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Review

# Molecular stacks as a common characteristic in the crystal lattice of organic pigment dyes

## A contribution to the "soluble–insoluble" dichotomy of dyes and pigments from the technological point of view

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## Abstract

This is the first attempt at trying to arrange industrial organic pigments into an order from the viewpoint of the formation of molecular stacks as the common characteristic of all their crystals. Some pigments additionally form networks of leaf-like structures, and others assemble themselves to construct a three-dimensional lattice. This approach is new in the field of pigments, but it permits differences in solubility behavior to be readily explained in a qualitative manner. Crystal engineering is undoubtedly the scientific basis for organic solids and may be vividly described as providing the building blocks, cement and brickwork for pigment dyes (heterocycles). Significant developments in organic pigments were admittedly, however—following the demands of both technology and market forces—made long before the new discipline of crystal engineering was called into being. The pigment dyes are thus an intimate point of contact between science and technology.

*Keywords:* Dyes; Pigments; Stack structures; Insolubility/solubility; Crystal engineering

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## Contents

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> *All pigments are bridges between organic and inorganic chemistry. Thus they do not separate, but connect.*

## 1. Foreword

In order to set the scene, the following three comments seemed appropriate:

1. From a scientific standpoint, the universal textbook from Klages today still provides a very readable introduction and compendium on organic dyes [1]. Particularly noteworthy is for example the linkage of the historical development of dyes with physical viewpoints. The development of color theory up until 1984 has been outlined by Griffiths, who goes into the PPP method [2].
2. The most modern monograph on this theme comes from Herbst and Hunger [3]. The present contribution will often refer back to this work, because it reflects 150 years of stringency between experiment and theory in chemistry which culminates in the structure of the individual molecules (the pigments) as the most important classification principle. At the same time, the reader submerges in the world of industrial relationships and values. The review articles on “Organic Pigments” (pp. 193–199) and “Phthalocyanines” (pp. 213–242) in Ullmann’s Encyclopedia [4] are also of great value. The most modern viewpoints on high-performance pigments (HPPs) are to be found in Smith [5]. As an indication of the new research component and the new approach “crystal engineering”, this monograph contains the relevant keywords “crystal engineering” and “crystal engineered pigments” in its register.
3. University scientists will want to know how it could be at all possible, outside of their own strict laws and rules, to carry out systematic research and reach their goals. The answer is that technological criteria (e.g. ISO and DIN norms)—but also customer requirements (of the market)—demanded extreme effort and selection [6]. Two statements from [6] are given here: “In spite of, or perhaps because of its importance to technology, standardization is not just a discipline for engineers. Standardization penetrates all areas of our lives—it is a prerequisite for the high standard of living of our society.” and “In the first instance, standards are an important **source of knowledge**[1] for professional behavior in normal cases.”

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[1] Bold print from the author of this publication.

For this reason, test standards (DIN, ISO) are also important for pigments. They result from the necessity to use a uniform basis for systems (preparations, formulations) that have several or many components. The physical equation (algorithm), with its high controlling value for the experiment, is replaced by the standard or norm.

Pragmatism is additionally demanded by the following fact: Technology (including chemistry) is dominated by thoughts and deeds that work—and indeed have to work—outside the area of validity of pure scientific laws. Standards such as DIN and ISO offer themselves as a common language. Important DIN norms for organic pigments are described and summarized in [3], pp. 119–123 and 190–191. The latest standard (DIN 55943, European norm—in preparation[2]) is called: "Pigment—substance consisting of particles, **practically insoluble** in the application medium, and used as colouring material or because of its corrosion-inhibiting, magnetic, electrical or electromagnetic properties". What does "practically insoluble" mean for the chemist? How does he deal with it? This is the task that the author of this article has set himself.

## 2. Introduction

### 2.1. A glance at the scientific roots

Desiraju put particular emphasis on the *chemistry* of organic solids (crystals) since 1983 [7]. This monograph put intermolecular chemical bonds, i.e. weak H-bridges and other intermolecular contacts (Cl...Cl; S...hetero atom; Cl...O, etc.), at the centre of attention. Thus, the contrast "intramolecular" and "intermolecular" is put into perspective for organic crystals—one could even practically say "levelled"—are places them alongside inorganic crystals. Also worthy of mention is the Taylor paper from 1983 [8]. The term "Crystal Engineering" was coined. The Taylor paper [8] later gave reasons for extensive studies on statistical chemical intermolecular bonds, and also for an increasing interest in organic hydrogen bonds. After this, the field of organic solid-state chemistry began to grow explosively. For a review on the important developments of crystal engineering see Desiraju [9]. The current article draws on the known stock of organic industrial pigments and orders these in accordance with their stack structure.

### 2.2. The technological basics

Industrial organic pigments are part of organic crystals (colloids), but they developed and kept their importance from the necessity for color printing inks, lacquers, plastics, fibres, etc. (mass coloration). *Parared* (1885) is the first organic pigment, Herbst/Hunger [3], p. 280. One pigment class demonstrates a clear transition to modern pigments—the azo condensation pigments, also known as disazocondensation pigments [3,5]. The plausible principle of molecular doubling with a simultaneous increase in the number of carbonamide groups in the molecule was consequently developed. The problems encountered in the synthesis due to insolubility—even as early as at the intermediates stage—are mentioned and characterize this class of pigments. The summarizing remark in [10], p. 255: "There is no doubt, that practice will set the appropriate standards on this group of pigments and assign a corresponding place for it. If these words should sound perhaps too optimistic: in a world full of pessimism, there is at least here, where the consumer is still able to have his say, no damage done" [10]. "...where the consumer is still able to have his say..."—this is real customer orientation. The producer is his customer's servant. This pigment class is treated in a modern fashion in [3,5].

Chemical technology is jointly developed by the community of producers and consumers and thus adheres to its own set of rules that extend into the analytics, testing techniques, and standards.

The origin of pigments lies in the dyes, so it is understandable that initially, in many presentations of the pigment field [11–13], the molecular viewpoints were emphasized in addition was mentioned about the solid-state. A further publication

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[2] Thanks go to the Norming Commission for Pigments and Fillers (NPF), Mrs. Ines Hiller, for her help in reference to the newest formulation of the pigment definition DIN 55943 (English version).

dealt with the significant increase in the stability of organic pigments from the point of view of intermolecular H-bridges (benzimidazolone–cyclic five-membered hetero rings) [14]. New developments are treated by Kaul in [15,16]: “Most of the original literature focuses on the molecular description of the pigments and very little is known about the solid-state arrangements of the molecules”.

It must be emphasized, however, that the one thing that all pigments have in common is their insolubility (and stability) in comparison to dyes. The authors of [11–14] therefore deal with test methods for pigments. The stabilities and colour fastnesses achieved were the underlying technological goals. Research into modern organic pigments is applied Crystal Engineering! Insolubility and other properties of use are relative terms, because there are continuous transitions even between dyes and pigments. *Because the molecular lattices of organic pigments hold the molecules stronger together than the corresponding molecular lattices of dyes, pigments need to be assigned to different fields of technology and research than dyes*. “Hold stronger together” means in this case: strong intermolecular forces. By their very nature, these can display considerable differences.

Because of continual changes in binders, plastics (e.g. PVC, other thermoplasts, powder lacquers), synthetic fibers (application medium!), etc., and due to higher processing temperatures, organic pigments have to be developed with ever-increasing insolubility. At the same time, everyday products have become more and more colorfull. The application technician is already very familiar with the insolubility of inorganic pigments (e.g. $TiO_2$, $Fe_2O_3$ or $Cr_2O_3$). When he says about organic pigments that “they have something inorganic about them”, then he is subconsciously building a bridge between inorganic pigments and extremely insoluble organic pigments and comes a step closer to the modern concept of crystal engineering: “This new discipline is perceived as cutting across the traditional barriers of organic, inorganic... chemistry.” [17].

Two contributions can be found in the literature; one from Baier [18] on thin-layer chromatography (i.e. quantified solvent stability) and one from Baier [19] on the temperature stability of organic pigments. Both give interpretations on Fig. 1, in particular on ② and ④. This gives a good overview of the currently possible molecular ways for increasing the insolubility. Fig. 1 is a modified depiction based on [20].

The relationships in practice are admittedly rather more intricate. Practice often demands multiple stabilities from pigments e.g. simultaneous stress caused by (temperature + solvent + time) or (temperature + plasticizer + time).

Thanks to the test methods already mentioned, industrial laboratories recognized newly prepared chemical compounds as being pigments. They were selectively targeted and both they themselves and their synthesis were optimized. Depending on the results, new pigments are classified according to the existing assortments e.g. Permanent H-types. Every now and then a new assortment is created e.g. Cinquasia-, Hostaperm-, Heliogen- or Cromophthal-. It is rare that a pigment can fulfil almost all criteria. These are then called universal pigments (allround pigments ~ HPPs). This is the highest goal of pigment technology. Quinacridones, phthalocyanines, carbon blacks and some others have managed to attain this goal.

High-performance pigments—and Pc, QA and DPPs in particular—come very close to the idea of scientific crystal engineering. Nowadays there are all kinds of stimuli, e.g. for surface treatments. The relationship between technology and crystal engineering is thus rather new:

> *The relationship between molecular and crystal structure to solubility, solvation, morphological quality and ease of growth are problems of both fundamental and practical importance, but these are largely uncharted waters* [7], p. 305.

Organic pigments owe their existence to their insolubility, i.e. to the strong interactive forces between the molecules. From a technological point of view, these are of decisive importance. It is a goal of this presentation to draw ties as far as possible to crystal engineering.

It is possible to visibly depict the stability of pigments with respect to solvents, re-coating, bleeding, and temperature by making a comparison with a wall (pigments) made up of stones (molecules) (Fig. 2).

