Dyeing Crystals

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I. Introduction

A. Dye Inclusion Crystals

Virtually every civilization has developed or appropriated technologies for dyeing animal or vegetable fibers; we desire the sensation of color. The historian of chemistry, Partington, made this point with the all too imperial observation, "Although savage peoples prefer music in the minor key, their colours are always bright".[2] The dyeing of textiles and parchments are protochemistries, technologies that encouraged an exploration of the material world and served as a foundation for the modern chemical sciences.[3] On the other hand, we do not often practice the dyeing of crystals. The reason for this distinction seems plain: fibrous materials such as wool, silk, cotton, wood pulp, or papyrus have large surface area-to-mass ratios compared with polyhedral crystals. However, the surface area of a *growing* crystal, the sum of the surface areas after the accretion of each new ionic or molecular layer, is enormous. For instance, the surface area of a 1 cm^3 cube is only 6 cm^2, while the surface area computed as a sum following the addition of each new 10 Å layer to a 1000 $Å^3$ seed is 10^9 cm^2.

As a matter of fact, one can find in the descriptive crystallographic literature of the last 150 years examples of simple transparent crystals stained by dyes during growth from solution. When dyes express different affinities for the various facets of a growing crystal, they produce striking patterns of color that are determined by the host crystal's symmetry. Since many faces are pairwise related to one another in centrosymmetric crystals, one frequently observes "bow-tie" patterns. Gypsum ($CaSO_4 \cdot 2H_2O$) stained by eosin, drawn by Vater in 1900,[4] is a typical example (Figure 1a). (Structures for dyes can be determined from Table 1 in section III.B by identifying the crystal with which they are associated, choosing the common names from the alphabetical list that follows, and then interpreting the associated symbolic names with Scheme 1.) For obvious reasons, Pelikan referred to the aforementioned figures as *sanduhrförmig* or more

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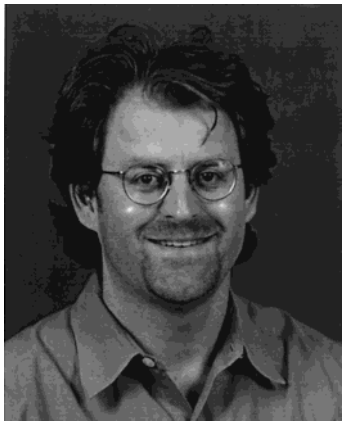


Bart Kahr was born in New York City in 1961. He attended Middlebury College in Vermont where he was introduced to research in chemistry by I. David Reingold. His graduate studies of the stereochemistry of unusual molecules with Kurt Mislow at Princeton University were followed in 1988 by postdoctoral research in crystal chemistry at the Yale University laboratory of J. Michael McBride. After two years he joined the faculty of Purdue University but spent 1996 in the New York City Public Library, where he collected some of the material for this review. In 1997, he moved to Seattle, where he is currently Professor of Chemistry at the University of Washington. His research group is studying the growth, structure, and physical properties of crystalline materials, with generous support from the U.S. National Science Foundation.

Richard W. Gurney was born in Chicago in 1972 and received his undergraduate degree from Illinois Benedictine College, also in Chicago. He was awarded his Ph.D. degree by Purdue University for research on mixed crystal growth carried out in the laboratories of Bart Kahr, in part in West Lafayette, IN, and in Seattle, WA. During this time he received an Alumni Award for teaching excellence. He is currently a postdoctoral research fellow in the laboratories of Meir Lahav and Leslie Leiserowitz at the Weizmann Institute of Science in Rehovot, Israel, where is studying stereoselective processes in two-dimensional crystals. He dedicates this review to the memory of Walter Jerome Zalarski.

commonly in English *hourglass inclusions*.[5] This label is not descriptive when other patterns emerge in high-symmetry hosts, like Maltese crosses (Figure 1b). Therefore, we adopt the general term *dye inclusion crystal* (DIC) for otherwise transparent single crystals that contain chromophores or luminophores oriented during growth from solution.

Colorful dyed crystal polyhedra naturally attracted the attention of scientists of past generations. However, they were more than artificial gems. Since neither the presumed shape nor the constitutions of the dye molecules were similar to the host molecules or ions, dyed crystals seemed to violate Mitscherlich's principle of isomorphism,[6] a cornerstone of structural crystallography. This inconsistency was the focus of much research on DICs. How did a dye molecule adopt an oriented position within an otherwise close-packed single crystal? How was the crystalline host able to accommodate these seemingly obtrusive impurities? What did such crystals mean for the developing science of crystal structure analysis?

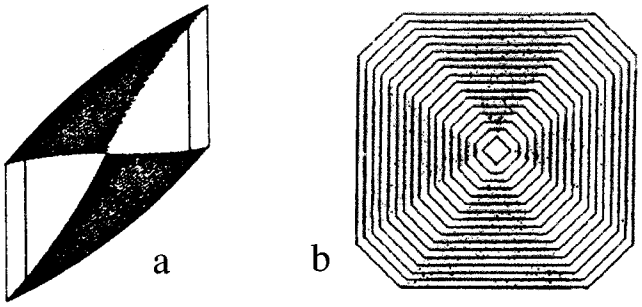


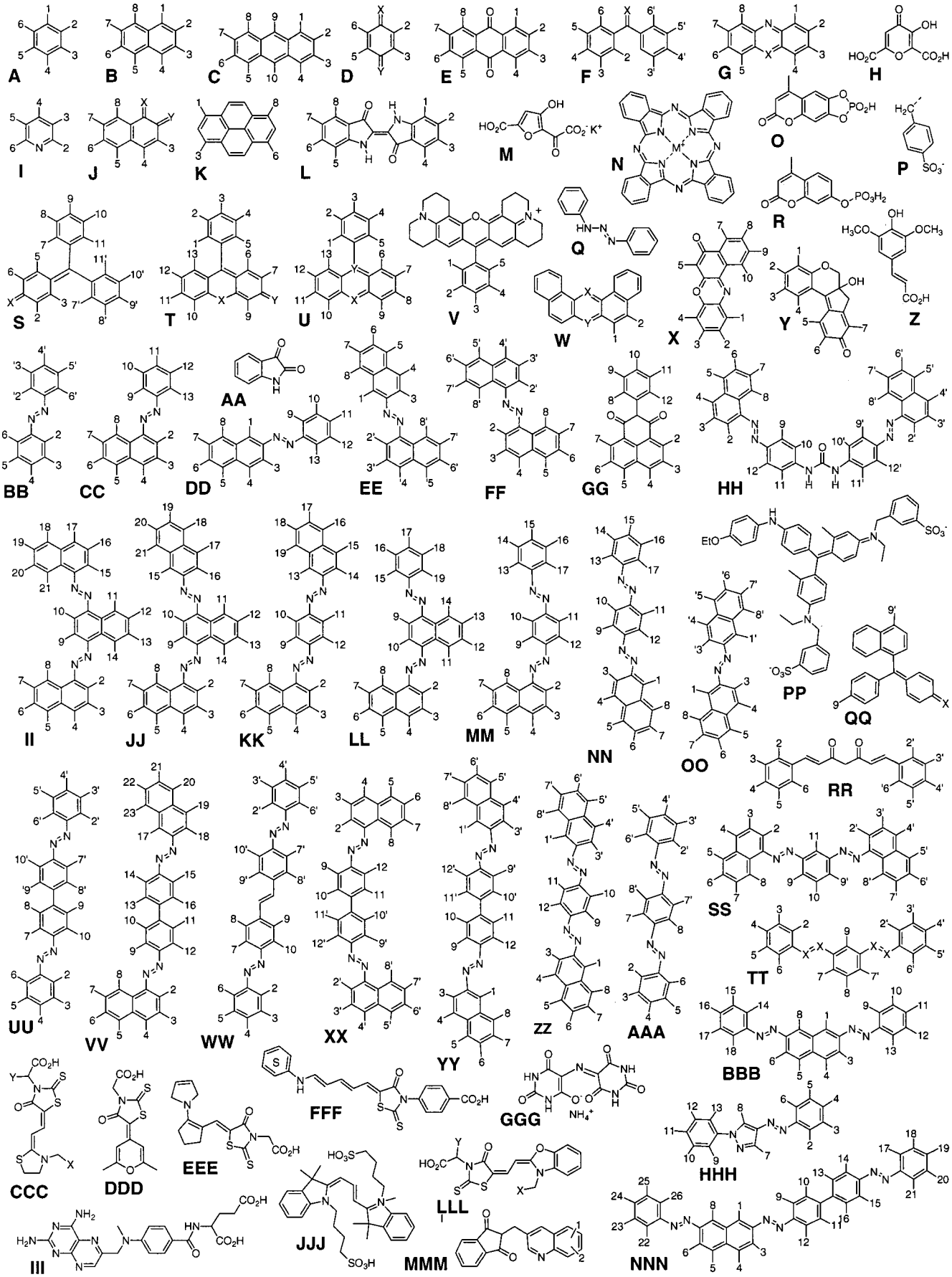
Figure 1. (a) Idealized representations of dyed crystals. (a) *Hourglass*: gypsum stained by eosin.[4] (Reprinted with permission from ref 4. Copyright 1900 Oldenbourg Wissenshaftsverlag, München.) (b) *Maltese cross*: barium nitrate stained with methylene blue.[187] (Reprinted with permission from ref 187. Copyright 1930 Manchester Literary and Philosophical Society, Manchester.)

In addition to violations of the principle of isomorphism, a variety of other scientific and technological concerns motivated research on dyeing crystals including the following: the nature of pleochroism, mechanisms of crystal growth, silver halide photosensitization, ceramics crystallization, colloid stabilization, habit modification, epitaxy, explosives preparation, and kidney stone inhibition, among others. In cursorily reviewing some of this territory, in 1959 Slavnova remarked that "the extensive topical literature is extremely scattered. It lacks a common purpose, and even a common terminology, so it is very difficult to survey".[7] Other reviews that in part cover some aspects of DICs include those by the following: Johnsen,[8] Gaubert,[9] Bunn,[10] Seifert,[11−13] Neuhaus and Spangenberg,[14,15] France,[16] and Buckley.[17]

Dyed crystals have not been objects of systematic study for several generations, but they will undoubtedly appeal to a new generation of scientists because of their rich stereochemistry and because transparent crystals containing oriented, monodispersed, organic dyes promise spectroscopic and photonic applications. Here we present an account of DICs including their emergence, disappearance, and restoration in the laboratory. This review assembles previous observations that make up the history of dyed crystals and translates the descriptive crystallographic observations of past generations into a form that may be readily applied by the modern researcher. We present recent contributions on dyed sulfates, chromates, phosphates, carboxylates and carboxylic acids, carbonates, nitrates, halates, halides, amines, amides, and sugars, and show how dyed crystals address issues of interest to contemporary crystallographers, materials scientists, and spectroscopists as well as physical organic, analytical, biostructural, and stereochemists. We have included a comprehensive table (Table 1) of dyed crystals in section III.B.

The material is divided between historical and contemporary studies. In many ways, this distinction

Scheme 1. Dye Frames with Codes for Substituent Positions



is an arbitrary one—the organization is not strictly temporal and narrative considerations are responsible for some overlap—but generally speaking, we have included in the historical section those studies

carried out before 1950, a time after which DICs ceased to be a subject for systematic research.

B. What This Review Excludes

What makes a "dyed crystal" is certainly open to interpretation. Here, we place justifiable and necessary limits on this review by excluding a variety of materials, apologizing to those whose work falls outside of the adopted definition. The citations in this section are meant to be illustrative rather than exhaustive; elsewhere we strive for completeness.

By dyeing, we typically mean a process whereby the absorbing properties of some support are modified, for example, by mordanting, so as to fix a colorant by means of a stable chemical union. In DICs, dyes are fixed by a growing crystal which plays the roles of support and mordant. Painted or casually applied colors cannot be described in this way.

