta-quinacridone indicate molecular stacks perpendicular (along the lengths) to the van der Waals surfaces (001). For details see Lincke [7, pp. 110–112].

A short time thereafter, single crystals of beta-quinacridone became available and the three-dimensional structure (Fourier synthesis) was analysed by E. Paulus, Hoechst, Fig. 12 and Paulus et al. [2].

Important results:

1. all the molecules are flat,
2. all molecules are connected within a plane and form small steps,
3. all molecules lie “along their lengths”,
4. the molecules additionally form stacks with lateral displacements.
5. the molecules are thus stacked above each other in a stair-like fashion, whereby each molecule lies on a diagonal with respect to a/b. Fig. 13 shows a tilted view of the van der Waals surface (001).

2.6. Alpha-quinacridone

This molecule displays a defect structure. As the colour shades of gamma- and alpha-quinacridone are very similar, it was deduced that the crystal structure of alpha-quinacridone is a criss-cross one, based on rigid, planar individual molecules and energy minimisation. Alpha-quinacridone is thus a variation of gamma-quinacridone, [7,13].

Section 2 reflects only a small part of the experiments performed over a 30 year period of research.

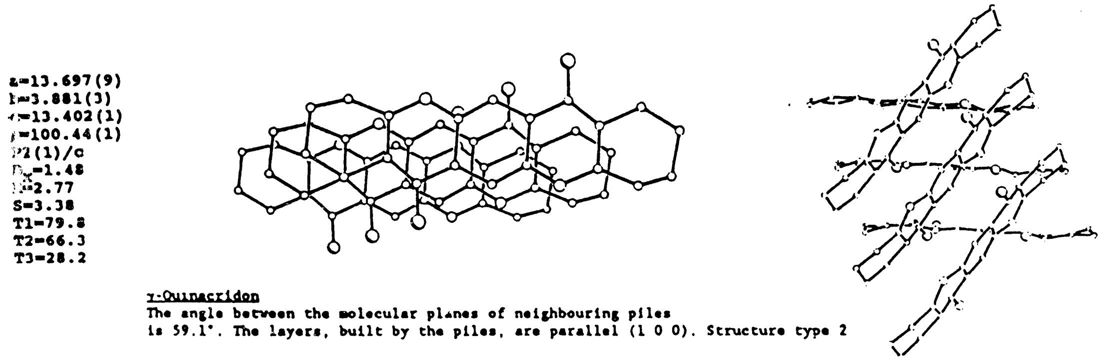


Fig. 9. Crystal structure of gamma-quinacridone. Criss-cross angle 59.1° [2].

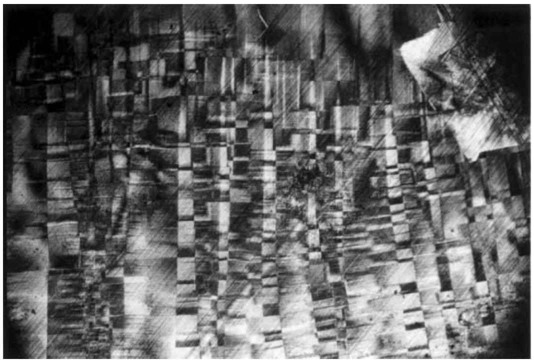


Fig. 10. Chequered lamellar crystals of beta-quinacridone.

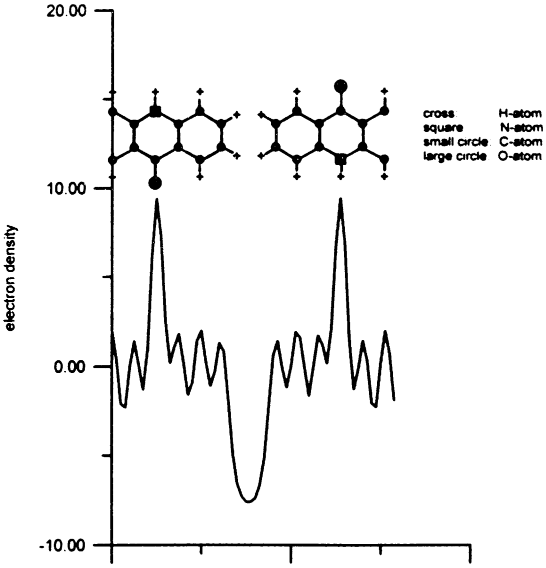


Fig. 11. One-dimensional Fourier-synthesis of beta-quinacridone.