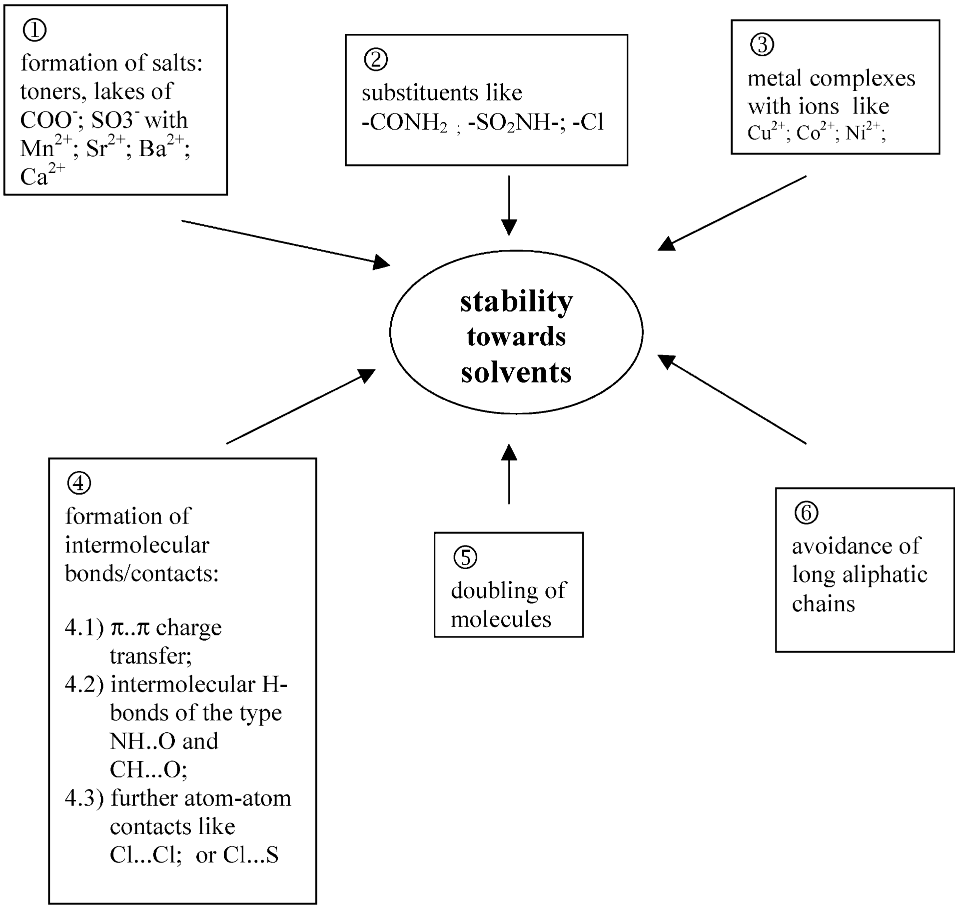

Fig. 1. Principles about unsolubility (adapted from Ref. [20], p. 137). The oldest way is the incorporation of inorganic parts within the body of soluble dyestuffs. This yields lakes and toners. They are very stable towards solvents, but not always stable towards weathering. The best toners are salts of $Mn^{2+}$. Well-known are the BON pigments and others, [3], pp. 6, 605–606 ①. The introduction of substituents was the first way of increasing the insolubility of organic pigments by organic syntheses, see Naphthol AS. Precursors are the GRELA-reds (1911), [3], pp. 290–324. In this respect, tetrachloroisoindolinones are very interesting [3], pp. 413–429 ②. The big success up until today are Pc pigments, therefore the first phthalocyanine dye was a phthalocyanine-polysulfonate. Today, other metal complexes are known, (see [3], pp. 400–429) ③. The formation of intermolecular bonds/contacts by H bonds and/or $\pi\ldots\pi$ charge-transfer is a new feature, especially in the case of QA, DPP, thiazines and others [5], pp. 317–330. Further intermolecular contacts are possible, see 4,4′,7,7′-tetrachlorothioindigo ④. An earlier (1955) route towards greater insolubility was by doubling the molecules disazocondensation pigments [3], pp. 380–398 [18], pp. 252–255, [5], pp. 195–209 ⑤. Substituents like long aliphatic chains should be avoided, see [126], pp. 490–493, [127], pp. 315–316. This is a shining example of the validity of the principles of organic chemistry within this survey ⑥.

Fig. 2 represents a brickwork assembly [21]. With the aid of this diagram, it is possible to explain the concept of different phases (modifications) even for the crystallographically untrained: **One and the same** building block may be used for similar, but not identical brickwork assemblies. The citations in Section 3.1 “0.4 (nm) Structures” make the bridge to certain pigments. Pc, QA and DPPs in particular are additional examples for different modifications. The mortar holding the stones together plays a significant role in determining the durability (service life) of the wall. Indeed, a special crystallographic type of the organic pigments is called “bricks in a brickwall” (see Section 4.1.1). The contributions of the intermolecular forces of the individual molecules are thus significant for the stability of organic

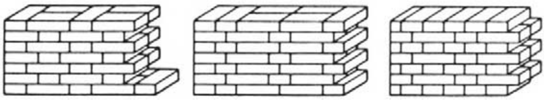

Fig. 2. Three distinct masonries (courtesy Ref. [21]).

pigments with respect to solvents, temperature, recoating, and migration. One could also say, that many of the above-mentioned tests indirectly check the properties of the (molecular) crystal lattice. It is not possible to make property predictions with DIN norms.

It should also be mentioned, that the "mortar" (lattice energy) between the molecules is of an electronic nature. The chemist, however, tends to depict the molecular building blocks in the form of chemical formulae. The physicist, on the other hand, describes the "mortar" with abstract mathematical equations. These are not a topic of this report. The methods of the chemist lead to Sections 3 and 4.

Up until now, Desiraju has carried out and published the most extensive studies on intermolecular interactions from a chemical point of view, e.g. in the monographs [7,22]. He was able to find subtle differences in the interactive forces of organic molecules [23].

This is particularly valid for heterocyclic compounds with the character of pigment dyes, which absorb visible light both in the form of a single molecule and in the crystal. Little has been published about this in the sense of crystal engineering. For certain organic pigments, it is sometimes only possible to differentiate them from dyes from a technological point of view, e.g. carbonyl pigments and vat dyes. An example is *Indanthrone Blue 60, CI 69800* (see Table 1).

The crystal structures of various compounds have admittedly been calculated in the past few years using fast computers with self-written software and these compared in a final step with powder diagrams. Organic pigments have almost exclusively found industrial interest [5,24,25].

In accordance with the technical demands placed on them, organic pigments are to be found strewn throughout chemistry. All pigments have in common the requirements of the application: hue/shade, colour range (palette), colour strength, stability (colour fastness), dispersibility. Chemistry and physics are only a bridge, an aid—admittedly indispensable—and that is since 1971 crystal engineering. The basis papers on the crystal structures of the phthalocyanines were published much earlier, however, by Robertson [26,27].

Initially, crystal engineering explains with hindsight. It is therefore descriptive. It could prove its quality as an exact science by making correct predictions and thus by having an influence on future research (see also [28]).

Today (2002) the crystal structures of many organic pigments are known, and these serve here as a basis (Table 1). There are also several reports to be considered (Pc, Perylene, QA, DPPs). Finally, the formal analogy between inorganic and organic pigments should be mentioned:

> *And yet, these 'organic' and 'inorganic' viewpoints are only parts of the whole, and another manifestation of the synthezising aspect of supramolecular chemistry is its ability to bridge organic and inorganic structural chemistry with the result that it will probably soon be difficult to distinguish between organic, inorganic and organometallic viewpoints in solid-state chemistry [29].*

Certain pigment classes have been especially worked on by certain companies in particular [4,5,30–36].

For both users and students, much of this is probably new. The present review article marks out the area requiring supplementation through additional experimental and calculable details.

Beyond the molecular lattices to be presented in the following, several novel, extremely insoluble and stable substances have become known in the past few years, e.g. quinophthalone, thiazine and oxazine (see Section 4.1.2 and [5], p. 307ff). There is no doubt about the principle of molecular stacking, however, it is not possible to make any exact details without knowledge of the crystal structure.

In the following section, intermolecular interactions and their qualitative graduations will be treated and the appendices A–D reorder the contrast between dyes and pigments—and thus also the "insoluble/soluble" dichotomy—in a novel manner, while at the same time enhancing them.

Table 1
Given crystal structures of organic pigments

| Chemical or pigment name (trivial) | C.I. name | C.I. no. | Ref. | Shortest distance of translation (lattice vector) (nm) | Translation type (∼stack type) | Flat portions of neighbouring mol. apart and pack in stacks (nm) |
|---|---|---|---|---|---|---|
| Para Red (alpha) | Pigment red 1 | 12070 | [49] | $a=0.3797$ | Simple | No indication |
| (beta) | | | [50] | $c=0.5854$ | Double | |
| (gamma) | | | [51] | $c=0.6964$ | Double | |
| Toluidine Red 3 (Hansa Red B) | Pigment red 3 | 12120 | [58] | $c=0.6960$ | Double | 0.334 |
| Naphthol AS derivative | Pigment red 2 | 12310 | [57] | $b=0.951$ | Double | No indication |
| Parachlor Red | Pigment red 6 | 12090 | [59] | $b=0.6958$ | Double | 0.339 |
| Permanentbraun FG | Pigment brown 1 | 12480 | [54] | $b=0.3963$ | Simple | No indication |
| Thioindigo, mod.II | Vat red 41 | 73000 | [45] | $a=0.3981$ | Simple | No indication |
| 6,6′-Dibromo-thioindigo | No indication | | [46] | $a=0.485$ | Simple | No indication |
| Flavanthrone | Vat yellow 1<br>pigment yellow 24 | 70600 | [47] | $b=0.380$ | Simple | No indication |
| Indanthrone | Vat blue 4<br>pigment blue 60 | 69800 | [48] | $b=0.3833$ | Simple | No indication |
| Hansa yellow type, methoxylated | No indication | | [36] | $c=0.4710$ | Simple | 0.331 |
| Hansa yellow type | Pigment yellow 4 | 11665 | [65] | $a=0.7691$ | Double | No indication |
| Hansa yellow 5G | Pigment yellow 5 | 11660 | [70] | $a=0.7593$ | Double | No indication |
| Hansa yellow G | Pigment yellow 1 | 11680 | [62] | $a=0.7587$ | Double | 0.3301 |
| | | | [63] | $a=0.7598$ | | 0.3320 |
| | | | [64] | $c(!)=0.7623$ | | No indication |
| Acetoacetanilide | Pigment yellow 6 | 11760 | [58] | $a=0.7462$ | Double | 0.3330 |
| Hansa yellow 10G | Pigment yellow 3 | 11710 | [69] | $a=1.3240$ | Fourfold | 0.3310 |
| Hansa yellow 5G | Pigment yellow 74 | 11741 | [93] | $c=0.7628$ | Double | 0.3318 |
| Hansa yellow 3RN | Pigment yellow 65 | 11740 | [94] | $a=0.7295$ | Double | No indication |
| Acetoacetanilide | Pigment yellow 98 | 11727 | [67] | $b=1.0551$ | Double | 0.3354 |
| Hansa yellow methyl derivative | No indication | | [68] | $c=0.8296$ | Double | 0.338–0.347 |
| Hansa yellow methoxy derivative | No indication | | [68] | $b=0.7481$ | Double | 0.330–0.358 |
| Pigment Yellow GG | α-Pigment yellow 5 | 11660? | [71] | $a=0.7572$ | Double | 0.3315 |
| Naphthol AS; Cl derivative | Pigment red 9 | 12460 | [52] | $b=0.4592$ | Simple | No indication |
| Pc-Blue, metal-free | Pigment blue 16 | 74100 | [26] | $b=0.471$ | Simple | 0.36–0.37 |
| Pc-blue, metal-free, 1 Cl-atom/mol | Pigment blue 16 | 74100 | [55] | $b=0.3760$ | Simple | 0.344 |
| Pc-blue (beta) | Pigment blue 15 | 74160 | [79] | $b=0.479$ | Simple | 0.34 |
| | | | [80] | | | 0.328 |
| | | | [81] | | | |
| | | | [82] | | | |
| Pc-blue (alpha) | Pigment blue 15 | 74160 | [80] | $b=0.38$ | Simple | 0.34 |
| Pc-green, 16 Cl-atoms/mol | Pigment green 7 | 74260 | [86] | $c=0.376$ | Simple | No indication |
| | | | [87] | | | |
| | | | [88] | | | |
| Perylene derivative | ? | ? | [31] | $a=0.4705$ | Simple | 0.351 |
| | ? | ? | [31] | $a=0.4739$ | Simple | 0.395/0.341 |
| | Pigment red 123 | 71145 | [31] | $a=0.4934$ | Simple | 0.370 |
| | Pigment red 178 | 71155 | [31] | $a=0.5291$ | Simple | 0.348 |
| | Pigment red 179 | 71130 | [56] | $a=0.3874$ | Simple | 0.3345–0.3476 |
| | Pigment black 31 | 71132 | [56] | $a=0.4741$ | Simple | |
| | Pigment black 32 | 71133 | [56] | $a=0.4390$ | Simple | |
| Perylenediimide | Pigment violet 29 | 71129 | [115] | $a=0.4872$ | Simple | No indication |
| Benzidine derivative | Pigment yellow 13 | 21100 | [24] | $a=0.8369$ | Double | No indication |
| | Pigment yellow 14 | 21095 | [24] | $a=0.8214$ | Double | No indication |
| | Pigment yellow 12 | 21090 | [76] | $b=0.737$ | Double | 0.343 |

(*continued on next page*)