For the purposes of this review, a dye is any water-soluble organic aromatic chromophore that strongly absorbs or emits visible light nondegradatively. Irreversible photochemistry is not considered.[18] No lower limits on energies or quantum efficiencies have been set. For example, we discuss aniline derivatives and naphthol as guests but not phenol; the latter has been studied extensively in alkali halides.[19−22]

The restriction to aqueous systems may seem arbitrary but maintains the analogy with the dyeing of cloth and paper. This restriction excludes photophysical studies on classic mixed crystal systems such as naphthalene in durene,[23,24] pentacene in *p*-terphenyl,[25] or Sh′polskii single crystals of *n*-alkanes.[26,27] Similarly, studies of intermolecular hydrogen-bond dynamics of benzoic acid crystals substitutionally doped by dyes are excluded.[28,29] These systems rely on host/guest isomorphisms and have been reviewed previously.

There are a great number and variety of materials containing preformed layers, channels, or pores that serve as hosts for dyes. Such materials may rightly be called dyed crystals, but they will not be discussed here. This omission in no way implies that the substances about to be named are less interesting. However, they do less to challenge our intuition about mixed crystal structure and crystal growth because materials that contain free or loosely solvated spaces may naturally be filled. Moreover, such materials stand outside of the historical themes that will be introduced in the next section. Given constraints of space, dyed clays as well as layered phosphates/phosphonates,[30] zeolites,[31−41] or molecular clathrate crystals[42−48] will be disregarded. We leave behind "norganics", dye monolayers interleaved with co-deposited salts,[51−54] or the deposition of dyes between semiconductor layers[49,50] because they are not crystals is the standard sense. We further exclude discussion of surface-adsorbed dyes interacting with F-centers in NaCl crystals.[55] Even though molecular or ionic cocrystals with dyes can help to identify noncovalent interactions in mixed crystals, these materials are also excluded.[56−59]

Stained biopolymer crystals are excluded since small dyes added to the solvent diffuse through solvent channels of as-grown crystals. In fact, Hampton Research sells a dye that can be used to distinguish protein crystals from buffer salt precipitates.[60] The protein crystals become colored by simple diffusion on application of the dye while the salt crystals do not.

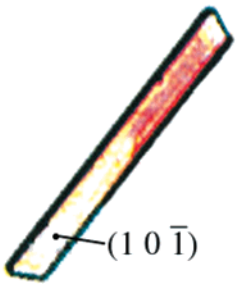


Figure 2. Transmitted light photograph of 1,4-dinitrobenzene crystal incubated with monoclonal antibodies and labeled with the vector red alkaline phosphatase kit. The red color reflects antibody binding to the (10$\bar{1}$) surface.[84] (Reproduced with permission from ref 84. Copyright 1998 Elsevier Science.)

Other examples of crystals dyed after growth include silver halides sensitized for color photography[61−63] and minerals.[64−71] Dyes have also been used for corrosion detection[72] or as markers for dislocations[73] and etch pits.[74] These processes are primarily adsorption phenomena and are not discussed here. Similarly, studies of dyes as crystal habit or growth rate modifiers are not included unless they relate to DICs. For example, quinoline yellow[75] and Bismarck brown,[76−78] shown to influence the growth rates of the potassium alum {111} faces, do under some conditions give DICs. The effects of dyes on crystal dissolution are not discussed.[79−82]

A variety of studies have focused on the binding of luminophore-labeled proteins to mineral surfaces. For example, fluorescein-labeled acid-rich proteins bind selectively to the {100} faces of hydroxyapatite, the cause of osteoarthritis when precipitated pathologically.[83] Antibodies raised to 1,4-dinitrobenzene are revealed when treated with vector red alkaline phosphatase preferentially on the {10$\bar{1}$} faces (Figure 2).[84] Despite the relevance and resemblance of this work to many of the papers discussed in section IV.E.1 on biomineralization, these studies of as-grown crystals incubated with dyes are not discussed.[85,86] However, it is likely that in a number of these cases conditions could have been found to encourage the overgrowth of the colored adsorbates.

Marc,[87,88] Paneth and co-workers,[89−91] and Kolthoff et al.[92−94] measured the adsorption of dyes on powdered, water-insoluble, alkaline-earth sulfates and carbonates that were stirred through premeasured pigment solutions. They found that these systems followed adsorption isotherms, expressions that relate the amount of adsorbate on a given crystalline surface to the solution concentration. These phenomena are to be regarded as distinct from the formation of DICs in which dyes are trapped by a growing crystal. Since adsorption is the first step in the overgrowth of a dye molecule by growing crystals, these chemisorption studies may nevertheless provide complementary information.

Polycrystalline materials (with exception of some relevant to section IV.E.1) are excluded due to the

difficulty in assessing the nature of the host/guest association.[95,96] For example, Gaubert reported dyed spherolites, aggregates of periodically precipitated crystals.[97−100] The cane sugar industry has generated substantial literature on colored molecules in crystalline sucrose. Most often the constitution of the chromophores are not known and we have avoided these problems.[101−104]

II. History

A. Artificial Pleochroism

1. Sénarmont

Dyeing crystals is an ancient practice. Sea salt and alum ($KAl(SO_4)_2 \cdot 12H_2O$) stained by indigo and safflower extracts long held a place in Egyptian superstition.[105] However, the scientific study of dyeing crystals was initiated by Sénarmont, best remembered for his pioneering analysis of the anisotropy of thermal conductivity in crystals[106,107] and for the invention of an optical compensator bearing his name.[108] In 1854, Sénarmont turned his attention to the mechanism of anisotropic absorption of light, pleochroism (linear dichroism), in minerals.

Many crystals are colored due to traces of foreign matter. Ruby and sapphire owe their value to red chromic and green ferric ions present in otherwise colorless Al_2O_3 crystals. Moreover, when these gems are viewed in linearly polarized light, their color depends on the orientation of the crystal with respect to the plane of polarization. Such crystals are said to exhibit pleochroism, a characteristic of most DICs.

Sénarmont contemplated whether pleochroism might analogously be imparted to an otherwise transparent crystal if a colored material present in solution should stain the crystal during growth. Sénarmont was satisfied by red, pleochroic crystals of $Sr(NO_3)_2 \cdot 4H_2O$ that he grew from an ammoniacal water solution containing logwood extract.[109−111] Logwood (*Haematoxylon campechianum*), a tree native to the Yucatan Peninsula,[112] contains hematoxylin,[113] a colorless compound that is air oxidized to a colored quinone, hematein. The crystals of $Sr(NO_3)_2 \cdot 4H_2O$ stained with hematein were red or violet in color depending upon their orientation with respect to the plane of incident linearly polarized light. Sénarmont announced "The Production of Artificial Pleochroism in Crystals" even though the physical basis of the absorption anisotropy was a mystery. Concluding his most extensive description of dyed crystals, Sénarmont lamented that he was undoubtedly seeing a superposition of a variety of inseparable effects and compared his position, with drama, to that of astronomers struggling with the *orbites troublées* of the planets prior to Kepler's organizing principles.[110]

2. Sénarmont's Salt

Strontium nitrate tetrahydrate stained with logwood extract has since been referred to as *Sénarmont's salt*, an appropriate name because when others tried to prepare it subsequently they most often failed. Rosenbusch was the first in 1873. In his famous petrology textbook he indicated that he succeeded only when logwood extract was replaced with fuchsin.[114]

Figure 3. Nineteenth century students of pleochroism frequently referred to their observation of *absorption brushes* shown here in tourmaline. A highly absorbing, anisotropic crystal viewed with the eye close to the surface along the optic axis reveals on a colored ground, two dark hyperbolic brushes. These come about in some crystals when absorption differs markedly for rays propagating along or obliquely to the optic axis.[119] (Reprinted with permission from ref 119. Copyright 1960 Consultants Bureau.)

Bertin, a successor of Sénarmont's at the École de Mines, reconsidered $Sr(NO_3)_2 \cdot 4H_2O$/hematein in the context of a general study of pleochroic minerals.[115] Bertin examined a collection of Sénarmont's stained crystals in 1877, but apparently none of the original samples showed acceptable absorption brushes[116−119] (Figure 3), even though they were protected by Canada balsam. Fortunately, Bertin recalled that a colleague possessed a singular plate from Sénarmont showing beautiful brushes. However, the act of transporting this crystal on a hot day from the École Normale was enough to make it foggy. After many attempts, an associate ultimately succeeded in reproducing Sénarmont's salt and these crystals were sectioned and distributed throughout collections in Europe.

Seherr-Thoss was motivated to determine whether even isotropic crystals—$Sr(NO_3)_2 \cdot 4H_2O$ belongs to the monoclinic system—could be made pleochroic by including dyes during growth from solution. He assumed that double refraction was a precondition for dichroism. In 1879, Seherr-Thoss tried a number of other cocrystallizations of salts and dyes but did not find a suitable cubic host crystal nor was he able to prepare Sénarmont's salt. He did nevertheless report that solutions of hematoxylin and *phosphorsaurem Ammoniak* produced pleochroic crystals in which the color was not equally distributed (more anon, section IV.A.3).[120]

No less a scientist than Henri Becquerel tried unsuccessfully to prepare Sénarmont's salt during his doctoral studies on pleochroism. Becquerel spiked $Sr(NO_3)_2$ solutions with other colorants such as *Persian blue* (throughout the text, dyes for which we cannot provide constitutions with confidence are named in italics) and ponceau red. He produced no additional inclusions. Since colorless hematoxylin may be readily crystallized from water as orange needles,[112] undoubtedly contaminated by hematein, Becquerel speculated that only those pigments that

could be obtained in the pure, crystalline state were likely to produce artificial pleochroism in transparent host crystals.

Ambronn, remembered for being the first to observe linear dichroism from dye-stained cell membranes,[121] also failed to prepare Sénarmont's salt. On the other hand, he did observe linear dichroism from Congo red, aligned within a sugar crystal.[122]

In 1893, Pelikan prepared Sénarmont's salt and reported that the hourglass was aligned along the *c* direction.[123] Unfortunately, we count ourselves among the scientists unable to make it. Kahr et al. tried growing crystals of Sénarmont's salt from solutions of varying pH in the presence of commercial hematoxylin, but we did not observe pleochroic or even colored crystals in this way.[112]

B. Limitations of the Principle of Isomorphism

In 1818, Mitscherlich demonstrated that similarly hydrated phosphate and arsenate salts had identical forms, thus establishing the principle of isomorphism and challenging Häuy's contention that crystal form was unique and specific to particular chemical compositions.[124] While extending his principle to other chemical systems, Mitscherlich realized that the identity of isomorphous crystal forms was more accurately described as a similarity between respective interfacial angles. This qualification then set off considerable theoretical and experimental research aimed at identifying the true nature of isomorphous crystals. Setting arbitrary angular differences as a measure of distinction between isomorphous and anisomorphous crystals was not satisfying. Moreover, all cubic crystals are isomorphous by the criteria of interfacial angles. Mitscherlich therefore favored a definition that restricts the use of *isomorphous* to crystals with an equal number of atoms similarly united. He further argued that the two substances should be miscible. Irrespective of the meaning of the term isomorphous, it was nevertheless widely assumed that the preparation of mixed crystals required hosts and guests of similar size and shape.

1. Retgers

Retgers proposed that for a mixture to qualify as isomorphous, the physical properties must vary systematically with composition. He correlated compositions of mixed crystals with refractive indices, specific gravity, thermal conductivity, elasticity, and electrical conductivity.[125] Retgers was attracted to DICs because they were mixed crystals with a physical property, pleochroism, absent in the pure host crystals. Like Rosenbusch, Becquerel, and Seherr-Thoss before him, Retgers appreciated the limitations of Sénarmont's singular study and attempted to produce a family of DICs by systematically adding colored compounds to solutions of growing salt crystals.[126] From some 962 experiments (assuming he crossed all 26 dyes with each of 37 salts listed in his paper), Retgers obtained four mixed crystals that he deemed worthy of further study: K_2SO_4/Bismarck brown, KNO_3/nigrosin, NH_4NO_3/indulin, and $BaCl_2 \cdot H_2O$/water blue. The paucity of successes suggests that the probability of staining an ionic crystal during growth with a randomly chosen dye is quite small.