3. Strong bridging hydrogen bonds and crystal engineering

Likely bridging hydrogen bonds play the role of the great unknown in a crystal lattice. Crystal engineering became a distinct field of research after it incorporated hydrogen bonding. The opinion of several researches should be aired at this point: "Recognising that the value of the hydrogen bond concept lies in the wilderness of idea and not in the wall of words" or "ideas of what constitutes a hydrogen bond are in a constant state of flux", "…the strong hydrogen bonds are the most interesting and intriguing category of hydrogen bonds…", Aakeröy and Seddon [14] "…the hesitating proton is a characteristic of strong hydrogen bonds", Jeffrey [15], "…the hydrogen bond in general can be regarded as the incipient state of a proton transfer process… however, only for strong hydrogen bonds do such proton transfer processes occur with significant rates", Desiraju and Steiner [16].

What about hydrogen bonds that are formed from heterocyclic, rigid, planar molecules like quinacridone (pigments)? That is the decisive question!

Here are two important experimental observations of industrial importance:

1. The Kitaigorodskii Principle (Law) states that: if a molecule contains a centre of inversion amongst its symmetry elements, it always keeps this in the crystal and loses the others.

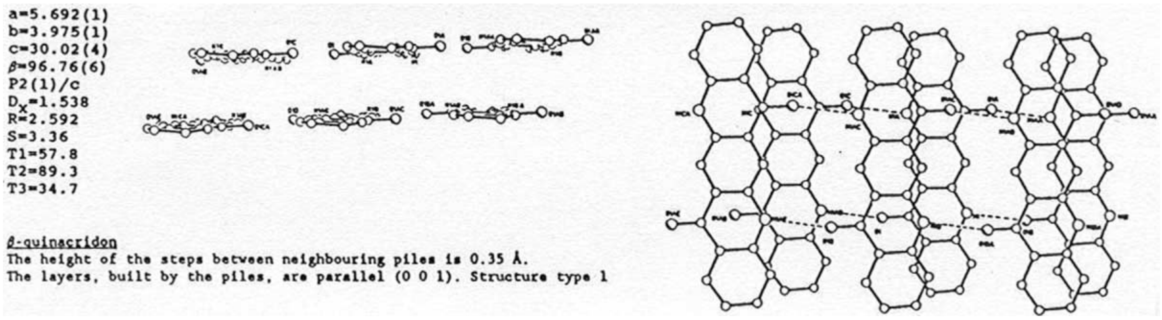


Fig. 12. Crystal structure of beta-quinacridone [2].

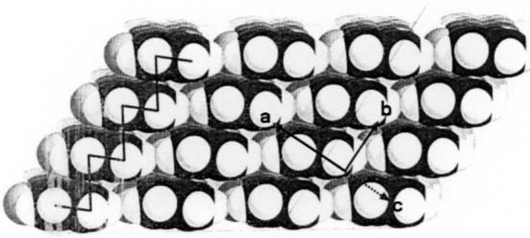


Fig. 13. Clinographic view on beta-quinacridone.

2. Let us take a look at the pigment finishing process. This is carried out on the crude product by means of mechanical shearing at higher temperature in the presence of solvent. The first patents on quinacridone pigments mentioned salt (NaCl), organic solvent and Cylpebs (steel rods $\frac{1}{2}$" × 1"), which were placed in a ball mill. The rigid, planar molecules thus slide over one another and formed more or less well-formed crystalline regions. The freedom of rotation leads to longitudinal and/or lateral displacements (Fig. 8a and b). At the same time, the geometry of the hydrogen bonds is altered, which act as connectors between the stacks.

In some quinacridone pigments the $\pi\ldots\pi$ and hydrogen bonds are inextricably connected with one another. The transformation from beta- to gamma-quinacridone and vice-versa necessarily requires the cleavage and re-formation of hydrogen bonds.

(1) and (2) are contributions to the interdisciplinary field of industrial crystal engineering.