Table 1 (*continued*)

| Chemical or pigment name (trivial) | C.I. name | C.I. no. | Ref. | Shortest distance of translation (lattice vector) (nm) | Translation type (~stack type) | Flat portions of neighbouring mol. apart and pack in stacks (nm) |
|---|---|---|---|---|---|---|
| Tetrachloroiso indolinone, | Pigment yellow 110 | 56280 | [106] | $c=0.726$ | Double | 0.341 |
| Benzimidazolone, | Pigment red 208 | 12514 | [95] | (0–11) | 4-fold | 0.342 |
| Isoindolinone derivative, $Co^{2+}$-complex | Pigment yellow 177 | 48120 | [90] | $b=1.2985$ | 4-fold | No indication |
|  | Pigment yellow 179 | 48125 | [91] | ? | ? | No indication |
| Ca4B-Toner | Pigment red 57:1 | 15850 | [92] | $b=0.58$ | ? | 0.343–0.346 |
| Anthrachinone derivative | Pigment red 177 | 65300 | [96]<br>[99] | $b=0.850$ | Double | 0.301–0.336 |
| Quinacridone, unsubstituated, gamma-phase (QA) | Pigment violet 19 | 73900 | [101] | $b=0.3886$ | Simple | 0.338 |
| Quinacridone, unsubstituated, (beta-phase) | Pigment violet 19 | 73900 | [101] | $b=0.3975$ | Simple | 0.336 |
| 2.9-Dichloro quinacridone | Pigment red 202 | 73907 | [101] | $a=0.3834$ | Simple | 0.333 |
| 2.9-Dimethyl quinacridone | Pigment red 122 | 73915 | [101] | $a=0.391$ | Simple | 0.342 |
| Diketopyrrolo pyrrole (DPP) | Pigment red 254 | 56110 | [111] | $b=0.3817$ | Simple | 0.336 |

## 3. The stacking arrangement in the crystal lattice (Intrastack forces)

The formation of stacks with a distant similarity to those of graphite is typical for organic pigments. The author has pointed this out in a previous publication [37]. A great deal more is known about these stacks today (see e.g. [7], pp. 92–96). Not all molecules in the lattice are completely planar, but certain parts of a molecule are, e.g. in the case of perylene pigments [30] or DPP (see [38–40] and many other articles elsewhere). Desiraju's classification principle [7] is valuable, but cannot fully account for the plethora of organic pigments. One could also say that molecules of the type pigment dye break through Desiraju's classification principle.

In the following, single and double layers in the stack will be presented (see Sections 3.1 and 3.2). It is the author's opinion that these are a not coincidence, but rather an indication of charge–transfer complexes in pigment dye molecules. A precise analysis of the stacks perpendicular to the planes would therefore be an advantage. It is certain that in single crystals, stacks are formed in accordance with the principle of attaining an energy minimum.

Within the framework of Fig. 1, the area ④, in particular 4.2, is meant.

### *3.1. The 0.4 (nm) structures (Intrastack forces)*

A review of all the crystal structures known today would be too extensive. However, some typical pigments (crystals) are described here. Additional pigments are summarized in Table 1.

The 0.4 (nm) structures take their name from the short spacing in the crystal lattice, which in turn refers to an important translation of the molecules—in the stack direction—in the lattice. Desiraju goes into these structures in detail in [7], pp. 92–96, 269. He also recognized their general importance. The 0.4 (nm) structure is also called the "beta structure". It is important, however, to clearly differentiate between these beta structures and the beta modifications of all kinds widely known in pigment chemistry. The latter characterizes differences *within* a particular pigment class (e.g. phthalocyanine or QA, etc.), whereas the former was first mentioned by Schmidt with reference to succinic acid derivatives [41] and further developed by Desiraju. It is interesting to note that Desiraju already mentioned some 0.4 (nm) structures in his monograph [7], p. 162, which later became important vat dyes; namely *pyranthron*, *violanthron*, and *isoviolanthron* [42]. Organic pigments of this type are called polycyclic. The chlorine and bromine derivatives are often industrially more important than the basic chemical and the stack spacings also differ from those of the basic chemical. This can also be seen in the case of *indigo* [43], but 6,6′-dichloroindigo [44], *thioindigo*, modific. II [45], and 6,6′-dibromoindigo [46] should also be mentioned (see Table 1).

There are probably many more in addition to *flavanthrone* [47] and *indanthrone blue* [48]. The short stack spacings are responsible for the emergence of the molecular piles—stacks. All pigments with the 0.4 (nm) structure have strong π...π-charge-transfer forces within the stack.

In addition, carbazoldioxazine—*CI Pigment Violet 23, CI 51319*—should be mentioned. Its crystal structure is known, but has not been published (see [3,5]).

The oldest pigment—called para red—is also of interest, and three modifications have been analyzed:

- *CI Pigment Red 1, CI 12070*, (alpha-Mod.) with $a = 0.3797$ nm [49].
- *CI Pigment Red 1, CI 12070*, (beta-Mod.) with $c = 0.5854$ nm [50].
- *CI Pigment Red 1, CI 12070*, (gamma-Mod.) with $c = 0.6964$ nm [51].

*Para red* is no longer of technical importance today.

Permanent brown FG—a naphthol AS pigment with $b = 0.3962$ nm—is also a member of this group of 0.4 (nm) structures [54] (see also Table 1).

All azo pigments have intramolecular H-bridges with formation of the hydrazone form (instead of the known azo form) in common [53].

A further azo pigment with the typical stack spacing of $b = 0.3963$ nm is a chlorine derivative of *Permanent Brown FG, CI 12480*, a naphthol AS pigment [54]. This molecule is also planar and only makes use of intramolecular H bridges. The publication makes no mention of the stacking or its bonding.

Both of these pigments thus develop stacks with π...π exchange between the molecules. The following also belongs in Section 3.1:

- The metal-free phthalocyanine (Pc) pigment, *Pigment Blue 16, CI 74100*, with b = 0.471 nm, crystallized as the beta-phthalocyanine modification [26].
- The mono-chlorinated metal-free phthalocyanine pigment, *Pigment Blue 16, CI 74100*, with $b = 0.3760$ nm constitutes the alpha modification [55].

The different stack spacings of the molecules in alpha Pc (~0.38 nm) and beta Pc (~0.48 nm) are remarkable. Details are given in Section 3.4.

An important pigment class is that of the perylenes [30,31]. From the plenitude of pigments mentioned in [31], there are four commercial types whose crystal structures are given here, and three of these belong in Section 3.1:

- $C_{32}H_{26}N_2O_6$, *Pigment?*, *CI?*, $a = 0.4705$ nm,
- $C_{36}H_{34}N_2O_6$, *Pigment?*, *CI?*, $a = 0.4739$ nm,
- $C_{40}H_{26}N_2O_6$, *Pigment Red 123*, *CI 71145*, $a = 0.4934$ nm.

Because of the layer spacing, the crystal structure will be dealt with in Section 3.3:

- $C_{48}H_{26}N_2O_6$, *Pigment Red 178*, *CI 71155*, $a = 0.5291$ nm, see there.

Hädicke und Graser have investigated 11 further perylene pigments [56]. Among these there are three commercial pigments:

- *CI Pigment Red 179, CI 71130*, with $a = 0.3874$ nm,
- *CI Pigment Black 31, CI 71132*, with $b = 0.4741$ nm,
- *CI Pigment Black 32, CI 71133*, with $a = 0.4390$ nm.

All three are thus also 0.4 (nm) structures.

In addition, carbazoldioxazine is also to be mentioned; *CI Pigment Violet 23, CI 51319*. Its crystal structure probably belongs in Section 3.1 (0.4 (nm) pigments).

### *3.2. Doubled 0.4 (nm) structures (Intrastack forces)*

Translations in a lattice are not always as simple as in Section 3.1. There are pigments that develop a doubled 0.4 (nm) structure, e.g. some azo pigments. They have been analyzed by Whitaker, e.g.:

- *CI Pigment Red 2, CI 12310* [57],
- *CI Pigment Red 3, CI 12120* [58] (toluidine red),
- *CI Pigment Red 6, CI 12090* [59].

One of Whitaker's review articles has been dedicated in particular to pigments of the type naphthol [60]. The second large pigment class is that of the acetoacetylanilides, called Hansa Yellows®. This class has been well investigated by means of X-ray crystallography, particularly by Whitaker. The first in this series is Hansa Yellow 1, *CI Pigment Yellow 1, CI 11680*, which was crystallographically analyzed by Mez in 1968 [61]. Due to the choice of the unit cell, this publication is not considered in Table 1. The same pigment was later studied independently by Whitaker [62], Paulus [63] and Brown [64]. The results in [62–64] with respect to the stack spacing are comparable and shown in Table 1. It is interesting that the space group in [63] is given as $P2_1/n$, in contrast to $P2_1/c$ in [62] and [64]. A further arrangement of the lattice with $c = 0.7623$ nm in [64] instead of $a = 0.7507$ nm in [62] is expressly mentioned here. In addition, the angle $\beta = 98.2°$ in [63] is different from that of $\beta = 120.68°$ in [62] and 120.5° in [64]. Whether or not this permits us to infer that Hansa yellow 1 has various modifications cannot be decided here. All three papers [62–64] appeared in 1994 and thus made no reference to one another. The formation of double stacks in Hansa yellow 1 seems certain, however.

Further structures are

- *CI Pigment Yellow 4* [65],
- *CI Pigment Yellow 5, CI 11660* [66].

The molecules in the lattice are virtually planar and form double stacks with $a = 0.7587$ nm, $a = 0.7691$ nm, [65] and $a = 0.7593$ nm [70]. Whitaker had also described *CI Pigment Yellow 98*, *CI 11727*, in this manner [67]. The molecules are stacked along $b$ (1.0551 nm). Two other yellow pigments of type Hansa yellow® with the typical double layer are described by Paulus et al. [68].

Whitaker has also described other pigments. An interesting variant with four molecules as a translation in the stack is

- *CI Pigment Yellow 3, CI 11710* [69].

One pigment with mixed crystal character has been analyzed by Whitaker

- *Hansa Yellow 5G*, *CI 11660* [70].

Both molecules form double layers parallel to a (= 0.7567 nm). A further pigment dedicated by Whitaker

- *Pigment Yellow GG* [71],

he describes as being a mixed crystal of *CI Pigment Yellow 6*, *CI 11760* [53], in *CI Pigment Yellow 5*, *CI 11660*, with $a = 0.7572$ nm.

An important publication for the acetoacetanilide pigments made in 1987 also comes from A. Whitaker [72]. Three further Hansa yellow pigments with intermolecular H bridges are described in [71]. These are more appropriately dealt with in Section 4.1.1 of this article.

At about the same time, Paulus and Rieper did a review on 12 acetoacetylanilides [73]. In this, a mesomeric structure (resonance formula) of the single molecule was proposed showing the distribution of the negative and positive charges. This in turn has consequences for the deviation from planarity.