2. Lehmann

Lehmann, the discoverer of liquid crystals,[127,128] spent the years following his important paper on the "two melting points" of cholesteryl benzoate studying the growth of organic acid crystals in the presence of both natural and coal−tar dyes. This emphasis at the expense of further liquid crystal research underscores the relative importance to Lehmann and his contemporaries of these two research subjects. Like Retgers, Lehmann was motivated to understand the limitations of the principle of isomorphism and described the crystallization of some 17 organic acids or alkaloids with up to 40 dyes.[129,130] He obtained many pleochroic crystals in this way that were often darker than the colored solutions from which they precipitated, thus mitigating against the color being due to fluid inclusions. Lehmann gave particular attention to crystal violet included in poppy acid (meconic acid) showing different colors in adjacent growth sectors. He surmised that dye molecules must be in different orientations in each sector, but his experiments are difficult to interpret because he paid little attention to crystallographic directions. Lehmann was primarily interested in the use of the microscope and hot stage to identify new crystalline substances and typically grew microcrystals on glass slides.[131]

Lehmann observed that dyed poppy acid lost none of its color when crystals were allowed to stand in gasoline and concluded that diffusion was not possible in the solid state.[130] However, this conclusion is most valid if pure poppy acid crystals are not dyed by a colored gasoline solution. S. Ruzicka later demonstrated that poppy acid crystals remained colorless even after soaking them in dyed gasoline solutions for extended periods.[132]

Tammann brought his deep appreciation of thermodynamics to the problems presented by DICs,[133] especially methylene blue and crystal violet in poppy and phthalic acids. All the mixed crystals that he grew were pleochroic but he distinguished between two cases. In the first case, for example, methylene blue did not bleed from the crystals into saturated alcoholic solutions of phthalic acid, while in the second case, crystal violet did bleed. He concluded that some DICs contain dyes in a molecular distribution while others contain microcrystalline dye particles. He stressed, therefore, that pleochroism alone cannot be seen as a sign of dyes in molecular distribution because crystallites themselves may be pleochroic.

Tammann further recognized that dyed crystals, despite their propensity to grow from some solutions, were not necessarily at equilibrium. This key insight was published to commemorate the 100th anniversary of Mitscherlich's principle of isomorphism.[134] Far from equilibrium, as in supersaturated solutions, it is possible to trap unusual chemical species that defy thermodynamic intuition.

C. Syncrystallization vs Epitaxy

1. Gaubert

Lehmann's DICs were studied further by Gaubert and by Billiet.[135] Gaubert was the first to describe the process of dyeing with respect to specific crystallographic directions. For example, he clarified that methylene blue recognized the {021} sectors of phthalic acid[136−142] and the {101} sectors of poppy acid.[143]

Like Seherr-Thoss, Gaubert questioned whether artificial pleochroism could be extended to isotropic hosts.[144] He was the first to describe a bona fide DIC made from cubic crystals: NaCl with murexide and $NH_4Br(Cl)$ with tartrazine.[145] Gaubert also prepared crystals of $Ba(NO_3)_2$, $Pb(NO_3)_2$, and the isomorphous anhydrous $Sr(NO_3)_2$ containing methylene blue.[146−152]

Through this work, Gaubert, like Tammann, came to distinguish two types of inclusions. In the first kind, the colored molecules entered the crystal in whatever their degree of dilution, while in the second kind, the colored material was only taken up when it was saturated in the solution. Studies of the pleochroism of the resultant colored crystals indicated that in the first case the colored molecules were as they would be in solution, monodispersed, while in the second case there was a regular grouping of crystalline dye particles within the colorless medium. Gaubert termed the latter phenomenon *syncrystallization*.[153] For example, ponceau red and Bismarck brown formed microcrystalline deposits in K_2SO_4.[154] After a 12-year hiatus, Gaubert returned to the subject of dyeing crystals with emphasis on luminescence.[155−159]

2. Neuhaus

Gaubert's concept of syncrystallization, a term that predated X-ray diffraction, gave way to *epitaxy*, the oriented overgrowth of one crystalline substance on another. Kopp expressed the opinion that oriented overgrowth, or epitaxy, ought to be a required feature of pairs of substances considered isomorphous.[160] Neuhaus brought this highly restricted view of isomorphism to studies of dye inclusion crystals and thereby carried some of Gaubert's results into the post diffraction era. By measuring lattice constants of crystalline dyes and the salts with which they had syncrystallized, Neuhaus was able to propose epitaxial relationships based upon the close matching of lattice dimensions. For example the lattice constants for crystalline methylene blue, a dye that colored poppy acid, were 9.5 Å × 31.3 Å × 6.85 Å. The poppy acid unit cell measured 19.5 Å × 16.0 Å × 6.48 Å. A match between the two sets (ignoring substantial angular differences) was achieved by multiplying the former set by 2, 0.5, and 1, respectively. Similarly, the *c* lattice constant of K_2SO_4 was equal to three times the *b* lattice constant of ponceau R.[161,162] This numerology, contrived in hindsight, was applied to those systems formerly studied by Gaubert and Lehmann.[163,164] While it may make sense in a limited number of genuine syncrystals, it is undoubtedly wrong in many other cases. That simple epitaxial relationships could be found for the great number of dyes that serve as guests for given crystallographic hosts argues against this mechanism on the grounds of probability. Recently, Ward and co-workers showed in images made by atomic force microscopy that simple geometric relationships between planar nets cannot be used to predict epitaxial phenomena, especially when kinks on growing surfaces are involved.[165,166]

Despite the fact that Neuhaus's interpretation may not be lasting, he did discover many new DICs. He identified 63 dyes that stained poppy acid. Some of his mixed crystals are sketched in Figure 4. Most showed complete linear dichroism.[167,168] Neuhaus's work on DICs ended abruptly in 1944 when his institute in Darmstadt was destroyed.[169]

Lindenberg reinvestigated a number of the Neuhaus's DICs but reiterated the essential features of the epitaxial interpretation of mixed crystal growth.[170,171]

D. Rate and Habit Modification

1. Marc

Any additive will affect the rate of crystal growth. Marc was the first scientist to use dyes quantitatively for this purpose. He came to the subject of dyeing crystals in order to test whether diffusion was a limiting factor in crystal growth rates.[172] He recognized that dyes that have the ability to color inorganic crystals such as K_2SO_4, $KAl(SO_4)_2 \cdot 12H_2O$, and others also greatly retarded growth rates whereas inactive colorants did not affect rate.[173] With Wenk he showed that dyes had a greater effect on rates of growth than on rates of solution and thus inferred that crystal growth was an adsorption process.[174] They observed linear dichroism in a number of dyed K_2SO_4 crystals; a fuller analysis containing photographs of a number of dyed crystals appeared in Wenk's dissertation.[175] Their system of K_2SO_4 and ponceau red was later the subject of a rather complete analysis by Neuhaus in the context of syncrystallization.[176] Marc's further study revealed that for each crystalline material there is an upper limit above which further adsorption does not take place.[177] In his final analysis, Marc despaired that his work could not be reduced to a single simple isotherm, as so many factors are at play in these complex phenomena.[178]

2. Buckley

Buckley was the first 20th century scientist to seriously study the effect of additives on crystal habit. Following a series of papers in which he discussed the influence of inorganic impurities, Buckley suddenly shifted his focus by using dyes as his habit modifying agents;[179−181] he was impressed with the earlier work of Marc and patterned his own studies likewise. Manchester, a textile center, afforded Buckley access to thousands of commercial dyes. During the next 10 years he recorded the results of 16,000 crystallizations of salts with dyes[182] that he exhaustively ranked according to their power to inhibit the growth rates of particular surfaces of various crystals.[183]

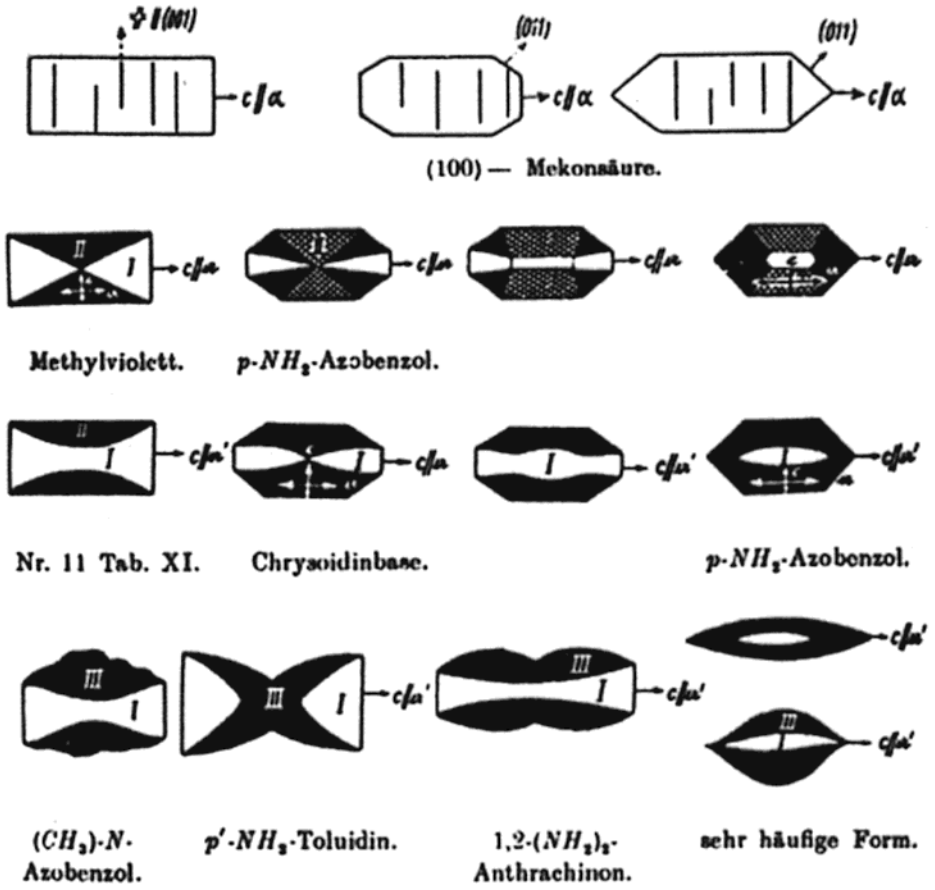


Figure 4. Neuhaus's sketch of dyed poppy acid (meconic acid or Mekonsäure) crystals.[163] (Reprinted with permission from ref 163. Copyright 1941 Oldenbourg Wissenshaftsverlag, München.)