4. $\pi\ldots\sigma$ Correlation—an hypothesis

"Much of what has been discussed in the preceding chapters would appear to be based on the hopeful assumption that a typical organic crystal my be visualised as a unique web woven from several types of intermolecular interactions." G.R. Desiraju, Crystal Engineering. The Design of Organic Solids, p. 285, Elsevier, 1989

What exactly is meant by this? If we were to consider the woven fabric linen, then this is made up through the so-called warp and weft threads, in short, warps and wefts. The woven fabric is held together by interweaving bonds i.e. through the intimate entwinement of the warps and wefts. We could say that this is a sort of "warp...weft correlation" and it is undoubtedly of mechanical nature.

Fig. 3 represents the transition to the QA crystal. The warp threads in our linen example correspond to the $\pi\ldots\pi$ stacks and the weft threads to the H-bridging bonds running through the lattice—the σ bonds. The two chemical bonding types meet up within each and every molecule. This in turn means that every molecule is involved in both a $\pi\ldots\pi$ bond (warp) and a σ bond (weft). This is a clear differentiation from the mechanical fabric. Instead of speaking clumsily of $\pi\ldots\pi$ stack/H bond (σ) interactions, we abbreviate this in calling the situation a $\pi\ldots\sigma$ correlation. A crystal sheet results which can be approximately compared with the woven fabric we call linen, but on a molecular dimension. There is admittedly a significant difference. The textile bonding in linen is of a mechanical nature, whereas the bonding in the crystal sheet is of chemical, physical, and crystallographic—i.e. of electronic nature. This is then taken into account by the expression "correlation', which may be regarded as a concession to the molecular chemical "sheet". These properties will now be dealt with.

In Section 3, the partial twists of the quinacridone molecules and their combined movement with stacks and hydrogen bonds were mentioned. Fig. 2 shows a twin in which the "wefts" on the twinning plane are bent and the "warps" are aligned in a mirror plane of symmetry to one another. The chemical-crystallographical viewpoint thus replaces that of the textile viewpoint. Changes in the geometry of the π stacks result in simultaneous changes in the geometry of the bonding of the hydrogen bridges—i.e. "warps" and "wefts" influence one another reciprocally. This is a purely geometrical and mechanical standpoint. But it is a $\pi \ldots \sigma$ correlation. At this point we now want to leave our comparison with the woven fabric. The range of gamma-quinacridone with respect to unit cell and hues is possibly due to this combined effect of the $\pi \ldots \pi$ and hydrogen bonds. The unit cells of single crystals of gamma-quinacridone—as determined by four independent laboratories—are connected by a straight line, (points 5,6,7,9, Fig. 14, see [17] for further literature). The parameters vary from lower to higher values along the body diagonal. This would also appear to be valid for all pigments, so there are apparently small systematic deviations present in the unit cells. This observation leads to the question as to how large deviations in the unit cell of a particular modification can be without resulting in polymorphism. It would seem appropriate at this point to mention the "forms" of the gamma-quinacridone, gamma$_{\mathrm{I}}$ and gamma$_{\mathrm{II}}$, which only differ slightly in the powder diffraction pattern and thus do not represent different modifications. They do play a technical role, however, and an investigation into the differences would be of interest within the sense of the publication [17].

There is a further chemical viewpoint, however. In a publication by Sharma et al. [18], acceptor/donor molecules are treated which form crystals from π...π stacks and intermolecular hydrogen bond bridges. The interested reader is expressly referred to this work. With respect to these crystals, Sharma writes "Stacking interactions influence the nature of hydrogen bonding and vice versa" and " Hydrogen bonds can act as channels (conduits) for charge transfer and may alter the polarization of atoms." For further statements see Sharma et al. [18]. These statements really do touch on the heart of the matter.