Within the framework of their X-ray structure analyses, Whitaker and Paulus often speak of pure van der Waals forces between the molecules in the stack. It is the opinion of the author of the present article that, irrespective of the precise crystallographic results, in view of the unequivocal pigment properties, e.g. of *CI Pigment Red 3* (toluidine red) and diverse Hansa yellows®, it should also be mentioned that weak charge-transfer forces between the molecules within a stack are possible. The previously mentioned charge differences in a single molecule [73] are a strong indication for $\pi\ldots\pi$-charge-transfer forces in the stack, possibly even the cause for the arrangement of the type "single", "double", or "four-fold". Van der Waals forces would lead to the formation of

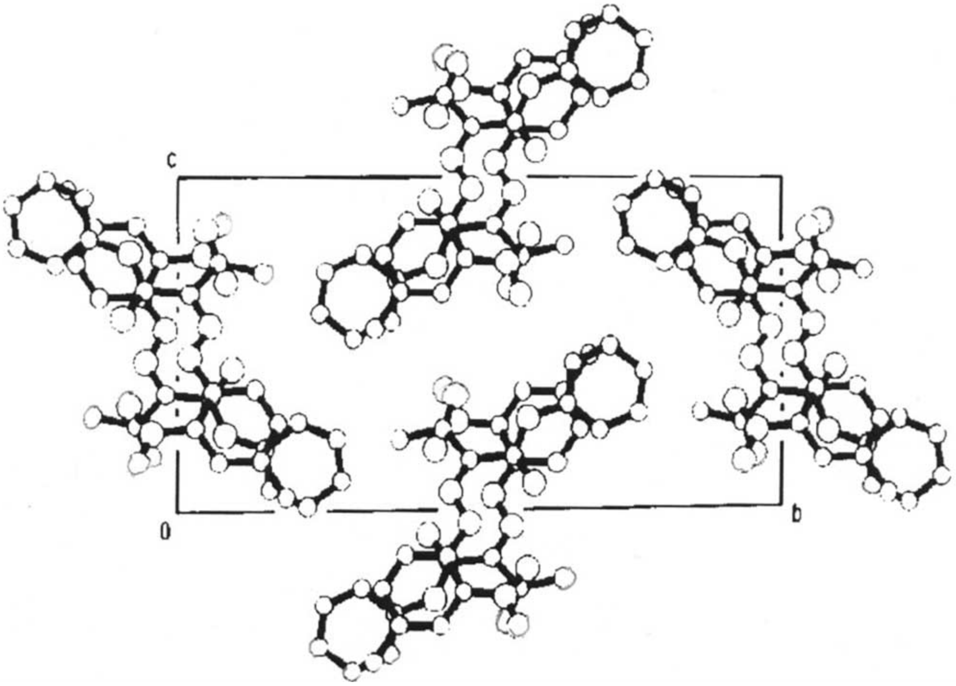

Fig. 3. The packing of C.I. Pigment Yellow 1 molecules in the unit cell, *a* axis projection (courtesy "Zeitschrift fuer Kristallographie", Oldenbourg Wissenschaftsverlag GmbH, Lektorat MINT, Munich).

disordered stacks. Strictly speaking, it is a question of the energetic difference between a single crystal and crystal with a statistical sequence of the molecules in the stack. From an experimental point of view, optical measurements with polarized light and possibly also conductivity measurements on crystals of the pigments parallel to the stack axis, could provide valuable information on the bonding states and their differences.

In actual fact, the decision whether one is dealing with van der Waals or charge-transfer forces between planar molecules in the stack is not an easy one [74]. But then again, even between aromatic molecules, it is assumed there are $\pi \ldots \pi$ charge-transfer forces present [75]. In the case of aceto-acetanilides, in comparison to poly-condensed aromatics, we are dealing with significantly more complicated hetero molecules. Fig. 4 from [74] and Figs. 3 and 4 from [62] may serve to demonstrate this:

- Fig. 4, *Pigment Red 3* (toluidine red), *c* axis projection
- Fig. 3, *Pigment Yellow 1*, *a* axis projection
- Fig. 5, *Pigment Yellow 1*, *b* axis projection

Figs. 3 and 4 are projections on the best plane of practically planar molecules. Fig. 5 shows the molecular stacks.

$\pi \ldots \pi$ charge-transfer forces between molecules in the stacks should therefore also be valid with regard to the technological properties as yellow pigments (Hansa yellows®). The temperature resistance is admittedly poor (120–150 °C), but the stability to solvents is acceptable for such a small molecule (fair–good). Admittedly, they do "bleed" in most solvents and migrate in plasticized synthetics. Solvents and high temperatures overcome the $\pi \ldots \pi$ charge-transfer forces in the stack and leads to its dissolution.

It can be seen, however, that when colouring synthetic materials, high temperatures can turn thermally stable pigments into dyes. This can be recognized from the resulting transparent colouration.

*Para Red* (*Pigment Red 1*) can show three(!) modifications of the same time, each of which has

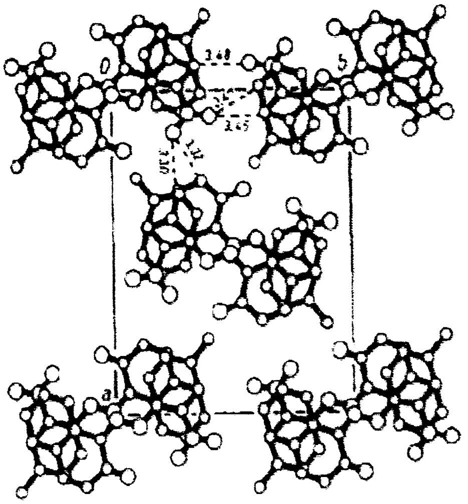

Fig. 4. The packing of C.I. Pigment Red 3 molecules in the unit cell, *a* axis projection (courtesy "Zeitschrift fuer Kristallographie", Oldenbourg Wissenschaftsverlag GmbH, Lektorat MINT, Munich).

different stacks (para red alpha, beta and gamma). One could even say that the different stacks and different modifications are in fact the same. Different stacks of the same compound are not trivial, but rather indicate that specific interactive forces are active between the molecules in the lattice. This all points to π…π charge-transfer forces between the molecules in the stacks.

This is a consequence of the comparison of the crystal structures with technological qualities.

A further naphthol AS pigment must be mentioned, a chlorinated derivative of permanent red FRLL with the stacking axis $b=0.4592$ nm [52]. The molecule is practically planar and almost certainly stacked parallel to *b*, even though this is not discussed in the publication. There are no intermolecular H bridges. The pigment dye molecule is admittedly enlarged around the NH–CO-phenyl group, but at the same time, the π…π charge-transfer forces in the stack are increased. This leads to improved stability against both temperature (up to 200 °C) and solvents in comparison with Hansa yellow®/toluidine red. The more NHCO groups are incorporated into the molecule, the higher is the stability against migration.

In the meantime, three benzidine yellows have become known. They all have double-layer spacings:

- *CI Pigment Yellow 13, CI 21100*, with $a=0.8369$ nm,
- *CI Pigment Yellow 14, CI 21095*, with $a=0.8214$ nm, both [24],
- *CI Pigment Yellow 12, CI 21090*, with $b=0.737$ nm [76].

In these there is no indication of intermolecular H bridges.

One case of a commercial pigment with a double stack spacing is *CI Pigment Red 149, CI 31137*, which together with three other perylene pigments was published by Hädicke and Graser in [77].

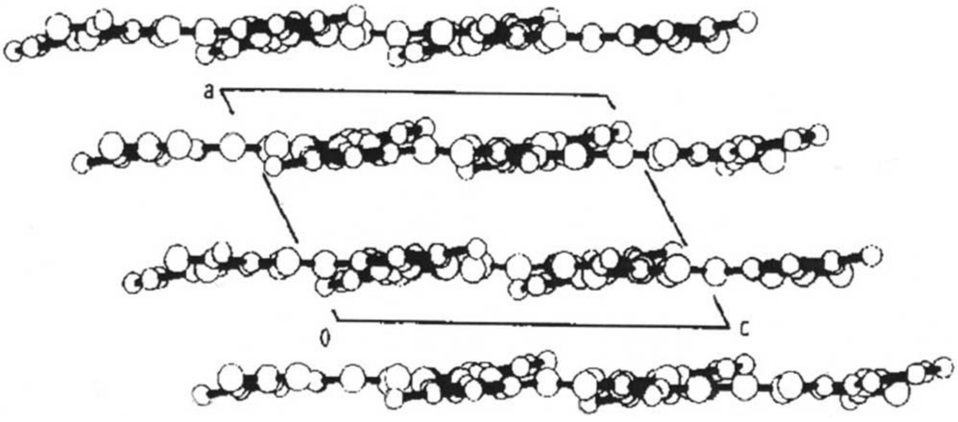

Fig. 5. The packing of C.I. Pigment Yellow 1 molecules in the unit cell, *b* axis projection (courtesy "Zeitschrift fuer Kristallographie", Oldenbourg Wissenschaftsverlag GmbH, Lektorat MINT, Munich).

### 3.3. Translations between 0.5 and 0.6 nm

Para red (beta-phase), *Pigment Red 1*, *CI 12070*, with $c = 0.5854$ nm can perhaps be classified here.

From the group of the perylenes, *Pigment Red 178, CI 71155* is to be mentioned, with its stack spacing of $a = 0.5291$ nm and a molecular layer spacing of 0.348 nm [5,31].

The extremely well-known indigo, *Pigment Blue 66*, *CI 73000*, [43] has an (unusually) large translation of the molecules in the stack ($b = 0.574$ nm), and in spite of the intermolecular H bridges is best included at this point. As a pigment it is industrially insignificant and is therefore not listed in Table 1.

Every pigment develops its own typical molecular structure, characteristics and stabilities, etc. Comparative research must, therefore, take the plethora of heterocycles into consideration.

It is only possible to make more detailed statements on the doubled layer spacings and the 0.5–0.6 nm translations with a precise knowledge of the crystal structures. The latter in particular give rise to questions. In all of these structures, contributions from $\pi \ldots \pi$ charge-transfer forces are to be reckoned with.

### 3.4. Complex compounds

Express reference is made to Fig. 1, in particular to ③ metal complexes which are an extremely important and growing field.

This type of pigment is still dominated today by the phthalocyanine compounds, in particular the Cu–Pc. Löbbert provides a review in [4] and Engel studied all kinds of phthalocyanine compounds right up until very recently [78] with 460 literature citations, including metal complexes. Within this framework, the copper complex of *beta-Pc* (0.479 nm), *Pigment Blue 15*, *CI 74160*, is of extraordinary practical importance, [79–82].

*Alpha-Pc*, *Pigment Blue 15*, *CI 74160*, crystallizes with a stack spacing of ~0.38 nm [80]. Amongst the metal complexes, phthalocyanine pigments are unrivaled.

The author of this paper draws attention to the stability rules of Irving and Williams, which—within the first row of transition elements of the periodic table (Ti to Zn)—demand the highest stability for copper complexes [83,84]. It enjoyed a worldwide career. It should be mentioned, that the central copper atom of each molecule with a [$CuN_6$] octahedral (metal complex) does not only serve to stabilize the individual molecule, but also to chemically stabilize the molecules linked above and below in the stack through hybridization (beta-stacking). It was only through detailed X-ray structure analysis by Brown [81], that it was first shown that the $Cu^{2+}$ ion in the [$CuN_6$] complex has differing $Cu \cdots N$ bond lengths, i.e. the complex is distorted in accordance with the Jahn–Teller effect [85]. It can thus prove very worthwhile to study stacked structures.

Polychlorinated Pc, *Pigment Green 7*, *CI 74260*, has 14–15 Cl atoms/molecule. The maximum would be 16. In this case, interactive forces between the molecules in the stack play a role. There is no beta-stack. Various publications give the stack spacing as $c = 0.376$ nm [86–88]. *Pigment Green 7* thus unequivocally forms alpha-stacks.

"To be borne in mind is the fact that in pigment chemistry the chlorinated pigments always show better pigmentary properties than the corresponding non-chlorinated derivatives. Examples can be cited of *Pigment Red 254* versus *Pigment Red 255*, *Pigment Violet 19* versus *Pigment Red 202*, chlorinated versus non-chlorinated THI, and last but not least *carbazole dioxazine violet 23* versus chlorine-enriched, modified *carbazole dioxazine violet 23*" [89]. But metal complex pigments with ions other than $Cu^{2+}$ also have to be mentioned.

The first to be mentioned here is *Pigment Green 10*, *CI 12775*, also known as green gold 10. It is a nickel complex of an azo compound and was the first metal complex with pigment character to be discovered after Pc blue. Its crystal structure has still not been entered in the CSD even today, so it is not possible to discuss its layer structure.