A fortuitous consequence of this great number of crystallizations was the discovery of several well-defined DICs (Figure 5).[184−186] Additional examples are illustrated in his book *Crystal Growth*.[17] In a summary article, Buckley published tables of pleochroic phenomena associated with dyes in borax ($Na_2B_4O_7 \cdot 10H_2O$), K_2SO_4, potassium hydrogen tartrate ($KHC_4H_4O_6$), and NH_4ClO_4.[187]

At the time of Buckley's research, the conformational analysis and electronic structure of dyes were poorly understood; spectroscopy was exotic rather than routine. Therefore, he was not able to provide a molecular view of dyes regularly included in the host crystals even though he realized that his observations undoubtedly contained structural information about the stereoselective interactions of organic dyes with growing crystal surfaces. Following an extensive report on the habit modification of K_2SO_4 with organic dyes, Buckley wrote, "Although all necessary data [*for understanding the recognition mechanism*] is included in the foregoing tables, much of it is not immediately obvious and many important features will remain hidden to all but the most careful scrutiny". He abdicated some responsibility for explaining the complex phenomena by describing himself as "an indifferent organic chemist".[182]

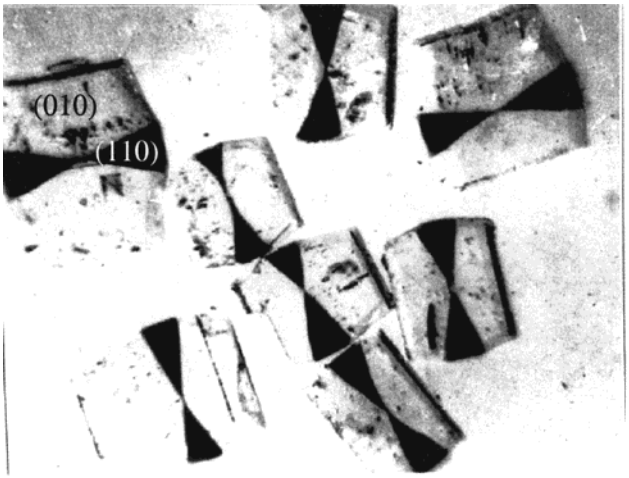


Figure 5. Photograph of Buckley's K_2SO_4 crystals dyed with azo-orseille R in the {110} growth sectors.[17,263] (Reprinted with permission from ref 263. Copyright 1934 Oldenbourg Wissenshaftsverlag, München.)

Buckley recognized that in DICs there need not be any fixed relationship between the directions in which the transverse electromagnetic wave can vibrate in the host crystal and the preferred absorption directions associated with the dye molecules. In a cubic crystal, in principle, he said there should be an equal number of absorption ellipsoids (Figure 6) in each direction and no distinction of color when the plane of polarization is rotated. In practice, in any sector, far more absorption ellipsoids will be oriented in one direction than in the others. Searching for words to express his observations of desymmetrization Buckley wrote that "For although it is comparatively easy for the crystal units themselves to fall into places which give the crystal isotropic properties, the

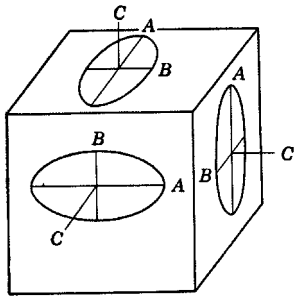


Figure 6. Buckley's illustration of the origin of linear dichroism in cubic crystals due to the oriented adsorption of dyes and their associated absorption ellipsoids.[17,184] In his view, desymmetrization arose because the colored molecules were not statistically "digested" by the surface. (Reprinted with permission from ref 187. Copyright 1939 Manchester Literary and Philosophical Society, Manchester.)

far larger impurity particles are not so readily digested".[17]

Buckley took advantage of the "incomplete digestion" of the impurity particles and produced the first photometric studies of DICs. In his final review, he showed optical absorption spectra for chromotrope 2B included in K_2SO_4 and NH_4ClO_4 obtained with the electric vector of the polarized light parallel to each of the three orthogonal directions (Figure 7).[32] There was marked pleochroism. So delighted by this observation, Buckley proclaimed that "A new branch of chemistry seems nearby". Unfortunately, as Deer remarked in Buckley's obituary, "There is no doubt that by some of his colleagues Buckley's work was considered outmoded by the methods of X-ray crystallography".[188]

3. Whetstone

Whetstone, a researcher at the Nobel Explosives Division of the Imperial Chemical Industries (ICI), took an interest in Buckley's work in the 1950s. Initially motivated to control the habit of NH_4NO_3 for use in explosives,[189] Whetstone tested 120 dyes as habit modifying agents.[190] Acid fuchsin was especially effective.[191] In the course of his habit modification work, he discovered several $(NH_4)_2SO_4$, $NaNO_3$, and KNO_3 DICs.[192] $NaNO_3$ DICs were earlier prepared by France (section II.E.2).[193]

Whetstone developed structural models for DICs on the basis of *qualitative* linear dichroism. He superimposed scaled dye molecules drawn on celluloid over projections of the salt lattices, consistent with the planes that he thought contained the dye molecules. Possible structures were suggested when the positively and negatively charged functionalities of the dyes were well matched to salt cation and anion positions, respectively.[194]

One of Whetstone's structural propositions was seemingly prescient, that for acid fuchsin superimposed on the (100) plane of NH_4NO_3 (Figure 8a).[195,196] He neither did calculations of molecular geometry nor quantitative spectroscopy, yet was able to fix intu-

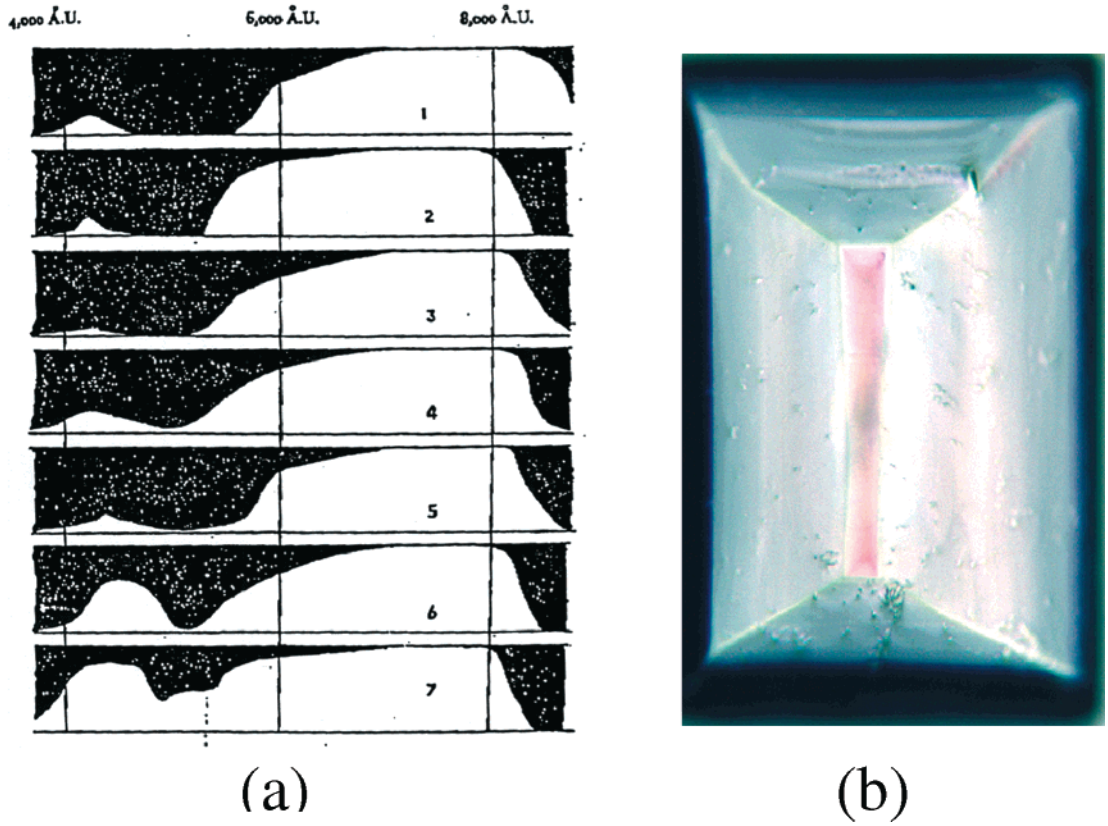


Figure 7. (a) First measurements of linear dichroism in dye inclusion crystals. Buckley's absorption spectra of chromotrope 2B: (1) in aqueous solution; (2,3,4) in NH_4ClO_4 with respect to the γ, β, α color axes; (5,6,7) in K_2SO_4 with respect to the γ, β, α color axes.[182] (Reprinted with permission from ref 182. copyright 1951 Manchester Literary and Philosophical Society, Manchester.) (b) Photograph of K_2SO_4 crystal grown by L. Bastin in the presence of chromotrope 2B. The red dye recognized the small (010) sector exclusively. The *a* axis is vertical. Crystal height = 3 mm.

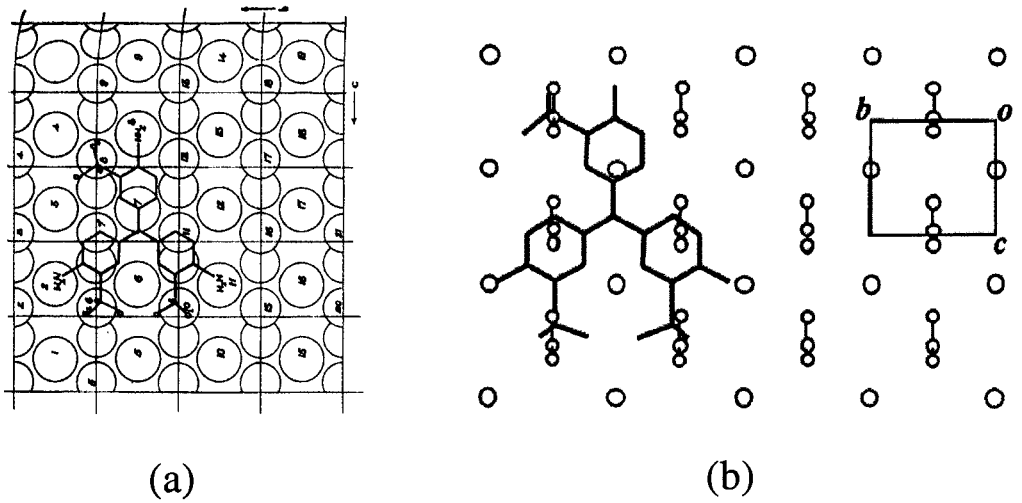


Figure 8. (a) Whetstone's drawing of acid fuchsin superimposed on the NH_4NO_3 lattice such that the sulfonate groups ($-SO_3^-$) groups fall upon nitrate (NO_3^-) positions.[196] (Reprinted with permission from ref 196. Copyright 1956 the Royal Society.) (b) Corresponding model constructed with an impossible planar triarylmethyl skeleton.[198] (Reprinted with the permission from ref 198. Copyright 1995 Kluwer Academic Publishers, Dordrecht.)

itively the stereochemistry of a very flexible molecule inside the crystal. As support of his model, he cited microfilm obtained from the British Intelligence Objectives Subcommittee (BIOS), an agency established at the end of the second world war to acquire technical information of military value.[197,198] The documents in question contained a 12-page report prepared by Krebs in 1943 on preliminary X-ray crystallographic studies of triarylmethyl cation dyes, especially crystal violet chloride.[199] Krebs's dye structure determinations could not be completed because he was summoned to the Wehrmacht. In haste, he implied that triarylmethyl cations are planar in that all the ring carbon atoms lie in a common plane, the trigonal coordination plane of the central carbon. These are impossible high-energy structures.[200]

Remarkably, Whetstone made a stereochemical choice in clearly representing a conformation of acid fuchsin in NH_4NO_3 that was essentially the same as the structure Kelley et al. chose for acid fuchsin in K_2SO_4 after quantifying the linear dichroism and comparing it with predictions made using semiempirical molecular orbital calculations.[201,202] To understand Whetstone's success, Kahr and Kelley mimicked his model by superimposing Krebs's planar model of acid fuchsin onto the NH_4NO_3 lattice such that ($-SO_3^-$) sulfur atoms of the dye were well fit to the nitrate (NO_3^-) nitrogen atoms (Figure 8b).[198] These analyses indicate that Whetstone, upon examining the Krebs/BIOS report, mistakenly concluded that triarylmethyl cation dyes are flat. He got the right structure, perhaps, for the wrong reason.