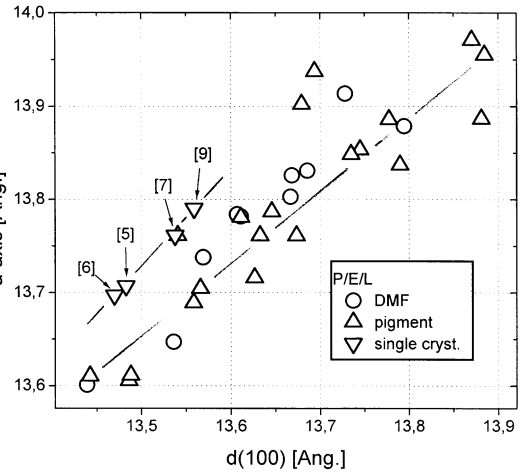
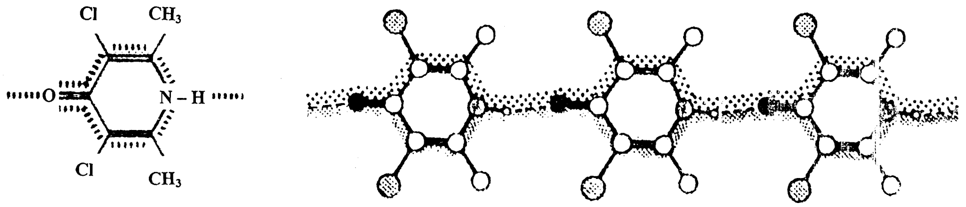


Fig. 14. Relationship between the innermost (100) peak and the *a*-axis as determined in the case of 21 industrial pigments (△), 10 DMF-treated pigments (○), and four single crystals (▽).

It is only fitting that the work of Gilli on resonance assisted hydrogen bonds (RAHB) also be mentioned at this point [19]. Some compounds with intermolecular N–H...O–H bridges form resonance structures: "...that all the shortest (or strongest) N–H π..π O intermolecular hydrogen bonds between neutral molecules are controlled and determined by a synergism of hydrogen bond strengthening and π delocalization enhancement called RAHB..." Bertolasi et al. [20]. Pyridinol is one example, Fig. 15. The authors call the intermolecular forces "a resonant chain". There is a series of compounds which follow this rule.

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?"



3.5-dichloro-
2.6-dimethyl-
4-pyridinol
(single molecule)

3 molecules forming a chain
(resonant chain is marked by
darker or lighter shading)

Fig. 15. Pyridinol, resonant chain.

Answer: It depends on one's point of view. The architecture of a graphite layer (Fig. 1) is associated with complete absorption of light. I suggest an experiment in thought: imagine now a graphite layer. Take some elongated quinacridone 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 (Fig. 13). In the case of quinacridone the graphite layer is extended from 3.36 to 15.0 Å. With regards to carbon black (stable up to 900 °C), the temperature stability of beta-quinacridone is considerably lower (420 °C). In this context—and this is my personal opinion—the effective "resonance" within the layers (001) is drastically lowered, but leads, however, to selective light absorption. It is in effect an example for "molecules, architecture and strategy".

Chemically speaking, the $\pi \ldots \sigma$ correlation is a resonance phenomenon (mesomerism) between two non-covalent bonds (H-bond and $\pi \ldots \pi$ charge transfer) within the crystal lattice. This could be the source of the excellent properties of the quinacridone pigments. For details see Lincke [7, pp. 118–119].

Mesomerism is a phenomenon of inorganic and organic chemistry. Stability (outstanding fastness) of quinacridones as a result of resonance (mesomerism). It looks like child-play, but in fact it was 30 years of hard work.

Chemists think in terms of chemical compounds and their analogies and relationships. These compounds are specially selected, then compared with CA and CSD data and evaluated. In this way still further properties (chemical behaviour) may be recognised. The logic of organic chemistry differs from that of physics and this can also be seen in the different experimentation techniques. Physicists tend to think in terms of potentials, energies, directions of transition moments etc. and study the degree of agreement between calculated values and the results of the physical experiment. The relationship between chemists and physicists is complementary, not contradictory. They resemble two different (separate) routes through the same mountain range which lead to the same goal. In favourable cases both routes meet at the same summit. The two routes touch on the question of reductionism [21].

5. Supramolecular synthons, mesomerism and quinacridones

The $\pi \ldots \sigma$ correlation mentioned in Section 4 has the disadvantage of being somewhat indistinct. Chemists are used to thinking in terms of structures. Pauling—the Nestor of chemical theory—said "The theory of resonance is a part of the chemical structure theory, which has an essentially empirical (inductive) basis; it is not a branch of quantum mechanics" and "The theory of resonance in chemistry is an essentially qualitative theory, which, like the classical structure theory, depends for its successful application largely upon a chemical feeling that is developed through practice", Pauling [22]. There are several more statements similar to these in this particular monograph. Confirming this, Griffith wrote "Dyes chemists rely mainly on intuition, an intuition borne of experiments and steeped in the ideas of Witt's theory and resonance theory", Griffith [23].