Somewhat more recent are the two tetrahedral(!) $Co^{2+}$ complexes of isoindolinone, *CI Pigment Yellow 177, CI 48120* and *CI Pigment Yellow 179*, *CI 48125*, both with very good stability. The crystal structure of the former has been published [90]. Frey and Lienhard discuss these pigments in an article from the aspect of application technology

[91]. The ligands of the $Co^{2+}$ complex are arranged in a tetrahedral fashion. There are four intermolecular H bridges per molecule and these serve to hold stacks together at the sides. Charge-transfer forces within the molecular stacks—between the isoindolinone ligands—provide the metal complex with additional stability. In the complex under discussion, the molecules build fourfold stacks ($b = 1.2985$ nm $\sim 4 \times 0.3256$ nm). This in turn would point to Section 4.1.2. The practical test methodology and its results are briefly described in [91]. This shows how accurately the stability—and thus indirectly the lattice energy—can be evaluated. With regard to the Irving–Williams rule [83,84], these $Co^{2+}$ complexes cannot be the most stable.

A modern pigment with the character of a metal complex is $Ni^{2+}$ thiazine indigo, *Pigment Red 257* (see [89]). The crystal structure has not been published.

A good overview on metal complex pigments, including azomethine, is given by Hunger and Herbst [3], pp. 399–412—admittedly without describing the crystal structures. An indication of modern metal complexes can also be found under Kaul [15], "Milestones in the Pigmentation in coloured paints", and the paper [16] goes still further. One can only hope that in future this field will become more accessible through the publication of the crystal structures of the pigments. This would surely be beneficial for the quality of organic pigments and a great deal can be expected here.

### 3.5. Toners

This field is characterized by the formation of salts from $SO_3^-$ or $COO^-$ groups, e.g. with $Ca^{2+}$ ions. Reference is made to Fig. 1, ①, which summarizes the possibilities for creating insolubility. An example is *Pigment Red 57:1*, *CI 15850*, *Ca4B-Toner* [92]. In this case, the eightfold coordination of the $Ca^{2+}$ ion with oxygen is particularly emphasized, i.e. the Ca–O bonds. Of these, two oxygen atoms belong to water of crystallization. In spite of this, express reference is made to the azo "ligands" (=azo molecules), that they are planar and lie parallel to one another with a spacing of 0.343–0.346 nm: "The azo ligands are parallel to their companions on the same side of the ladder,...The closest contacts between parallel ligands falls just within the range usually accepted as indicating π-stacking...All the azo ligands in a chain run...along the *b*-direction...". The *b* axis has a length of 0.58 nm, so the translation here is simple.

This pigment would appear to break ranks with the other pigments described until now, because the $Ca^{2+}$ ion, also providing good solvent stability, does not impart temperature stability. The tendency for the formation of $CaCO_3$ or $CaSO_4$ is pronounced and thus also is the decomposition of the lattice. The role of the π...π charge-transfer forces in the lattice is interesting, however, and these are readily recognizable, albeit somewhat weaker. For this reason, *Pigment Red 57:1* is a typical color print pigment, but not an HPP. It is rather untypical for the sequence of pigments presented here.

## 4. Linking between the stacks (Interstack forces, directional interactions)

When the stacks are linked to one another, a new type of pigment is formed. This would without doubt provide access to a new field of technical pigments, see Fig. 1, ④ specially 4.2.

### 4.1. Via intermolecular hydrogen bridges

#### 4.1.1. Simple intermolecular H-bridges in the lattice

Side linking of the stacks is a chemico-crystallographic route to further increase the insolubility, see Fig. 1, especially 4.2.

To begin with, two acetoacetanilide pigments are considered. In addition to intramolecular H bridges, they also make use of weak intermolecular(!) H bridges of the type C–H...O–C. In this case, it is not easy to recognize this H bridge type by means of X-ray crystallography. Based on their technical behavior, the pigments belong in the series of the above-mentioned coupling components (Hansa series) and in no way stand out due to improved color fastness. Their temperature stability does not surpass 150 °C. Using the systematics of the present article, they do belong in the group of side-linked pigments.

*Hansa Brilliant Yellow 5G*, *Pigment Yellow 74*, *CI 11741* [93] and *CI Pigment Yellow 65*, *CI 11740* [94], are all worthy of mention. In this connection, *CI Pigment Yellow 65*, *CI 11740*, must also be mentioned, [94]. It also forms double layers with $a=0.7295$ nm. It is noticeable that Whitaker speaks of intermolecular H bridges in [93] and [94], apparently of the type CH...OC. In the case of [94], this leads to the formation of molecular dimers in the unit cell. For this reason, these pigments are incorporated in Section 4.1.1.

Only the two pigments *Pigment Yellow 74* and *Pigment Yellow 65* have intramolecular H bridges in addition to intermolecular ones. The influence on the crystal structure is recognizably different from those of the usual Hansa yellows. At a push, *Pigment Yellow 3*, *CI 11710* [69] might also be considered to form intermolecular H bridges, although this type of intermolecular H bridge is very weak. As a result, they represent an initial stage of organic pigments with intermolecular H bridges and are certainly not HPPs. One could also say, that the molecular lattice in the narrowest sense dominates.

Now we turn our attention to heterocyclic molecules with intermolecular H bridge bonds. These are:

- Benzimidazolones,
- Tetrachlorisoindolinones,
- Quinacridones,
- Diketopyrrolopyrroles,
- Peryldiimide, and
- Thiazine, THI.

It is characteristic of the inventiveness of the synthetic chemist, that a benzimidazolonedioxazine has also been prepared [25].

Finally, the diazocondensation pigments should also be mentioned, although strictly speaking, they do not belong to the heterocyclic pigments.

The pure carbonyl pigments (see 3.1, 0.4 (nm) structures) are characterized by strong $\pi\ldots\pi$ charge-transfer forces, which lead to high stabilities. Anthraquinone derivatives, which all form stack structures, are particularly worthy of mention [4], pp. 335–417. Carbazole dioxazine, *CI Pigment Violet 23*, *CI 51319*, should also be mentioned. In this case, the linkage of the one-dimensional stack to two-dimensional layers is significant.

> *The arrangement of the molecules within a stack influences the arrangement of the stacks next to one another and vice versa*

A comparison of diverse pigment crystal structures clearly shows that the pigment quality can be improved in particular by the presence of intermolecular H bridges; examples are provided by the single or double stacked azo pigments (Whitaker) through to benzimidazolone [95]. This is *CI Pigment Red 208*, *CI 12514*, with the commercial name PV-Rot HF2B. The molecules are planar and the layers 4-fold(!), but no longer at a spacing of one axis length, but rather parallel to the crystal surface (0 –2 3). A further publication on a yellow benzimidazolone appeared in ‘‘Farbe and Lack’’ in 1982, [96]. In this case too, apparently, the molecules do not lie parallel to an axis of the unit cell, but rather askew to the axis system. This bears resemblance to *CI Pigment Red 208*.

It could well be, that both intermolecular forces in the lattice are of about equal size and that they ‘‘agree to meet somewhere in the middle’’. In order to reinforce this assumption, the study of more pigment crystals is necessary.

Dioxazine has—in the form of *Pigment Violet 37*, *CI 51345*—experienced an extension, in that it contains substituted $NH_2$ groups and is thus capable of forming intermolecular H bridges [97]. The crystal structure is not described. The principle of intermolecular H bridges was also used successfully on benzimidazolone dioxazine [5], pp. 317–320. Its crystal structure is apparently known, but not published.

The pigment Cromophthalrot A3B, *Pigment Red 177*, *CI 65300*, from the anthraquinone series also forms side-linked intermolecular H bridges in addition to the $\pi\ldots\pi$ stacks. Double layers with $b=0.850$ nm are present in the direction of the stack. However, this pigment belongs to that group, that at the same time also form intramolecular H bridges [98,99]. The individual molecule also displays two peculiarities. The first is that it contains "free" $NH_2$ groups, which as every chemist knows, are very reactive in individual molecules. In spite of this, it belongs in the cromophthal assortment, i.e. to the top group of stable pigments (industrial lacquers, fibre dyes, polyolefin and PVC colorants). It is the only organic pigment with a free $NH_2$ group! The two anthraquinone residues also open themselves just as far as the carbonyl groups permit (~107°). The chemist would say that both of the anthraquinone residues, which are covalently bonded via the 4,4′ position, interact mesomerically and approach planarity as closely as possible.

If one agrees with literature, then one would have to be of the opinion that disazocondensation pigments owe their increased solvent stability exclusively to the doubled molecule [3], p. 380, 10,11]. It was only recently that the question of the crystal structure was thrown up and thus indirectly the subject of intermolecular H bridges [5], p. 206. Within the framework of this report the reader is once more referred to Fig. 1. The disazocondensation pigments were still conceived in the spirit of the chemistry of dyes. Due to their insolubility, however, they are already breathing certain elements of solid-state chemistry.

One of the most important pigment classes with side-linked intermolecular H bridges is that of the quinacridones. Their colour tone lies between yellow and red–violet. An overview is given in the article [100] and modern works in [3], pp. 462–481, [5], pp. 279–306. The colour tones in the region purple, red-violet and yellow, combined with outstanding stability filled a gap in the market. Their crystal structures are known for the most part [101]. More recent papers are [102–105].

The crystal structures of the quinacridones are most completely summarized in [101]. The molecules are exactly planar and form infinite stacks. The characteristic *trans*-position of the NH...CO groups is the reason for **inter**molecular H bridges in the crystal lattice. The spacing of the molecules in the stack is simple (short axis), e.g. in the case of *Pigment Violet 19*, *CI 73900*, $b = 0.3886$ nm, layer spacing = 0.338 nm (beta-modification). Gamma-QA forms a surprising criss-cross angle. The beta-modification, *Pigment Violett 19*, *CI 73900*, crystallizes with $b = 0.3975$ nm, layer spacing = 0.336 nm. The 2,9-dichloro-QA, *Pigment Red 202*, *CI 73907*, crystallizes with $a = 0.3834$ nm, layer spacing = 0.333 nm. The dimethyl-QA, *Pigment Red 122*, *CI 73915*, crystallizes with $a = 0.3901$ nm, layer spacing = 0.342 nm. The four quinacridones are listed in Table 1. It was decided not to take up alpha-quinacridone [103], because although it is an intermediate product, it is not a commercial pigment.

In the QA pigments known to date, single layers are present with strong $\pi \ldots \pi$ charge-transfer forces at work in the stack, probably due to heterocyclic molecules.

The large variety of hues in QA pigments, even with one and the same modification is due to the following

- different particle size, but also
- somewhat different positions of the molecules in the stack, and
- physical mixtures of similar, but not identical crystals.

The crystal structure of the real solutions (mixed crystals) is not known.

From the tetrachloroisoindolinones, the crystal structure of CI *Pigment Yellow 109*, *CI 56284* is known [106]. This significant point is that the entire molecule cannot be planar [107]. The pigment forms a double layer with $c = 0.7226$ nm, see also Fig. 6. Further details will be provided in a later publication [108]. Review articles on tetrachloroisoindolinone pigments can be found in [3], pp. 415–430, [5], pp. 231–249.

A further class of pigments has caused quite a sensation since 1998—the DPPs—the so-called diketopyrrolopyrroles. Reviews appeared in [5], p. 159 and [109]. The DPPs have been well characterized crystallographically (see e.g. [38–40,110–113]). In this case too, $\pi \ldots \pi$ charge-transfer forces are present, however, in the stack *two* different positions of the molecules in the crystal are exchanged [114].

There is a similarity, both chemically and crystallographically, between quinacridones and diketopyrrolopyrroles.