Whetstone suggested that in some cases adsorption of foreign matter occurs on step risers that are actually perpendicular to the face that had increased markedly in area as illustrated in Figure 9.[203] This idea was consistent with developing theories of solution crystal growth involving spirals.[204,205]

Phoenix carried on Whetstone's studies of dye-induced NH_4NO_3 habit modification to much the same effect.[206] Most recently, Lacmann and coworkers adopted Whetstone-like models of salt dye

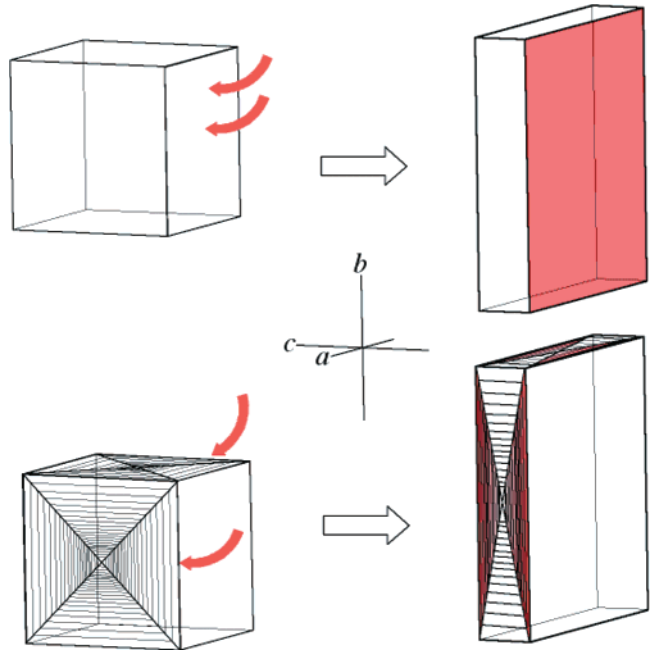


Figure 9. Two ways in which a crystal's habit can be modified by an additive (indicated with arrows). (Top) Additive adsorbs on *c* which grows in area relative to *a* and *b*. (Bottom) Precisely the same change of shape is affected by adsorption to one of two types of vicinal slopes on *a* and *b*, faces orthogonal to that which grows in area.

interactions to explain the habit modification of KNO_3 (Figure 10.)[207−209]

E. Photosensitization and Colloid Stabilization

1. Reinders

Colloid science[210] and photography based on the reduction of silver halides[211] developed rapidly in the beginning of the 20th century. Colloidal suspensions of gelatin containing silver halide crystals were of immense practical importance for the developing photography industry and also squarely addressed this new "intermediate state" of matter. Photosensitization whereby silver halide emulsions are sensi-

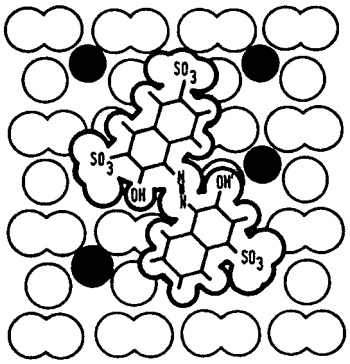


Figure 10. Model of amaranth adsorbed to the (010) face of KNO_3 according to Kipp, Lacmann, and Rolfs.[208,209] Black atoms are K^+. (Reprinted with permission from ref 208. Copyright 1997 Elsevier Science, Oxford.)

tized to the frequencies in daylight through the adsorption of dyes involved increasingly complex colloidal suspensions and raised questions about the nature of the interaction of the dyes with the crystal surfaces.

Gaubert was the first to dye AgCl and AgBr.[212] Reinders described the growth of large silver halide crystals with 22 different dyes, which he suggested were not just adsorbed on surfaces but contained within.[213−215] Erythrosin and rose bengal solutions deposited well-formed AgCl crystals with homogeneous red/violet color. Dye was indicated even in crystals that had no visible coloring because they reacted with light faster than did pure AgCl.

2. France

France, a ceramicist, tried to come to some understanding of the mechanisms of complex silicate crystallizations by studying the growth velocities of simple inorganic salts in the presence of colloidal gelatins and dyes. Additives perturbing the outer adsorbed layer of solute molecules upon the surfaces of growing crystals were thought to determine eventual form.[218] Any information on growth velocities and adsorption occurring at crystal faces should therefore promote our understanding of the fineness of structure in porcelain, the setting of cements and plasters, crystallization of glass, and many other processes in which the control of crystal growth is requisite.

France, familiar with the colloidal chemistry of photography, began his education as a crystallographer by recording the growth rates of cupric sulfate pentahydrate, famous for its large crystals, with a motion picture camera.[216,217] Following the work of Marc, Wenk, and Reinders, he then attempted to determine the effect of dye additives but faced difficulties with blue crystals; his observation of the effect of quinoline yellow was limited to "turned crystals greenish".[218] France then turned to transparent potassium alum.[219] His first definitive DIC, potassium alum stained on the {100} faces with *diamine sky blue FF*, was discovered in 1928[220−222] and was later the subject of the first X-ray measurements of DICs (Figure 11a).[223] France determined that the lattice constants for pure alum and dyed alum were the same within experimental error.[223,224] He studied other alum DICs subsequently.[225,226]

Potassium alum is structurally similar to NaCl; both have two distinct planes, one checkerboard like ($(111)_{alum}$ and $(100)_{NaCl}$) and one with alternating layers of cations and anions ($(100)_{alum}$ and $(111)_{NaCl}$). The alternating facets were presumed to grow faster due to stronger attractive electrostatic forces. Analogously, France believed that charged dye molecules or foreign materials would be more strongly attracted to faces comprised of like ions.[219,226] Buckley nevertheless found dyes that recognized both types of faces in K_2SO_4.[17] Moreover, Frondel found that the checkerboard {100} faces of NaF adsorbed a great number of ionic dyes.[227]

The theses of France's students are valuable resources that contain examples of DICs not found in the published papers.[228−235] A common feature of many of them are criticisms of Saylor's proposal, later characterized by Buckley as an oversimplification,[17] that some faces only adsorbed acidic impurities while others preferred basic impurities.[236] France with Paine-Davis showed that lead nitrate grown in the

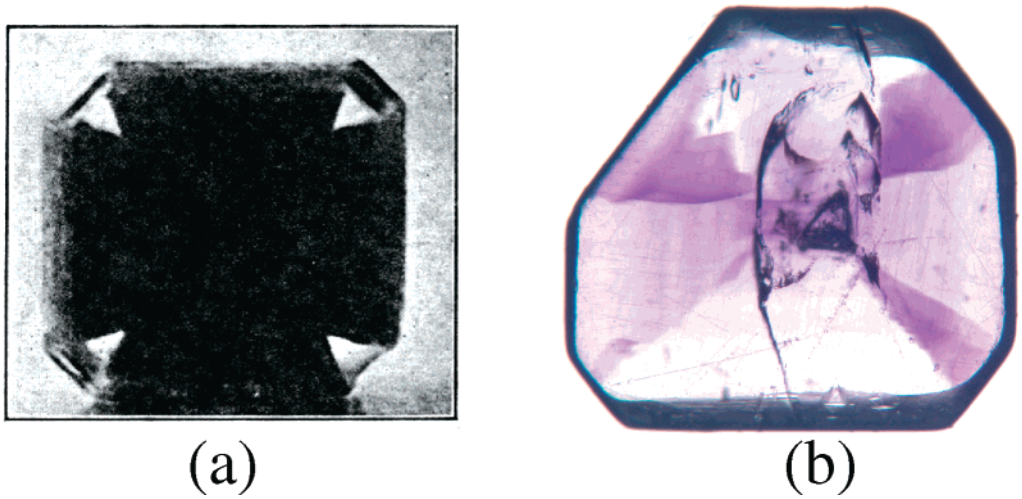


Figure 11. (a) France's photograph of a "Maltese cross" pattern (absence of dye) formed when *diamine sky blue FF* colors the {100} growth sectors of $NH_4AlSO_4 \cdot 12H_2O$.[225] (b) Thin section (70 μm) of a Maltese cross of K_2SO_4 dyed with Evan's blue in the {111} growth sectors. View along [010]. Width = 5 mm.

presence of two basic dyes, Bismarck brown and methylene blue, produced octahedral and cubic DICs, respectively, in contrast to Saylor's proposition. However, equally presumptuous was France's determination to use his observations of face selectivity to choose among competing models for the crystal structure of $Ba(NO_3)_2$ and $Pb(NO_3)_2$.[237]

France stressed the need to experiment with pure dyes.[226] With Ritgerink, France compared 11 purified isomeric dyes, some which produced well-defined hourglasses in K_2SO_4.[238] However, despite this care, France ultimately conceded that there might not be a simple rule with which to predict the formation of DICs. The work of Buckley and France in the 1930s on either side of the Atlantic represented the last comprehensive analyses of DICs. France died in 1947.[239] Buckley retired in 1951. Thereafter, contributions to the literature on DICs were incidental or highly restricted in scope and most often divorced from their antecedents.

III. Guide for the Contemporary Researcher

A. Cautions

Recent decades have been barren times for the discovery and study of DICs. One bright spot is the work of Hartmann, who described lead, barium, and cadmium acetates as hosts for fluorescent dyes.[240−243] Some of Hartmann's inclusions illustrate the varieties of order that are possible when cocrystallizing a salt in the presence of a dye. For example, methylene blue makes an hourglass pattern of color in the {100} growth sectors of lead acetate trihydrate. However, after quick inspection, it becomes obvious that the dye has merely filled fluid inclusions[244] that have a propensity to form in these sectors (Figure 12). There are no specific chemical interactions here that we deem worthy of further study. By contrast, fluorescein does form a face-specific, mixed crystal with lead acetate trihydrate that shows strong fluorescence anisotropy. These two mixed crystalline objects may

Figure 12. Lead acetate trihydrate crystals containing methylene blue in solution inclusions confined to the (100) growth sector. View along [010]. Horizontal dimension = 9 mm.

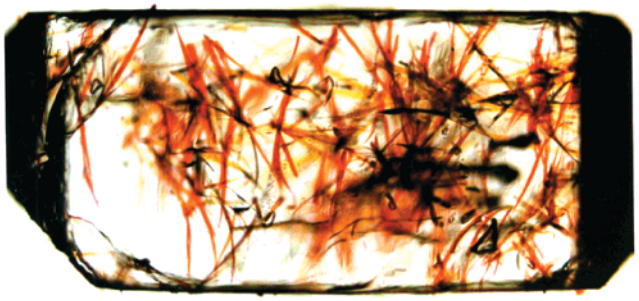


Figure 13. Synthetic "rutile-in-quartz" phenomenon. KH_2PO_4 crystals having overgrown needles of **CC**-2-OH-6,9-SO_3.[247] Pyramid {101} faces are sharply attenuated. View along [100]. Horizontal dimension = 1 cm. Crystal grown by J. A. Subramony.

appear alike at first glance; however, only the chromophores in the latter case are oriented and restricted by lattice. In either case, Hartmann, influenced by Neuhaus, searched for small whole numbers that would reconcile the dimensions of the host and guest lattices determined by X-ray diffraction. At about the same time, Kleber also doped lead and cadmium acetates with a variety of fluorescent dyes. His interpretations of mixed crystal growth were consistent with those of Neuhaus and Hartmann.[245]

Sometimes whole dye crystals are "swallowed-up" by single host crystals during growth. Buckley called this the synthetic "rutile-in-quartz" phenomenon, referring to those quartz samples prized by collectors that have golden TiO_2 needles running through them.[246] Buckley obtained orange needles of a 1:1 resorcinol ($C_6H_4(OH)_2$)/saffranin complex that radiated randomly through the transparent K_2SO_4. Similarly, Subramony observed this phenomenon in KH_2PO_4 crystals that had enveloped needles of the dye **CC**-2-OH-6,9-SO_3 (refer to Scheme 1) during growth (Figure 13).[247] Sometimes dye crystallites or aggregates are incorporated in the host in a preferred orientation. This is Gaubert's syncrystallization or Neuhaus's epitaxy. Two examples are K_2SO_4/ponceau red and $Ba(NO_3)_2$/methylene blue (see section IV.B.1).[248]

In the course of studying dyed crystals, a researcher will undoubtedly discover colored crystals that are highly dichroic but the deposition of the colored material may seem quite inhomogeneous and difficult to associate with a particular face. Samples sometimes lack a well-defined form and on close inspection with an optical microscope, appear fractured with many high-index surfaces. While in some cases these objects are undoubtedly worthy of careful analysis, we have restricted ourselves as much as possible to investigations of homogeneous, growth-sector specific, monodispersed, dichroic inclusions.