The autonomy of chemistry as a "pure" science is expressed in a remark made by Weygand, who said "Now (1955) the structures of the benzene ring and the methane molecule are being confirmed by quantum mechanics. But we've known them already for 80 years!", Weygand [24].

If structures are employed in the treatment of the mesomerism of individual molecules in chemistry, then it should come as no surprise when the treatment of the mesomerism of organic molecular lattices also makes use of structural elements. This is precisely what Desiraju did in his publication. Organic molecular lattices are regarded as equivalent entities to supramolecules and supramolecular synthons introduced. These are defined as follows[2], Desiraju [25]:

"Thus supramolecular synthons are structural units within supramolecules which can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions", "Supramolecular synthons are spatial arrangements of intermolecular interactions and play the same focusing role in supramolecular synthesis that conventional synthons do in molecular synthesis", "A supramolecular synthon is an identifiable design element and should be ... distinguished from an intermolecular interaction" and "Synthons are derived from designed combinations of interactions and are not identical to the interactions".

The tradition of organic structural chemistry is reflected in the concept of supramolecular synthons. They form the connecting bridge coming from the low-molecular organic chemistry to organic solid-state chemistry.

The succinct structure of the quinacridone lattice contains two non-covalent bonds which are connected in the narrowest of space. The extreme properties are inextricably connected with these two non-covalent bonds. Anyone who comes across quinacridone is automatically dealing with these bonds, whether it be as a scientist in fundamental research, or as an engineer or technician in the application.

The succinct structure of the individual molecule in the crystal lattice of quinacridone proves to be advantageous in the determination of the supramolecular synthons. The structure is that of the aryl...aryl synthon (No. 34 in Desiraju [25]), reinforced by two pyridone centres in the molecule, i.e. by heterocyclic components. These then lead to the H bridging synthon (No. 4 in Desiraju [25]). The situation in beta-quinacridone is shown in Figs. 16 and 17. Two similar synthons can also be identified in gamma-quinacridone (Figs. 18 and 19). It should be noted that the (chemical) supramolecular synthons are not identical to the (crystallographic) asymmetric units. It should not be forgotten that the determination of the supramolecular synthons is not unequivocal, Desiraju [25]. In Figs. 16 and 18 of this article, the regions between the horizontal dotted lines (see also the arrow on the right) are regarded as supramolecular H bridging synthons.

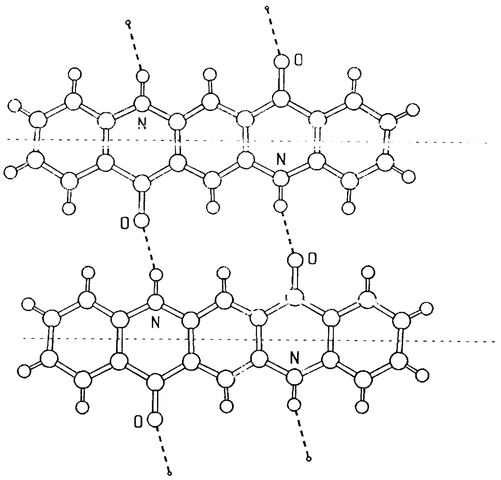


Fig. 16. Supramolecular H-bond synthon of beta-qa.

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[2] Because of their importance, they are cited as originally written.

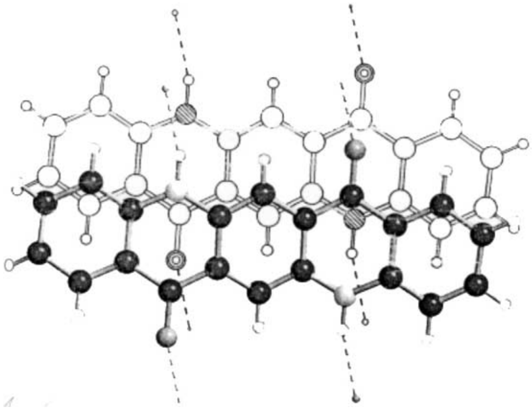

Fig. 17. Supramolecular aryl. . .aryl synthon of beta-qa.