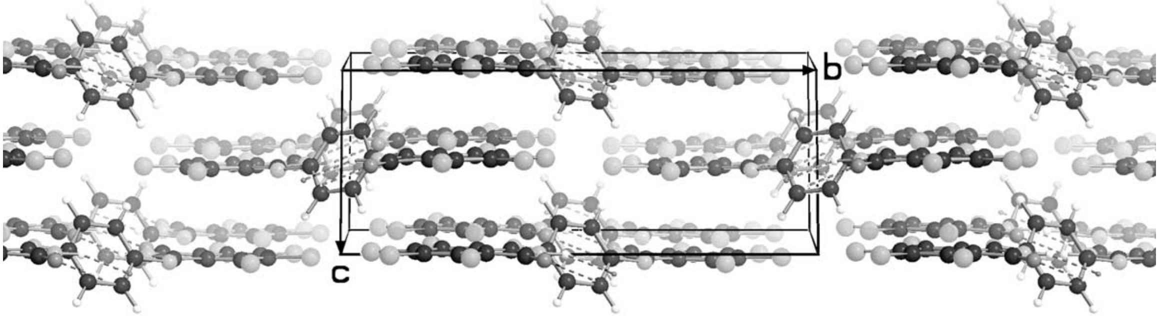

Fig. 6. View on layers of molecules of tetrachloroisoindolinone, beta-modification (made with SCHAKAL 97 by E. Keller, Freiburg (Breisgau), Kristallographisches Institut).

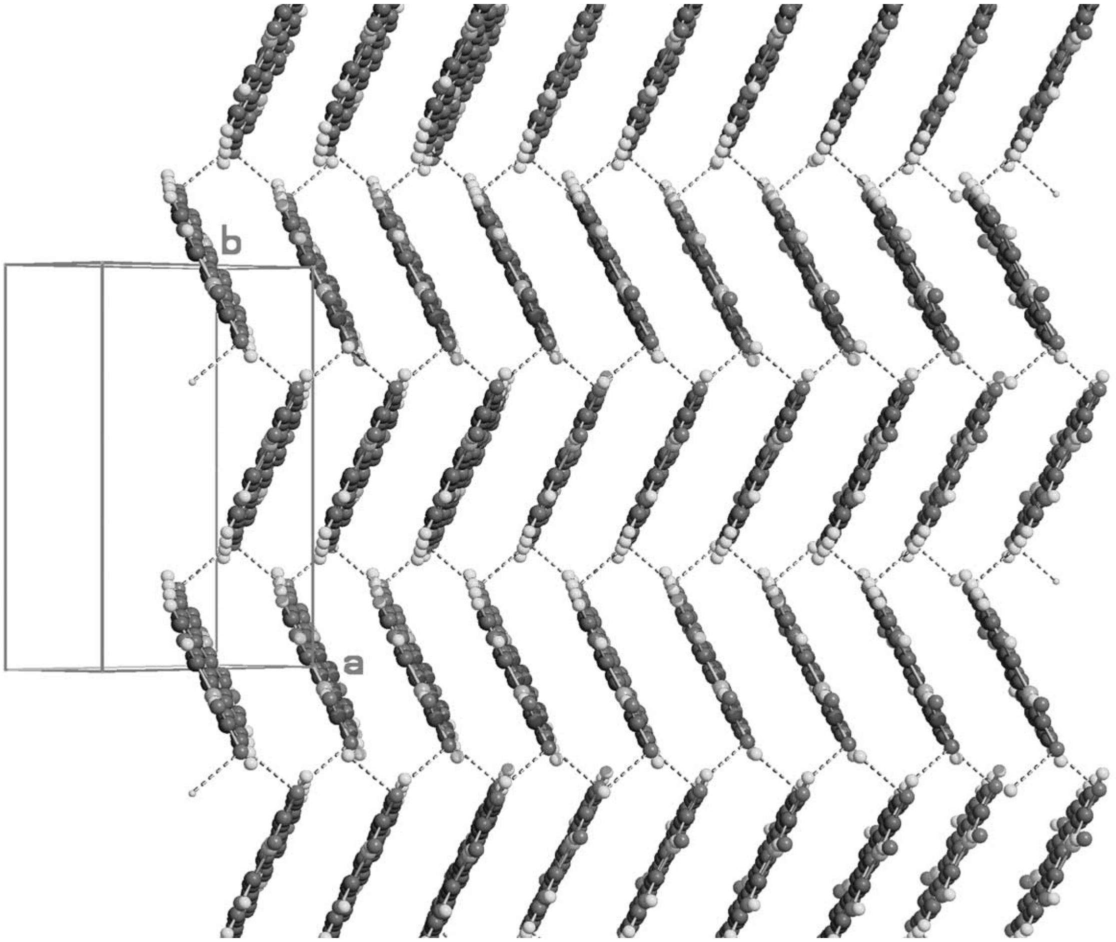

Fig. 7. View on layers of coin-rolled molecules of perylimid (made with SCHAKAL 97 by E. Keller, Freiburg (Breisgau), Kristallographisches Institut).

Disazobenzimidazolone pigments were recently reported by Kaul. In a similar manner, the imidazolone residue can be modified by oxalindione. This leads to the incorporation of an additional cyclic amide group and the pigment becomes even more insoluble [89].

In order to make these changes more tangible for the practical person, one can imagine this type of modification as the application of the new (modified), i.e. mechanically more stable building blocks, from which a more stable wall could be built (see Fig. 2, Section 2.2).

A new group is that of the thiazines (THIs), which were presented by Kaul in [5], pp. 317–330.

The introduction of solid solutions, i.e. the construction of molecular stacks from two or three different organic molecules. These also form $\pi \ldots \pi$ charge-transfer forces and some of them have considerably different colour hues, e.g. in the case of QAs and thiazines. It is interesting to note the H bridges sticking out of the sides and linking to form two-dimensional networks (see also Section 4.1.2).

Mixed crystals of Hansa yellow [70] remind one of lattices with "isolated" individual molecules. New pigments of the mixed crystal type are similar to inorganic alloys. One very well-known pigment of this type is

- Pc blue, which contains partially chlorinated Cu–Pc molecules in a minority proportion in a host lattice of Cu–Pc. This is already a "solid solution".

Molecules of new pigments of the mixed crystal type are for example

- Quinacridone/quinacridone quinone [5], pp. 296–300,
- Thiazine/diketopyrrolopyrrole [5], p. 319,
- Substitution variants of diketopyrrolopyrrole [5], pp. 175–178 or
- Perylene diimide [5], p. 256.

### *4.1.2. Multiple (different) intermolecular H-bridges in the lattice: perylene diimide*

Good overviews on the perylene pigments can be found in [5], p. 249 and [3], p. 482.

Perylene diimide, *P V 29*, *CI 71129*, can be regarded as the mother substance of all perylene pigments. Perylene diimide has a simple layer with $a = 0.4872$ nm [115]. It has an unusual translation and considerably exceeds the beta structure in magnitude (in the sense of Desiraju [7]).

The perylene diimide molecule is completely planar (see Fig. 7, view on the stacked "rolls of money". The linkage of molecules through H bridges over the type CH...OC (see also [7,116]) has today become self-evident. This type of H bridge can be easily recognized by the perpendicular dotted zigzag line in Fig. 7. Further details can be found in the publication [108].

It would of course be very interesting to phenomenologically integrate modern HPPs in this review, but their crystal structures are not yet accessible to the public. It is considered certain, however, that they have a distinct layered lattice, probably with intermolecular H bridges or metal complexes, or both. The interactions in the molecular stack begin with Hansa yellow in the sense of Section 4.1.1, an increase in strength up to the HPPs. Phenomenologically, this is certainly true as regards their pigment character.

## *4.2. Via other contacts*

Any chemist trained in the synthesis of organic molecules would exile intermolecular Cl...Cl contacts to the land of fables (this statement is pure fabrication). This is why Desiraju's monograph is of importance [7], pp. 175–194: "The chloro group may be therefore easily identified as a good 'steering group' in crystal engineering,...", p. 192, and "By implication, Cl...Cl contacts and not C...Cl and hydrogen bonding are the interactions of significance", p. 194.

For this reason, it is fitting to give a pigment example here using a derivative of the long-known thioindigo. It—and indeed all of its derivatives—are vat dyes. Of particular interest is the 4,4′,7,7′-tetrachlorothioindigo (thioindigobordeaux), *Pigment Red 88*, *CI 73312*. This is the only one that substantially fulfills the requirements of the pigment consumer [11]. All other tetrachlorinated thioindigos with displaced Cl atoms on the molecule are less stable with respect to solvents. This is also valid when one Cl atom is removed from or added to the thioindigobordeaux molecule. It would appear logical to infer that, within the crystal lattice, Cl...Cl contacts are sterically favourable so that the molecular stacks can be connected to one another in a stable manner and thus serve additionally to stabilize the crystal (the pigment). See also Fig. 1, starting point 4.3.

> ***Crystal engineering is, in reality, crystal synthesis and one tries therefore to design and construct a crystal structure with specified physical and chemical properties...So, while classical structure determination ends with the list of (x, y, z) of all the atoms in the asymmetric unit, crystal engineering begins at this point [117].***

## 5. Conclusion

A basic publication by Desiraju and Gavezzotti [74] is fundamental for the evaluation of van der Waals forces between planar molecules within the stack. It is possible to discern from this, that molecular stacks with short axes belong to the $\pi...\pi$ charge-transfer type and not to the van der Waals type [75].

Modern organic pigments are, in a subtle way, "walls" made up of building blocks (molecules). **Chemistry and crystallography are prerequisites for understanding the fastness and stabilities. The latter go far beyond the limits of known chemistry and crystallography, however**. The resolution of a previously unknown crystal structure is thus an additional bridge that is crossed on the way to understanding organic solids.

It is often a source of amusement for the author of these lines when he sees in otherwise first-class publications that scientists make no distinction between dyes and pigments. It is admittedly only through the technology of dyes and pigments, i.e. the industrial application, that the difference becomes apparent. **If academic research makes no distinction between dyes and pigments, then it will not find one**.

The publications considered here [3,5] describe organic pigments from the point of view of individual molecules and syntheses, and these justifiably play a central role. Even modern overviews on the coloration of synthetic materials with organic pigments limit themselves to the classification according to individual molecules [16].

This is of great importance—possibly even a prerequisite—for the comprehension of the rudimentary conception presented here from the solids point of view. There is no doubt that the art of the pigment chemist in organic synthesis imparts the creative spirit to the field of pigments. It should not be surprising, therefore, that many synthesis chemists point to the relationship to dyes and consider pigment dyes as "their" field. Even extremely insoluble pigments (e.g. QA, Pc, DPP) still retain some of the character of the individual molecule: How else could such pigments be soluble in certain solvents (e.g. $H_2SO_4$) and yet still be able to recrystallize? However: The synthesis route itself lays down the subsequent aftertreatment method, and it is crystals that are subject to this treatment—not individual molecules.

From the point of view of material science, the interdisciplinary character of organic solid-state chemistry—of which organic pigments are just one constituent—has to be expressly emphasized. One should remember that the chemistry of colors has always had fascinating aspects and was once the basis of technical chemistry—indeed the very origin of the chemical industry itself. Perhaps organic pigments will also prove to be the basis for something completely new.

Until now, only Desiraju has systematically studied and summarized "organic solid-state *chemistry*", and he has done this in deliberate analogy to "inorganic solid-state *chemistry*" [7]. His anomalous perception is expressed in the words:

> *However, the concept that the molecule is at the 'heart of chemistry' is so deeply ingrained that drawing a distinction between intramolecular and intermolecular properties has become almost an act of faith for chemists* [7], p. 27.

With reference to pigments in their entirety, one can say positively that pigments form a bridge between inorganic and organic chemistry—but a bridge that does not separate the two parts, but rather connects them.

One can only hope that crystal engineering will provide an impulse to create new pigment classes and also new pigment variants. If it should prove possible to reduce the number of compounds to be synthesized, while at the same time retaining the same number of technically useful pigments (hits), then this would be a result of more theory and less empirical work in pigment research.

The smaller a molecule and the more insoluble the related crystal lattice, the simpler are the rules that govern its properties. This was valid for benzene and it is valid for the individual molecule of quinacridone up to the associated leaflike structure.

This last point of view in particular is an extreme one. But the creation of ever more stable and insoluble pigments infers a continual convergence on the world of graphite. This convergence finds its limit in that selectively absorbing compounds are desired and are to be prepared. With regard to stability and total absorption of light, carbon black remains unmatched.