Dyes are often named descriptively or sometimes to honor a person or place. "Acid yellow" describes a yellow compound carrying one or more sulfonic acid groups; "crystal violet" is literally a purple stain that can be obtained in a crystalline state. Many substances might meet either of these descriptive requirements, even though the coiner may have had a particular molecular constitution in mind. The names "Bismarck brown", "Victoria scarlet", "Congo green", and "Texas red" tell us more about what people like

to call dyes than about the compounds themselves. Hurst's *Dictionary of the Coal Tar Colors* is a useful reference for interpreting dye nomenclature.[249] Travis has pointed out that it contains no less than 12 synonyms for Perkin's mauve, widely regarded as the first synthetic colorant, and including the following: aniline purple, rosolane, chrome violet, indisin, Perkin's violet, aniline violet, violein, purpurine, tyrian purple, harmaline, tyralin, and anileine.[250]

The 19th century literature can be impenetrable because researchers provide common names for synthetic preparations or natural extracts. While trying to reproduce historical DICs we have many times been uncertain whether a dye commercially available to us and having the same name as a substance referred to in an old procedure is indeed the material that produced the noteworthy mixed crystal. Moreover, since natural dyes are often obtained as impure extracts—even commercially available synthetic dyes are often impure—the molecule responsible for coloring a crystal is often in doubt. Surely the difficulty in obtaining Sénarmont's salt had to do in large measure with different researchers using dissimilar extracts of logwood whose chemical actions on $Sr(NO_3)_2 \cdot 4H_2O$ were highly variable (section II.A.2.).[112]

Buckley's data, unlike that of some of the 19th century researchers, can be tackled with some confidence because he is careful about assigning *Colour Index*[251] numbers to each compound. The *Colour Index* was established by the Society of Dyers and Colourists in order to obviate confusion regarding dye composition and constitution. For example, Buckley described acid fuchsin (CI No. 692) in K_2SO_4 crystals.[17,184] The constitution of this dye may be found in the current 3rd edition of the *Colour Index* according to its *five*-digit CI number (42685). Buckley used the three-digit codes in the 1st edition. Conversion tables can be found in the 2nd edition. We were especially keen on the appearance of azo orseille R (CI No. 34) in the {110} growth sectors of K_2SO_4 first reported by Buckley.[17,184] Plates with sharply delineated growth sectors well suited to spectroscopy are illustrated in Figure 5. We could not, however, find any commercial product called azo orseille R. We could track the CI No. 34 through successive editions of the Color Index; it is reclassified as CI No. 17160 (2nd and 3rd editions) and the structure is provided in Table 1.

Even with the *Colour Index* Buckley had his troubles. He lamented that he had been too reliant "on the uninstructed counter assistant who was unaware of the existence of, say, 50 odd 'Fast Reds' and nearly as many 'Acid Yellows' and, ready to oblige in the least possible time, would hand over the wrong sample so that the investigator had the wrong molecular configuration without knowing it".[182]

Buckley's habit modification data contain many examples where two or more dyes carrying the same name and the same *Colour Index* number, but supplied by different manufacturers, showed remarkably varied actions on a particular crystalline surface. For example, the activity of a dye with CI No. 246 for the (010) face of K_2SO_4 was 15 times greater, according to Buckley's scale, when supplied by Leopold Casella that when supplied by British Dyestuffs Inc. Whetstone, in his reevaluation of some of Buckley's work, was convinced of the necessity of using "specially laboratory prepared dyes made from purified dye intermediates".[195]

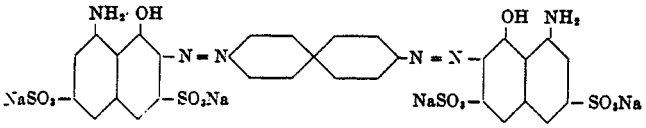


Figure 14. Mistaken molecular constitution: France's "spiro" biaryl dyes.[223]

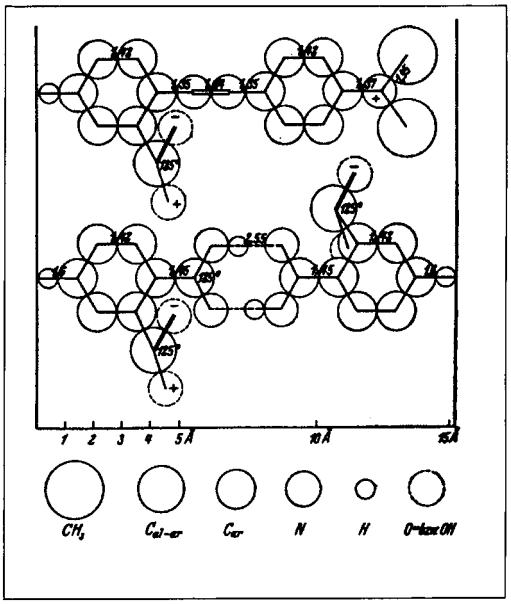


Figure 15. Neuhaus's illustration of a hypothetical isomorphism between a phthalic acid dimer and methyl red with a linear azo linkage betweem aryl rings.[164] (Reprinted with permission from ref 164. Copyright 1941 Oldenbourg Wissenshaftsverlag, München.)

Buckley published photographs showing brilliant Congo R in the {111} growth sectors of K_2SO_4 producing a Maltese cross pattern. We synthesized this compound because {111} inclusions were historically the rarest. Unfortunately, we never did produce crosses with brilliant Congo R. We nevertheless did succeed with Evan's blue and trypan blue (Figure 11b).

Other scientists used incorrect constitutions and conformations in their estimates of dye dimensions. France omitted the central bond in some biaryl ring systems and calculated their dimensions as if they were spiro compounds (Figure 14). He also thought,[252] as did Neuhaus,[164] that azo bonds were linear (Figure 15). Thus, structural propositions that were developed before conformational analysis was a mature discipline should be regarded critically. Of course, infelicities are to be forgiven. Whetstone, France, and Neuhaus were struggling with complex problems of molecular recognition at a time when structural organic chemistry was not sufficiently well developed to routinely address the specificity of noncovalent interactions.

B. The Table

In Table 1 we have accumulated all DICs reported during the past 147 years. In order for a mixed crystal to qualify for inclusion in the table, evidence of dichroism or growth sector/subsector specific

Table 1. Comprehensive Index of Dye Inclusion Crystals

host crystal	formula	space group	lattice constants			
commercial name of dye	formula		Color Index #	growth sector	D (i)	Reference (ii)
ammonium alum	$NH_4AlSO_4 \cdot 12\ H_2O$	$Pa\bar{3}$	a=12.240 Å			
Anthraquinone Green (iii)	**E**-1-NH(Ph-SO_3)-4-NH(Ph)-6-SO_3		1081	{100}	x	220
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{100}	x	226,233
Crystal Violet	**S**-9,9'N(CH_3)$_2$-(X=N(CH_3)$_2$Cl)		42555	{100}	d	220,221,233
Diamine Sky Blue FF (iv)	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410	{100}	d	220P,221,226,228,233
France Dye #4	**LL**-4-NH_2-13,17-SO_3			{100}	x	228
France Dye #11	**BB**-3-SO_3-4'-NHPh		13065	{100}	n	221,226,228,233
Oxamine Blue B	**YY**-1,1'-OH-3,4'-SO_3-5-NH_2-9,9'-OCH_3		24170	{100}	x	220,226,228
Pontamine Blue BBF (v)	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2		22610	{100}	x	228
ammonium bromide	NH_4Br	$Fm\bar{3}\ m$	a= 6.90 Å			
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH		19140		d	145
ammonium chloride	NH_4Cl	$Fm\bar{3}\ m$	a= 6.52 Å			
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH		19140		d	145
ammonium dihydrogen phosphate	$(NH_4)H_2PO_4$	$I\bar{4}\ 2d$	a=7.4997, b=7.5494 Å			
Hematein	**Y**-1,2,6-OH		75290	{100}	d	120,284
ammonium hydrogen tartrate	$NH_4\ H\ C_6H_4O_6$	$P2_12_12_1$	a=7.648 b=11.066 c=7.483 Å			
Azogrenadine L	**CC**-2-OH-3,6-SO_3-11-NHC(O)CH_3		16130		d	17
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180		d	17
Naphthol Red S	**FF**-2-OH-3,4',6-SO_3		16185		d	17
ammonium nitrate IV	$(NH_4)NO_3$	$Pmmn$	a=5.757, b=5.451, c=4.935 Å			
Acid Magenta (vi)	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3		42685	{100}	d	190,195I,197
Acid Magenta N.D.	**S**-2,8,8'-SO_3-6,10,10'-CH_3-9,9'-NH_2-(X=NH_2)		42520	{100}	d	190,195,197
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{100}	d	195,196
Azofuchsin G	**DD**-1,8-OH-4,11-SO_3		16540		x	190
Chlorazol Sky Blue FF	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410		x	190
Chromazol Yellow CRS	**UU**-3,3'-CO_2-4,4'-OH-8,8'-SO_3		22880		d	197
Diaminoanthraquinonesulfonate	**E**-1,4-NH_2-2-SO_3				d	190,197
Disulfonated Dobner's Violet					d	196,197
Indulin (vii)	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & (-SO_3)$_x$		50405		d	126
Ink Blue	**S**-9,9'-NH(Ph-*p*-SO_3)-(X=NH(Ph-*p*-SO_3))		42780		d	197
Naphthol Red S (viii)	**FF**-2-OH-3,4',6-SO_3		16185		d	197
Nigrosin (vii) (ix)			50420		d	126
Trisulfonated Dobners Violet					d	196,197
Trisulfonated Methylviolet	**S**-2,8,8'-SO_3-9-N(CH_3)$_2$-9'-$NHCH_3$-(X=N(CH_3)$_2$)Cl		42535		d	196
Trisulfonated Pararosaniline	**S**-2,8,8'-SO_3-9,9'-NH_2-(X=NH_2)Cl		42500	{100}	d	195,196,197
Trypan Red	**XX**-2,2'-NH_2-3,3',6,6',9-SO_3		22850		d	196
Whetstone Dye (viii)	**FF**-2-NH_2-3,6,4'-SO_3				d	196,197
Whetstone Dye (viii)	**JJ**-2-OH-3,6,13,18,20-SO_3				d	196,197
Whetstone Dye (viii)	**JJ**-2-OH-3,6,18,20-SO_3				d	197
Whetstone Dye (viii)	**II**-2-OH-3,6,13,16,19,21-SO_3				d	196,197
Whetstone Dye (viii)	**II**-2-OH-3,6,13,16,17,19,21-SO_3				d	196
Whetstone Dye (viii)	**FF**-2-NH_2-3,3',6,6'-SO_3				d	196

(i) Measurement of linear dichroism. d = dichroic, x = not dichroic, n = dichroism not observed.
(ii) P= Photograph, I = Illustration
(iii) Assumed to be anthraquinone green GX or GXN.
(iv) Also France Dye #13, pontamine sky blue 6B, chlorazol sky blue FF, direct pure blue, direct sky blue, and Chicago sky blue.
(v) Also France Dye #12
(vi) Also trisulfonated roseaniline.
(vii) Form not specified.
(viii) Structure deduced from synthesis reagents.
(ix) Aniline, aniline hydrochloride and nitrophenol or nitrobenzene heated with an iron catalyst, and sulfonated.