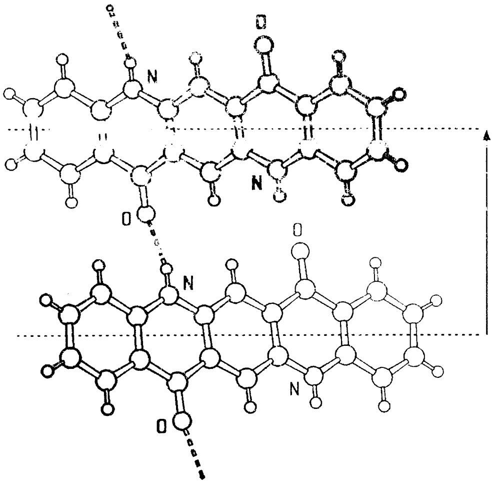

Fig. 18. Supramolecular H-bond synthon of gamma-qa.

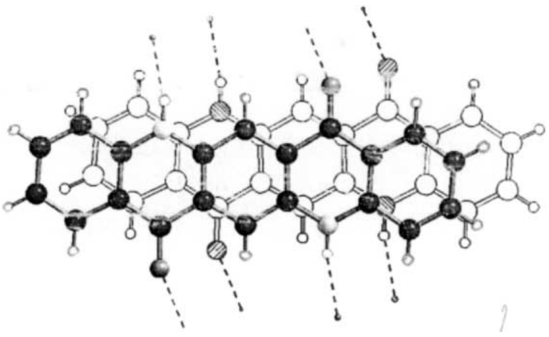

Fig. 19. Supramolecular aryl. . .aryl synthon of gamma-qa.

If the crystal lattices of beta- or gamma-quinacridone are also taken into account, then one can say that "Every quinacridone molecule is capable of forming two different supramolecular synthons. Every supramolecular synthon is capable of mesomerism with the other within the entire crystal grain. They may also be considered as limiting structures. "A pair of supramolecular synthons make up one whole" and "Quinacridones consist of supramolecular synthons". This is the same as saying: "Every quinacridone molecule in the lattice is part of the two (different) supramolecular synthons" or "In the lattice there is mesomerism between the two (different) supramolecular synthons" and "It is only possible to distinguish between covalent and non-covalent bonds in a quinacridone lattice by means of formal criteria".

This is the connection between the concept of supramolecular synthons and the (lattice) properties of the quinacridones, and represents at the same time the core statement of this publication. Fig. 20 shows a compilation.

The top third shows the general knowledge status (atoms, mesomerism, molecules). The middle third replaces atoms with molecules and non-covalent bonds, which lead via mesomerism to the crystal lattice (molecules, mesomerism, crystal lattice (= supramolecule)). The last third sets the $\pi \ldots \sigma$ correlation—which was introduced in Section 4—in relation to Desiraju's supramolecular synthons.

It is reasonable to make a comparison of other organic pigments with quinacridone at this point. No other red pigment with such low molecular weight is currently known which displays the stabilities mentioned with the brilliance of the colour shades in scarlet/red-violet—not even diketopyrrolopyrrole (DPP) or perylene. Each individual quinacridone molecule is—strictly speaking—made up solely of the two supramolecular synthons. Is, in the case of quinacridone, the mesomerism of the two particularly well-balanced? Or is the *relationship* between the two just right?[3]

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[3] It is of particular value to take a look at other pigment classes in this respect, e.g. Dr. K. Hunger, "High Performance Organic Pigments in Europe—An Historical Perspective", a lecture held on 12th September 2000 in the Grand Hyatt Hotel, Berlin, Germany within the framework of the High Performance Pigments 2000 (Intertech, Portland, Maine, USA).