Due to reasons of conciseness, many publications that would further clarify the soluble–insoluble dichotomy could not be mentioned here. The interested reader is referred to the articles [118–127]. All literature on pigments in connection with crystallinity will be taken into consideration in a future article.

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## Appendix A. Association of dyes

Complete experimental studies on associations of dyes on X-rays have been made by the team around Kratky “Putting it in the molecular terms: The ribbon-like molecules with their large surface arranged to one another such that the length and breadth of the aggregates are determined by the length and breadth of the molecule, whereas the thickness of the aggregate is determined by the number of molecules connected [118–120].

## Appendix B. Scheibe polymers

Scheibe polymers contain a higher degree of aggregation of the individual molecules (dyes). “. . .that one is dealing in the case of these polymers with high molecular entities, that are formed by stacking several thousands to several millions of plate-like dye molecules on top of one another” [121–123]. Fig. 8 has been taken from [123].

## Appendix C. Decomposition of pigments to dyes

See [124,125].

## Appendix D. Soluble quinacridones

The importance of Fig. 1, starting point ⑥, becomes clear thanks to two publications [126,127]. The authors synthesized soluble quina-

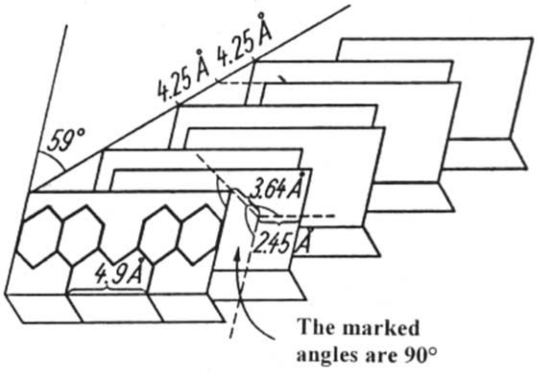

Fig. 8. View on a stack of molecules of pseudoisocyanine (G. Scheibe) [courtesy Wiley-VCh, Publ. GmbH & Co. KgaH, Weinheim (Germany). Zeitschr. fur Elektrochemie 1952; 56:727].

cridones by substitution of the H atoms at the 2- and 9-positions with dodecyloxy groups $O–C_{12}H_{26}$ (alkoxy groups). The aim was to process the **quinacridone solutions** for the preparation of light-emitting materials by means of spin-coating or solution casting. From the technical point of view, the opposite of insolubility can thus also be very important.

This is a shining example for the validity of the principles of organic chemistry within this survey.

## References

[1] Klages F. Lehrbuch der organischen Chemie, vol III. Berlin: Walther de Gruyter; 1967.

[2] Griffiths J. In: Griffiths J, editor. Developments in the chemistry and technology of organic dyes. Blackwell Scientific; 1984. p. 1–30.

[3] Herbst W, Hunger K. Industrielle organische pigmente. Weinheim: VCH; 1995.

[4] Herbst W, Hunger K. In: Elvers B, Hawkings St, Schulz G, editors. Ullmann's encyclopedia. 5th ed. VCH; 1992. p. 213–42.

[5] Smith HM, editor. High performance pigments. Weinheim: Wiley-VCH; 2001.

[6] Krieg GK. Einführung in die DIN-Normen. Berlin: Beuth; 1989.

[7] Desiraju GR. Crystal engineering. Amsterdam: Elsevier; 1989.

[8] Taylor R, Kennard O, Versichel W. Geometry of the N-H...O = C hydrogen bond lone pair directionality. J Am Chem Soc 1983;105:5761–6.

[9] Desiraju GR. Crystal engineering: outlook and prospects. Current Science 2001;81:1038–42.

[10] Schmid M. Neue organische Pigmentfarbstoffe, ihre Herstellung und Anwendung. Defazet 1955;9:252–5.

[11] Gaertner H. Modern chemistry of organic pigments. JOCCA 1963;46:13–46.

[12] Geissler G. Fortschritte in der Entwicklung von Azopigmenten. Verbesserung der Lösemittelechtheit. Defazet 1973:464–73.

[13] Geissler G. Überblick über die Geschichte der organischen Pigmente. Defazet 1977;31:190–6.

[14] Dietz E, Fuchs O. Neue echte Monoazopigmente. Farbe + Lack 1973;79:1058–63.

[15] Kaul BL. Milestones in the pigmentation of coloured paints. In: 22nd Proc. 18th Fatipec Congress, vol. 3, Venice, 1986. p. 73–93.

[16] Kaul BL. Coloration of plastics using organic pigments. Rev Prog Coloration 1993;23:19–35.

[17] Desiraju GR. The intermolecular concept as a bridge between organic, inorganic and organometallic crystal chemistry. J Mol Struct 1996;374:191–8.

[18] Baier E. Ueber die Duennschichtchromatographie organischer Pigmente. Farbe + Lack 1974;80:614–28.

[19] Baier E. Einige Betrachtungen zur Temperaturbestaendigkeit organischer Pigmente. Farbe + Lack 1977;83:599–610.

[20] Radtke V. In: Bartz WJ, editor. Pigmente + Farbstoffe in der Lackindustrie. Ehningen (Germany): Expert Publishing, 1992. p. 134.

[21] Brockhaus FA, editor. Mauerwerk, vol. 14. Bibliographisches Institut & F.A. Brockhaus; 1991. p. 324.

[22] Desiraju GR, Steiner T. The weak hydrogen bond in structural chemistry and biology. Oxford: University Press; 1999.

[23] Steiner T, Desiraju GR. Distinction between the weak hydrogen bond and the van der Waals interaction. Chem Commun 1998:891–2.

[24] (a) Schmidt MU. Kristallstrukturen organischer Pigmente aus Pulverdiagrammen. Nachrichten aus der Chemie 2002;50:812–8 [referring to];
(b) Schmidt MU. Dye and pigment chemistry. In: Griffiths J, editor. Colour science 98, vol. 1. University of Leeds; 1999. p. 72–81.

[25] Schmidt MU. In: Braga D, Orpen G, editors. Crystal engineering: from molecules and crystals to materials. Dordrecht: Kluwer; 1999. p. 331–48.

[26] (a) Robertson IM. An X-ray study of the structure of the phthalocyanines part 1. J Chem Soc 1935:615–21;
(b) Robertson IM. An X-ray study of the phthalocyanines part 2. J Chem Soc 1936:1195–209;
(c) Robertson IM. An X-ray study of the phthalocyanines part 3. J Chem Soc 1937:219–31;
(d) Robertson IM. An X-ray study of the phthalocyanines part 4. J Chem Soc 1940:36–48.

[27] Linstead RP, Robertson IM. The stereochemistry of metallic phthalocyanines. J Chem Soc 1936:1736–8.

[28] Sarma JA, Desiraju GR. The supramolecular synthon approach to crystal structure prediction. Crystal Growth Des 2002;2:93–100.

[29] Desiraju GR. In: Desiraju GR, editor. The crystal as a supramolecular entity, perspectives in supramolecular chemistry, vol. 2. Chichester: John Wiley and Sons; 1996. p. IX–XI.

[30] Graser F, Hädicke E. Kristallstruktur und Farbe bei Perylen-3,4:9,10-bis(dicarboimid)-Pigmenten. Liebigs Ann Chem 1980:1994–2011.

[31] Klebe G, Graser F, Hädicke E, Berndt J. Crystallochromy as a solid state effect. Acta Cryst 1989;45:66–77.

[32] Freeman HC Jr, editor. In: DUPONT Innovation, vol. II, DUPONT, 1970. p. 14–7.

[33] Lincke G. A review of thirty years of research on quinacridones X-ray crystallography and crystal engineering. Dyes Pigments 2000;44:101–21.

[34] See [14].

[35] Paulus EF, Hunger K. Ueber die Molekuel- und Kristallstruktur eines roten Mono-“azo”-Pigmentes. Farbe + Lack 1980;86:116–20.

[36] Hunger K, Paulus EF, Weber D. Ueber die Molekuel- und Kristallstruktur gelber Mono-“azo”-Pigmente. Farbe + Lack 1982;88:453–7.

[37] Lincke G. Strukturelle Betrachtungen zur Kristallsation der Chinacridone. Farbe + Lack 1970;76:764–75.

[38] Mizuguchi J, Grubenmann A, Wooden G, Rihs G. Structures of 3,6-diphenylpyrrolo[3,4-c] pyrrole-1,4-dione and 2,5-dimethyl-3,6-diphenylpyrrolo[3,4-c] pyrrole-1,4-dione. Acta Cryst 1992;B48:696–700.

[39] Mizuguchi J, Grubenmann A, Rihs G. Structures of 3,6-bis(3-chlorophenyl)pyrrolo[3,4-c]pyrrolo-1,4-dione and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrolo-1,4-dione. Acta Cryst 1993;B49:1056–60.

[40] Mizuguchi J. Correlation between crystal and electronic structures in diketopyrrolopyrrole pigments as viewed from exciton coupling effects. J Phys Chem A 2000;104:1817–21.

[41] Schmidt G. Photodimerisation in the solid state. Pure Appl Chem 1971;27:647–78.

[42] Bolton W. The crystal structure of isoviolanthrone. Acta Cryst 1964;17:1020–4.

[43] Gribova EF, Zhdanow GS, Gol‘der GA. An X-ray structural study of indigo and thioindigo. Soviet Physics Crystallography 1956;1:39–43.

[44] Süsse P, Wäsche R. Parallel molecular arrangement in the crystal structure of 6,6′-dichloro-indigo. Naturwiss 1978;65:157.

[45] Haase-Wessel W, Ohmasa M, Süsse P. Thioindigo: crystal strucural data for modification II. Naturwiss 1977;64:435.

[46] Süsse P, Crampe C. 6,6′-dibromo-indigo, a main component of tyrian purple. Naturwiss 1979;66:110.

[47] Stadtler HP. The crystal structure of flavanthrone. Acta Cryst 1953;6:540–2.

[48] Bailey M. The crystal structure of indanthrone. Acta Cryst 1955;8:182–5.

[49] Grainger CT, Mc Connell JF. The crystal structure of 1-p-nitrobenzeneazo-2-naphthol (para red) from overlapped twin-crystal data. Acta Cryst 1969;B25:962–70.

[50] Whitaker A. The crystal structure of a second polymorph (β) of C.I. pigment red 1,1-[(4-nitrophenyl)azo]-2-naphthol. Zeitschr Krist 1980;152:227–38.

[51] Whitaker A. The crystal structure of a third polymorph (γ) of C.I. pigment red 1, 1-[(4-nitrophenyl)azo]-2-naphthol. Zeitschr Krist 1981;156:125–36.

[52] Kobelt D, Paulus EF, Kunstmann W. Röntgeneinkristallstrukturanalyse eines Chlorderivates von Permanentrot FRLL. Zeitschr Krist 1974;139:15–32.

[53] Whitaker A. The crystal structure of aceto-acetanilide azo-pigments II. C.I. Pigment Yellow 6. Zeitschr Krist 1983;163:139–49.

[54] Kobelt D, Paulus EF, Kunstmann W. Röntgeneinkristallstrukturanalyse von 1-(2,5-Dichlorphenylazo)-2-hydroxy-3-naphthoesäure-(4-chlor-2,5-dimethoxy-anilid) (Chlorderivat von Permanentbraun FG). Acta Cryst 1972;B28:1319–24.

[55] Yase K, Yasuoka N. Structure of metal-free phthalocyanine stabilized by the addition of its 4-chloroderivative. Acta Cryst 1988;C44:514–6.

[56] Hädicke E, Graser F. Structures of eleven perylene-3,4:9,10-bis(dicarboximide) pigments. Acta Cryst 1986; C42:189–95.

[57] Whitaker A. The crystal structure of C.I. Pigment Red 2. Zeitschr Krist 1977;146:173–84.

[58] Whitaker A. The crystal structure of C.I. Pigment Red 3. Zeitschr Krist 1978;147:99–112.