Table 1 (Continued)

ammonium perchlorate	NH_4ClO_4	*Pnma*	*a*=9.282, *b*=5.816, *c*=7.449 Å			
Azofuchsin G	**DD**-1,8-OH-4,11-SO_3		16540		d	187
Azogrenadine L	**CC**-2-OH-3,6-SO_3-11-NHC(O)CH_3		16130		d	17,187
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180		d	17
Chromotrope 2B	**DD**-1,8-OH-3,6-SO_3-11-NO_2		16575	{*hkl*}	d	17,182,187,202
Chromotrope 10B	**EE**-1,8-OH-3,6-SO_3		16640		d	187
Diphenyl Citronine G	**WW**-8,8'-SO_3		40045		d	187
Fast Red Extra	**FF**-2-OH-4',6-SO_3		16045		d	187
Methyl Blue (x)	**S**-9,9'-NH($PhSO_3$)-(X=NHPh)		42770		x	212
Methylene Blue	**G**-3,6-N(CH_3)$_2$-(X=S)		52015		x	212
National Fast Wool Blue B	**FF**-3,5',6-SO_3-4'-NH(Ph-*p*-CH_3)-8-OH		13405	{001}	d	17
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3		16150		d	17,187,333
Quinoline Yellow	**MMM**-1,2-SO_3		47005	{110}	d	182,187,202
St. Denis Red (xii)			604		x	212
aragonite	$CaCO_3$	*Pmcn*	*a*=4.9611, *b*=7.9672, *c*=5.7407 Å			
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3		22120		x	458
L-ascorbic acid	$C_6H_8O_6$	$P2_1$	*a*=17.299, *b*=6.353, *c*=6.411 Å, β=102.5°			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		d	410
Bismarck Brown R	**TT**-2,2'-NH_3Cl-4,4'-NH_2-5,5',7-CH_3-(X=N)		21010		d	410
barium acetate	$Ba(CH_3CO_2)_2$	$I4_1a$	*a*=9.010, *c*=27.3620 Å			
2-aminobenzoic acid	**A**-1-CO_2-2-NH_2			{10*l*),{01*l*}	d	270
3-aminobenzoic acid	**A**-1-CO_2-3-NH_2			{10*l*),{01*l*}	d	270PI
4-aminobenzoic acid	**A**-1-CO_2-4-NH_2			{10*l*),{01*l*}	d	270PI,419PI
barium acetate trihydrate	$Ba(CH_3CO_2)_2 \cdot 3\ H_2O$					
Auramine O	**F**-4,4'-N(CH_3)$_2$-(X=NH_2Cl) • H_2O		41000	{010}	x	240,243
Crystal Violet	**S**-9,9'-N(CH_3)$_2$-(X=N(CH_3)$_2$Cl)		42555	{010}	x	240,243
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380	{010}	x	240,243
Ethyl Green	**S**-9-N(CH_3)$_2$-9'-N(CH_3)$_2$(Et)Br-(X=N(CH_3)$_2$Cl)		42590	{010}	x	240,243
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350	{010}	x	240,243
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)		42500	{010}	x	240,243
Methylene Blue	**G**-3,6-N(CH_3)$_2$-(X=S)		52015	{010}	x	240,243
Naphthol Yellow	**B**-1-OH-2,4-NO_2-7-SO_3		10316	{010}	x	240,243
Rhodamine B	**T**-1-CO_2-8-N(Et)$_2$-(X=O,Y=N(Et)$_2$)		45170	{010}	x	240,243
Water Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-SO_3)$_3$		42755	{010}	x	240,243
barium chloride dihydrate	$BaCl_2 \cdot 2H_2O$	$P2_1/c$	*a*=6.717, *b*=10.900, *c*=9.696 Å, β=132.7°			
Water Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-SO_3)$_3$		42755		n	126
barium nitrate	$Ba(NO_3)_2$	$Pa\bar{3}$	*a*=8.11 Å			
Anthraquinone Green (iii)	**E**-1-NH(Ph-SO_3)-4-NH(Ph)-6-SO_3		1081	uniform	x	232, 237
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{111}	x	232, 237
France Dye #4	**LL**-4-NH_2-13,17-SO_3			{210}	x	232, 237
France Dye #5	**DD**-1-NH_2-3,6-SO_3-8-OH-11-N_2O			{210}	x	232
France Dye #6	**CC**-4-NH_2-9,12-SO_3			{210}	x	232, 237
France Dye #8	**BB**-2-CH_3-4-NH_2-3'-SO_3			{111}	x	232
France Dye #16	**NNN**-1,19-OH-3,5-SO_3-8-NH_2-24-NO_2			{210}	x	232
Methylene Blue	**G**-3,6-N(CH_3)$_2$-(X=S)		52015	{100},{111}	d	136,143,144,146,147, 148,153,163,164,179, 202,232,233,263,305, 313PI 317,321,322, 323
Methylene Green				{100},(111}	d	310
Oxamine Blue B	**YY**-1,1'-OH-3,4'-SO_3-5-NH_2-9,9'-OCH_3		24170	{210}	x	232,237
Picric Acid	**A**-1-OH-2,4,6-NO_2			{111}	x	232

(x) Parent structure for methyl blue. May have additional sulfonate on the –NHPh group (42780).
(xi) Parent fuchsin framework. May have either (8-CH_3) or (2,8,8'-CH_3) substituents.

Table 1 (Continued)

benzamide	$C_6H_5C(O)NH_2$	$P2_1/c$	a=5.449, b=5.033, c=21.548 Å β=89.22°			
Nile Red	**X**-3-N(Et)$_2$			{10$\bar{2}$}	x	This paper, section IV.A.3.
borax	$Na_2B_4O_7 \cdot 10H_2O$	$C2/c$	a=11.858, b=10.674, c=12.197 Å, β=106.68°			
Acid Bordeaux B	**FF**-2-OH-3,6-SO_3		16180	{100}	d	17,187
Acid Brown R	**FF**-4-OH-4'-SO_3		20075	{100}	d	187
Brilliant Congo R	**XX**-2,2'-NH_2-3,6,6'-SO_3-9,9'-CH_3		23570	{100}	d	187
Chlorazol Fast Orange D (xii)	Stilbene derivative (undetermined structure)		40015	{100}	d	187
Diamine Sky Blue A	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3		24400	{100}	d	187
Diamine Sky Blue FF	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410	{100}	d	187
Diphenyl Citronine G	**WW**-8,8'-SO_3		40045	{100}	d	187
Hessian Yellow	**WW**-3,3'-CO_2-4,4'-OH-8,8'-SO_3		24910	{100}	d	187
Naphthol Red S	**FF**-2-OH-3,4',6-SO_3		16185	{100}	d	17,187
Orange R	**CC**-2-OH-9-CH_3-11-SO_3		15575	{100}	d	187
Solochrome Black A	**FF**-2,2'-OH-4-SO_3-5-NO_2		15710	{100}	d	187
Trypan Blue	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3		23850	{100}	d	187
cadmium acetate trihydrate	$Cd(CH_3CO_2)_2 \cdot 3H_2O$					
Auramine O	**F**-4,4'-N(CH$_3$)$_2$-(X=NH_2Cl) • H_2O		41000	{010}	x	240,243
Brilliant Gold				{100}	x	240,243
Crystal Violet	**S**-9,9'-N(CH$_3$)$_2$-(X=N(CH$_3$)$_2$Cl)		42555	{010}	x	240,243
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380	{100}	x	240,243
Erythrosin Bluish	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)		45430	{100}	x	240,243
Ethyl Green	**S**-9-N(CH$_3$)$_2$-9'-N(CH$_3$)$_2$(Et)Br-(X=N(CH$_3$)$_2$Cl)		42590	{010}	x	240,243
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350	{100}	x	240,243
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)		42500	{010}	x	240,243
Isatin	**AA**			{100}	x	240,243
Methylene Blue	**G**-3,6-N(CH$_3$)$_2$-(X=S)		52015	{010}	x	240,243
Naphthol Yellow	**B**-1-OH-2,4-NO_2-7-SO_3		10316	{010}	x	240,243
Phenol Red	**S**-7-SO_3-9-OH-(X=O)			{010}	x	240,243
Rhodamine B	**T**-1-CO_2-8-N(Et)$_2$-(X=O,Y=N(Et)$_2$)		45170	{010}	x	240,243
Water Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-SO_3)$_3$		42755	{010}	x	240,243
calcite	$CaCO_3$	$R\bar{3}\,c$	a=6.361 Å, α=46.1°			
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3		22120		x	458
calcium oxalate monohydrate	$CaC_2O_4 \cdot H_2O$	$P2_1/n$	a=9.9763, b=14.5884, c=6.2913 Å, β=107.05°			
Aniline Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl		42775		x	434
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380		x	434PI
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350		x	434
Cesium alum	$CsAlSO_4 \cdot 12\ H_2O$	$Pa\bar{3}$	a=12.363 Å			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{100}	x	226,228
France Dye #11	**BB**-3-SO_3-4'-NHPh		13065	{100}	x	226,228
Oxamine Blue B	**YY**-1,1'-OH-3,4'-SO_3-5-NH_2-9,9'-OCH_3		24170	{100}	x	226,228
Pontamine Blue BBF (v)	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2		22610	{100}	x	226,228
cesium orthosulfobenzoate	$Cs(C_6H_4(CO_2H)(SO_3))$	$Pca2_1$	a=10.988, b=12.665, c= 7.193 Å			
Benzoflavin	**U**-7,12-CH_3-8,11-NH_2-(X=NH,Y=C)Cl			uniform	x	424,426
cinnamic acid	$C_6H_5CH{=}CHCO_2H$		Form and stereochemistry not specified.			
Carminic Acid (xiii)	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3		75470		d	129
Purpurin (xiii)	**E**-1,2,4-OH		58205		d	129
copper sulfate	$CuSO_4 \cdot H_2O$	$P\bar{1}$	a=6.1130, b=10.7121, c=5.9576 Å, α=82.30°, β=107.29°, γ=102.57°			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		x	218

(xii) For preparation see: US Patent 395 115.
(xiii) Only the unstable modification is colored.