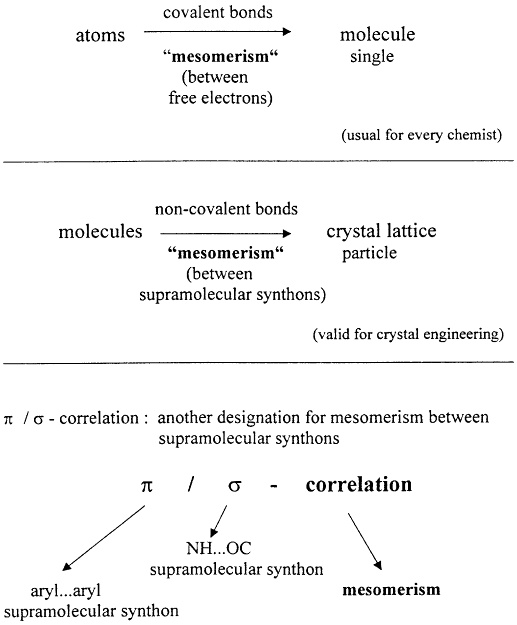

Fig. 20. Schematic comparison of different bond types.

The surface of the crystal is of higher energy because one (or more) faces of the *molecule* is not interacting with another molecule. It will still be able to participate in both hydrogen bonding and aryl...aryl interactions, just fewer of them.

In Section 1, the Mie theory approach was mentioned, according to which the entire particle vibrates with the impacting electromagnetic waves. This theory stems from the period before quantum mechanics (1908). The supramolecular synthon concept used here on the quinacridones can be considered as an organo-structural analogue to the Mie theory.

A further development on quinacridones led to "solid solutions", i.e. to mixed phases. Although already well-known in inorganic chemistry, these were entirely new in the field of quinacridones Ehrich [26]. It is appealing to see how Ehrich's patent describes the stable mixed phases of ternary systems with the aid of conventional ternary diagrams (composition diagrams). This underlines the similarity between the quinacridones and inorganic pigments (and metal alloys) and is once again a sign of insolubility. This development is qualitatively readily accessible in the light of supramolecular synthons. The planar quinacridone molecules stack in varying arrangements, i.e. the stack is built up of not just one molecule, but rather from two or even three molecules. For example, a stack may be made up of quinacridone and quinacridonequinone (+ sub. quinacridone). Every variation of the supramolecular aryl...aryl synthon is directly connected with a variation in the supramolecular H bonds in the lattice. This leads to additional colour shades (hypsochromic shift) within the quinacridone series.

6. Finale

"The historical molecular bias of organic chemistry necessitates the reiteration that supramolecules are not just collections of molecules and that their structures and characteristic properties are distinct from the aggregate properties of their molecular constituents. Such a statement is, however, *hardly necessary in inorganic crystal chemistry where structures have traditionally been viewed in terms of networks and connectivities and where the very definition of molecularity is excitingly different*. And yet, these 'organic' and 'inorganic' viewpoints are only parts of the whole, and another manifestation of the synthesizing aspect of supramolecular chemistry is its ability to bridge organic and inorganic structural chemistry with the result that it will soon probably be difficult to distinguish between organic, inorganic and organometallic viewpoints in solid-state chemistry".

"Again, is it possible to distinguish clearly between a chemical bond and an intermolecular interaction? *Even as supramolecular chemistry has sought to demarcate between what is within and without the molecule it has demonstrated as deficient the classification of forces as 'bonded' and 'nonbonded'*. The weakest covalent bonds are indeed feebler than the strongest intermolecular interactions such as those between some metal atoms in organicmetallic crystals, interactions which confound attempts at distinguishing between molecules and supramolecules". G.R. Desiraju, editor. The Crystal as a Supramolecular Entity, Perspectives in Supramolecular Chemistry, Preface, pp. IX–XI, J. Wiley & Sons, Chichester (1996).

Acknowledgements

Fig. 1 (Reflections of Symmetry. Weinheim–Basel, VCH, 1993) was reproduced with the kind permission of E. Heilbronner, Grütstr. 10, CH-8704 Herrliberg, (Switzerland). The definitions of supramolecular synthons were also used with the kind permission of G.R. Desiraju, School of Chemistry, University of Hyderabad, Hyderabad 500 046, India. Both are gratefully acknowledged. Figs. 6, 13, 16–19 were made using the program SCHAKAL from E. Keller, Hebelstr. 25, D-79104 Freiburg i. Br., Germany, Crystallographic Institute of the University Freiburg.

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