[59] Whitaker A. The crystal structure of C.I. Pigment Red 6. Zeitschr Krist 1977;145:271–88.

[60] Whitaker A. crystal structure analysis of azo pigments involving β-naphthol: a review. JSDC (Communications) 1978:431–5.

[61] Mez HC. Zwei planare Farbstoffmolekuele mit intramolekularen Wasserstoffbrueckenbindungen. Ber Bunsenges Phys Chem 1968;72:389–93.

[62] Whitaker A. The crystal structure of aceto-acetanilide azo-pigments III C.I. Pigment Yellow 1. Zeitsch Krist 1984;166:177–88.

[63] Paulus EF. Molecular and crystal structure of C.I. pigment yellow 1. 11680, (Hansagelb G). Zeitsch Krist 1984; 167:65–72.

[64] Brown CJ, Yadav HR. α-(4-Methyl-2-nitrophenylhydrazono)acetoacetanilide, $C_{17}H_{16}N_4O_4$. Acta Cryst 1984; C40:564–6.

[65] Whitacker A. The crystal structure of aceto-acetanilide azo-pigments VI C.I. Pigment Yellow 4. Zeitsch Krist 1985;171:7–15.

[66] Whitaker A. The crystal structure of aceto-acetanilide azo-pigments VII a polymorph (α) of C.I. Pigment Yellow 5. Zeitsch Krist 1985;171:17–22.

[67] Whitaker A. The crystal structure of aceto-acetanilide azo-pigments IV C.I. pigment yellow 98. Zeitsch Krist 1984;167:225–33.

[68] Paulus EF, Rieper W, Wagner D. Molecular and crystal

structure of two hydrazone pigments. Zeitschr Krist 1983;165:137–49.

[69] Whitaker A. The crystal sructure of, C. I. Pigment Yellow 3. Zeitschr Krist 1983;163:19–30.

[70] Whitaker A. The crystal structure of aceto-acetanilide azo-pigments, V. Hansa Yellow 5G, a mixed crystal. Zeitschr Krist 1985;170:213–23.

[71] Whitaker A. 583 Pigment Yellow GG. A mixed crystal of CI Pigment Yellow 6 and α-CI Pigment Yellow 5. Acta Cryst 1986;C42:1566–9.

[72] Whitaker A. Crystal structures of azo pigments derived from acetoacetanilide. JSDC 1987;104:294–300.

[73] Paulus EF, Rieper W. Derivatives of hydrazone acetoacetyl anilide. Acta Cryst 1984;A40(Suppl):C-277.

[74] Desiraju GR, Gavezzotti A. From molecular to crystal structure: polynuclear aromatic hydrocarbons. J Chem Soc, Chem Commun 1989:621–3.

[75] Desiraju GR. Private commnication, July 2002, University of Hyderabad, India.

[76] Barrow MJ, Christie RM, Lough AJ, Monteith JE, Standring PN. The crystal structure of, C. I. Pigment Yellow 12. Dyes and Pigments 2002;45:153–60.

[77] Hädicke E, Graser F. Structures of three perylene-3,4:9,10-bis(dicarboximide) pigments. Acta Cryst 1986; C42:195–8.

[78] Engel MK. Single crystal and solid state molecular structures of phthalocyanine complexes. Kawamura Rikagaku Kenkyusho Hokoku 1997;8:11–54 [in English].

[79] Honigmann B. Modifikationen und physikalische Formen organischer Pigmente. Farbe + Lack 1964;70:787–91.

[80] Honigmann B, Lenné HU, Schrödel R. Beziehungen zwischen den Strukturen der Modifikationen des Platin- und Kupferphthalocyanins und einiger Chlorderivate. Zeitsch Krist 1965;122:85–205.

[81] Brown CJ. Crystal structure of platinum Phthalocyanine: a re-investigation. J Chem Soc (A) 1968:2488–93.

[82] Brown CJ. Crystal structure of β-copper phthalocyanine. J Chem Soc (A) 1968:2494–8.

[83] Irving H, Williams RJP. Order of stability of metal complexes. Nature 1948;162:746–7.

[84] Irving H, Williams JRP. The stability of transition-metal complexes. J Chem Soc 1953:3192–210.

[85] Krebs H. Grundzüge der Anorganischen Kristallchemie. Stuttgart: Enke; 1968.

[86] Kirkland EJ. Nonlinear high resolution image processing of conventional transmission electron micrograpgs. Ultramicroscopy 1982;9:45–64.

[87] Saito Y, Shiojiri M. Molecular energetics of the epitactical growth of chlorinated copper phthalocyanine on KCl surfaces. J Cryst Growth 1984;67:91–6.

[88] Dorset DL. The accurate electron crystallographic refinement of organic structures containing heavy atoms. Acta Cryst, A 1997;53:356–65.

[89] Kaul BL. In: Intertech editor. High performance pigments. A review of progress in chemistry, technology, application and delivery systems of high performance pigments. 19 Northbrook Drive, Portland, ME 04150, USA: 2000.

[90] L'Eplattenier FA, Frey C, Rihs G. Metallkomplexe von N-substituierten 3-Imino-isoindolinonen. Helv Chim Acta 1977;60:697–709.

[91] Frey C, Lienhard P. In: Schweizerische Vereinigung der Lack- und Farbenchemiker, editor. XVII. Congress Fatipec Lugano: 1984;283–301.

[92] Kennedy AR, McNair C, Smith WE, Chisholm G, Teat SJ. The first red azo lake pigment whose structure is characterized by single crystal diffraction. Ang Chem Int Ed 2000;39:638–40.

[93] Whitaker A. Acta Cryst 1987;C43:2137–41.

[94] Whitaker A. C.I. Pigment Yellow 74, α-(2-methoxy-4-nitrophenylhydrazono)-α-aceto-2′-methoxyacetanilide. Acta Cryst 1987;C43:2141–4.

[95] Paulus EF. Molecular and crystal structure of, C.I. Pigment Red 208, 12514 (PV-Rot HF2B). Zeitschr Krist 1982;160:235–43.

[96] Hunger K, Paulus EF, Weber D. Ueber die Molekuel- und Kristallstruktur gelber Mono-"azo"-Pigmente. Farbe + Lack 1982;88:453–8.

[97] Pugin A. The influence of the chemical structure on the color and properties of dioxazine pigments. Off Dig Fed Soc Paint Tech 1965;37:782–802.

[98] Kojama H, Scheel HJ. The crystal structure of 4,4′-diamino-1,1′-bianthraquinone, $C_{28}H_{16}N_2O_4$. Zeitsch Krist 1969;130:405–19.

[99] Lincke G. Stuart-Briegleb-Kalotten als Arbeitshilfe beim Studium des Kristallbaus von 4,4′-Diamino-1,1′-dianthrachinonyl Eine Anwendung der Dichtpackungs-methode auf Cromophtalrot A3B. Chem Zeitg 1984;108:177–84.

[100] Jaffe EE. Quinacridone and some of its derivatives. Surface Coatings Int 1967;75:24–31.

[101] Paulus EF, Dietz E, Kroh A, Prokschy F, Lincke G. In: Winiti, editor. 12th European Crystallographic Meeting, Moscow, 1989. Collected papers: Collected abstr. vol. 2. p. 23–24.

[102] Potts GD, Jones W, Bullock JF, Andrews SJ, Maginn SJ. The crystal structure of quinacridone: an archetypal pigment. J Chem Soc Chem Commun 1994:2565–7.

[103] Lincke G, Finzel HU. Studies on the structure of alpha-quinacridone. Cryst Res Technol 1996;31:441–52 , 31: 658.

[104] Lincke G. The quinacridones: structure and colour: a study by powder diffraction. J Mat Sci 1997;32:6447–51.

[105] Mizuguchi J, Sasaki T, Tojo K. Refinement of the crystal structure of 5,7,12,14-tetrahydro[2,3-b]-quinolinoacridine (γ-form), $C_{20}H_{12}N_2O_2$ at 223 K. Zeitsch Krist NCS 2002; 217:249–50.

[106] Private communication, 2002. Ich danke Herrn Dr. O. Wallquist, CIBA Spezialitätenchemie, Basel (Schweiz), für die Genehmigung zur Bekanntgabe dieses Ergebnisses.

[107] Pugin A, von der Crone J. Chemie und eigenschaften von neuen Pigmenten der 4,5,6,7-tetrachlorisoindolin-1-on-Reihe. Farbe + Lack 1966;72:206–17.

[108] Lincke, G. Dyes Pigments [in preparation].

[109] Iqbal A, Cassar L, Rochat AC, Pfenninger J, Wallquist O. New heterocyclic pigments. J Coat Techn 1988;60:37–45.

[110] Mizuguchi J, Wooden G. A large bathochromic shift from the solution to the solid state in 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-c]-pyrrole. Ber Bunsenges Phys Chem 1991;95:1264–74.

[111] Mizuguchi J, Arita M, Rihs G. A new crystal structure of 3,6-diphenylpyrrolo[3,4-c]pyrrolo-1,4-dithione. Acta Cryst 1991;C47:1952–6.

[112] Mizuguchi J, Rihs G. Electronic spectra of 1,4-diketo-3,6-diphenyl-pyrrolo-[3,4-c]-pyrrole in the solid state. Ber Bunsenges Phys Chem 1992;96:597–606.

[113] Mizuguchi J. 3,6-Bis(4-tert-butylphenyl)-1,2,4,5-tetrahydropyrrolo[3,4-c]pyrrole-1,4-dione. Acta Cryst 1998; C54:1482–4.

[114] Mizuguchi J. Correlation between crystal and electronic structures in diketopyrrolopyrrole pigments as viewed from exiton coupling effects. J Phys A 2000;104:1817–21.

[115] Erk P. Private communication 1999. Ludwigshafen (Germany): BASF; 1999.

[116] Desiraju GR. The C-H...O hydrogen bond in crystals: what is it? Acc Chem Res 1991;24:290–6.

[117] Desiraju GR. Crystallography. Quo vadis? Zeitschr Krist 2002;217:297–8.

[118] Kratky O, Ledwinka H, Pilz I. Röntgenkleinwinkeluntersuchungen an Lösungen von β-Naphtholorange. Die Makromolekulare Chemie 1967;105:171–92.

[119] Kratky O, Ledwinka H, Pilz I. Röntgenkleinwinkeluntersuchungen unter Verwendung der absoluten Streuintensität an Lösungen des Azofarbstoffes Chlorantinlichtviolett 2RLL. Ber Bunsenges Phys Chem 1966; 70:904–12.

[120] Kratky O. Röntgenkleinwinkelstreuung zur Erforschung von Faserfeinstrukturen. Austria: Universitaet Graz Selbstverlag; 1972.

[121] Hoppe W. Über eine aus dem reversibel polymeren Zustand von N-N′-diethylpseudoisocyaninsalzen entstehende kristallinische Modifikation. Kolloid-Zeitschrift 1942;101:300–5.

[122] Hoppe W. Beziehungen zwischen Struktur und Lichtabsorption der reversiblen Polymerisate aus der Pseudoisicyaninreihe. Kolloid-Zeitschrift 1944;109:21–37.

[123] Scheibe G. Zum Problem der photochemischen Sensibilisierung. Zeitschr Elektrochem 1952;56:723–8.

[124] Herrmann E. Kunststoffeinfärbung. Speyer am Rhein. Zechner and Hüthig; 1976.

[125] Kaufmann G. In: Bildungswerk VDI, editor. Bildungswerk BW 1520. Düsseldorf: Einfärben von Kunststoffen; 1969.

[126] Keller U, Muellen K, de Feyter St, Frans Schryer F. Hydrogen-bonding and phase-forming behaviour of a soluble quinacridone. Adv Mater 1996;8:490–3.

[127] Geerts Y, Keller U, Scherf U, Schneider M, Muellen K. New organic light emitting materials. Polym Prep Am Chem Soc Div Polym Chem 1997;38:315–6.