Table 1 (Continued)

Methylene Blue	**G**-3,6-N$(CH_3)_2$-(X=S)		52015		d	153,218
Quinoline Yellow	**MMM**-1,2-SO_3		47005		x	218
glycine	$HOOCCH_2NH_2$	$P2_1/n$	a=5.1020, b=11.9709, c=5.5475 Å, β=111.70°			
Naphtholsulfonate	**B**-1-OH-5-SO_3				x	17
gypsum	$CaSO_4 \cdot H_2O$	$C2/c$	a=10.47, b=15.15, c=6.37 Å, β=150.1°			
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380	{101}	x	4
Hematein	**Y**-1,2,6-OH		75290	{101}	x	4
Methylene Blue	**G**-3,6-N$(CH_3)_2$-(X=S)		52015	{101}	d	147,305
hemimellitic acid	**A**-1,2,3-COOH	$P\bar{1}$	a=11.02, b=9.12, c=8.72 Å, α=106.2° β=140.2°, γ=84.2°			
Methyl Yellow	**BB**-4-N$(CH_3)_2$		11020		d	277,430
hippuric acid	$C_6H_5C(O)NHCOOH$	$P2_12_12_1$	a=10.586, b=9.123, c=8.880 Å			
Alizarin	**E**-1,2-OH		58000		d	130
Alkali Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph-*p*-SO_3)-(X=NH(Ph))		42750		d	130
Aloësäure					d	130
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		d	130
Blaue Fettfarbe					d	130
Bordeaux Roth					d	130
Chrysamine Acid (xiv)	**UU**-3,3'-CO_2-4,4'-OH		22250		d	130
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl		11270		d	130
Corallin	**S**-9,9'-OH-(X=O)		43800		d	130
Curcuma	**RR**-3,3'-OCH_3-4,4'-OH		75300		d	130
Diazoamidobenzol	**Q**				d	130
Drachenblut (xv)	Sanguis draconis		75200		d	130
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350		d	130
Frangulinsäure					d	130
Gentiana Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl		42775		d	130
Grüne Fettfarbe					d	130
Hofmann's Violet	**S**-8-CH_3-9,9'-NH(Et)-(X=NH(Et)Cl)		42530		d	130
Magdala Red	**W**-2-NH_2-(X=N,Y=N(α-**B**))Cl		50375		d	130
	& **W**-2,2'-NH_2-(X=N,Y=N(α-**B**))Cl (Mixture)					
Malachite Green	**S**-9-N$(CH_3)_2$-(X=N$(CH_3)_2$Cl) • ZnCl		42000		d	130
Marine Blue	**S**-9-N$(CH_3)_2$-(X=N$(CH_3)_2$Cl)		42000		d	130
	& **S**-9,9'-N$(CH_3)_2$-(X=N$(CH_3)_2$Cl) (mixture)		42535			
Methyl Green	**S**-9-N$(CH_3)_2$-9'-N$(CH_3)_3$Cl-(X=N$(CH_3)_2$Cl)		42585		d	130
	& **S**-9-N$(CH_3)_2$-9'-N$(CH_3)_2$(Et)Br-(X=N$(CH_3)_2$Cl)		42590			
Methyl Orange	**BB**-4-N$(CH_3)_2$-4'-SO_3		13025		d	130
Methyl Violet	**S**-9-N$(CH_3)_2$-9'-NHCH_3-(X=N$(CH_3)_2$Cl)		42535		d	130
Methylene Blue	**G**-3,6-N$(CH_3)_2$-(X=S)		52015		d	130
Phenylblau					d	130
Purpurin	**E**-1,2,4-OH		58205		d	130
Rosolic Acid	**S**-9,9'-OH-(X=O)		43800		d	130
Rothe Fettfarbe					d	130
Safranin	**U**-8,11-CH_3-7,12-NH_2-(X,Y=N)		50240		d	130
	& **U**-1,8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)					
Santalin (xviii)	$C_{24}H_{22}O_8$		1245		d	130
Tropäoline O	**BB**-2,4-OH-4'-SO_3		14270		d	130
Violette Fettfarbe					d	130
***meta*-hydroxybenzoic acid**	$C_6H_4OH(COOH) \cdot H_2O$	$P2_1/a$	a=17.752, b=6.412, c=6.731 Å, β=105.48°			
Alkali Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph-*p*-SO_3)-(X=NH(Ph))		42750		d	129
Carmine	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3 (Al,Ca)		75470		d	129
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl		11270		x	129
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380		d	129
Gentian Violet (xvi)	**S**-9-N$(CH_3)_2$-9'-NHCH_3-(X=N$(CH_3)_2$Cl)		42535		d	129
	& **S**-9,9'-N$(CH_3)_2$-(X=N$(CH_3)_2$Cl & dextrin		42555			
Karthaminsäure					x	129
Malachite Green	**S**-9-N$(CH_3)_2$-(X=N$(CH_3)_2$Cl) • ZnCl		42000		d	129

(xiv) Parent structure for chrysamine acid. May have additional 7,7'-CH_3 substituents (23640).

(xv) The resinous secretion from the fruits of *Doemonorops propinqus* and similar species found in Sumatra and Borneo.

(xvi) Genitan violet is a mixture of 1 part of dextrin with 1 part hexa- and penta-methylpararosaniline hydrochloride.

Table 1 (Continued)

Mode Braun				d	129
***para*-hydroxybenzoic acid**	$C_6H_4OH(COOH)$	Polymorph not specified.			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000		d	129
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl	11270		x	129
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)	45380		n	129
Karthaminsäure				d	129
Malachite Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) • ZnCl	42000		d	129
Methyl Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2Cl$)	42535		d	129
Mode Braun				d	129
Naphthalene Red	**NN**-1-OH-4-SO_3	26660		n	129
ice	H_2O				
2-Naphthol	**B**-2-OH			x	405,406
α-lactose monohydrate	$C_{12}O_{11}H_{22} \cdot H_2O$	$P2_1$	a=7.982, b=21.562, c=4.824 Å, β=109.57°		
Carminic Acid	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3	75470	{010}	d	359
lead acetate trihydrate	$Pb(CH_3CO_2)_2 \cdot 3\ H_2O$	$C2/m$	a=15.803, b=7.269, c=9.049 Å, β=109.55°		
Auramine O	**F**-4,4'-$N(CH_3)_2$-(X=NH_2Cl) • H_2O	41000	{010}	x	240,243
Brilliant Gold			{100}	x	240,243
Crystal Violet	**S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)	42555	{010}	x	240,243P
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)	45380	{100}	x	240,243
Erythrosin Bluish	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)	45430	{100}	x	240,243
Ethyl Green	**S**-9-$N(CH_3)_2$-9'-$N(CH_3)_2$(Et)Br-(X=$N(CH_3)_2Cl$)	42590	{010}	x	240,243
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)	45350	{100}	x	202,240,243,245
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)	42500	{010}	x	240P,243
Isatin	**AA**		{100}	d	240,242,243
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)	52015	{100}	x	240P,243
Naphthol Yellow	**B**-1-OH-2,4-NO_2-7-SO_3	10316	{010}	x	240,243
Phenol Red	**S**-7-SO_3-9-OH-(X=O)		{010}	x	240,243
Rhodamine B	**T**-1-CO_2-8-$N(Et)_2$-(X=O,Y=$N(Et)_2$)	45170	{010}	x	240P,243
Water Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-SO_3)$_3$	42755	{010}	x	240,243
lead nitrate	$Pb(NO_3)_2$	$Pa\bar{3}$	a=7.853 Å		
Acide Rosalique				x	152
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000	{111}	x	232
Capri Blue	**G**-3-$N(CH_3)_2$-6-$N(Et)_2$-7-CH_3-(X=O)	51015	{111}	x	320PI
France Dye #4	**LL**-4-NH_2-13,17-SO_3		{210}	x	237
France Dye #5	**DD**-1-NH_2-3,6-SO_3-8-OH-11-N_2O		{100}	x	232
France Dye #6	**CC**-4-NH_2-9,12-SO_3		{100}	x	237
France Dye #7	**MM**-2-OH-6,8-SO_3	27290	{100}	x	237
France Dye #16	**NNN**-1,19-OH-3,5-SO_3-8-NH_2-24-NO_2		{100}	x	237
France Dye: M-α-NH_2-(4 or 6)	**DD**-1-NH_2-(4 or 6),10-SO_3		{100}	x	234
France Dye: M-α-OH-3	**DD**-1-OH-3,10-SO_3		{100}	x	234
France Dye: M-α-OH-3:8	**DD**-1-OH-3,8,10-SO_3		{100}	x	234
France Dye: P-α-OH-5	**DD**-1-OH-5,11-SO_3		{100}	x	234
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)	52015	{100}	d	136,140,143,144,146, 147,153,163,164,202, 232,233,305,313PI, 317,321,322,323,337, 372,
Oxamine Blue B	**YY**-1,1'-OH-3,4'-SO_3-5-NH_2-9,9'-OCH_3	24170	{100}	x	232
Picric Acid	**A**-1-OH-2,4,6-NO_2		{111},{210}	x	232
Thionine Blue	**G**-3-$N(CH_3)_2$-6-$N(CH_3)$(Et)-(X=S)	52025	{100}	x	315,318
lithium fluoride	LiF	$Fm\bar{3}\,m$	a=4.0271 Å		
Acid Anthracene	**XX**-2,2'-OH-10,10'-SO_3	22890	{100}	x	227
Acid Violet 4BN	**S**-2,8-SO_3-9-$N(CH_3)_2$-9'-$N(CH_3)$(**P**)-(X=$N(CH_3)_2$)	42561	{100}	x	227
Anthraquinone Green GX	**E**-1-NH(Ph-SO_3)-4-NH(Ph)-6-SO_3	1081	{100}	x	227
Auramine G	**F**-3,3'-CH_3-4,4'-$NHCH_3$-(X=NH•HCl)	41005	{100}	x	227
Azo Blue	**YY**-1,1'-OH-4,4'-SO_3-9,9'-CH_3	23680	{100}	x	227
Azorubin	**EE**-1-OH-4,4'-SO_3	14720	{100}	x	227
Benzopurpurin 4B	**YY**-1,1'-NH_2-4,4'-SO_3-9,9'-CH_3	23500	{100}	d	227
Brilliant Crocein 9B	**KK**-2-OH-(3 or 8),6,17,19-SO_3-9-CH_3 (mixture)	27300	{100}	x	227

Table 1 (Continued)

Brilliant Yellow R	**BB**-4-NHPh-4'-SO_3 & (-SO_3)$_1$	13085	{100}	x	227
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3	22120	{100}	d	227
Croceine Orange	**CC**-2-OH-6-SO_3	15970	{100}	x	227
Croceine Scarlet 3B	**MM**-2-OH-8,15-SO_3	27155	{100}	x	227
Croceine Scarlet 7B	**MM**-2-OH-8,15-SO_3-9,13-CH_3	27165	{100}	x	227
Crystal Ponceau	**FF**-2-OH-6,8-SO_3	16250	{100}	x	227
Cyanol Extra	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NH(Et)	43535	{100}	x	227
Diamine Blue 6G	**JJ**-2-OH-9-OEt-19,21-SO_3	26980	{100}	x	227
Diamine Blue BX	**YY**-1,1'-OH-3,4',6-SO_3-8-NH_2-9,9'-CH_3	23710	{100}	d	227
Fast Yellow G	**BB**-3,4'-SO_3-4-NH_2	13015	{100}	x	227
Formyl Violet S4B	**S**-9,9'-N(Et)(**P**)-(X=N($Et)_2$)	42650	{100}	x	227
Metanil Yellow	**BB**-3-SO_3-4'-NHPh	13065	{100}	x	227
Methylene Violet 2RA	**U**-7-N($CH_3)_2$-12-NH_2	50205	{100}	x	227
Naphthol Black 3B	**JJ**-2-OH-3,6,19,21-SO_3	27260	{100}	x	227
Naphthol Green B	(**J**-6-SO_3-(X=NO,Y=O))$_3$Fe	10020	{100}	x	227
Naphthol Yellow S	**B**-1-OH-2,4-NO_2-7-SO_3	10316	{100}	x	227
Newport Direct Blue 3B	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3	23850	{100}	x	227
Orange G	**CC**-2-OH-6,8-SO_3	16230	{100}	x	227
Orange I	**CC**-4-OH-11-SO_3	14600	{100}	x	227
Orange III	**BB**-4-N($CH_3)_2$-4'-SO_3	13025	{100}	x	227
Orange IV	**BB**-4-NHPh-4'-SO_3	13080	{100}	x	227
Palatine Scarlet	**DD**-1-OH-3,6-SO_3-9,11-CH_3	14900	{100}	x	227
Ponceau 3R	**CC**-2-OH-3,6-SO_3-9,11,12-CH_3	16155	{100}	x	227
Ponceau 6R	**FF**-2-OH-3,4',6,8-SO_3	16290	{100}	x	227
Pontacyl Carmine 2G	**DD**-1-OH-3,6-SO_3-8-$NHCOCH_3$	18050	{100}	x	227
Pontacyl Carmine 6B	**DD**-1-OH-3,6-SO_3-8,11-NHC(O)CH_3	18055	{100}	x	227
Pontamine Fast Pink BL	**HH**-2,2'-NH_2-6,6',9,9'-SO_3-8,8'-OH	25380	{100}	x	227
Quinoline Yellow	**MMM**-1,2-SO_3	47005	{100}	x	227
Resorcin Yellow	**BB**-2,4-OH-4'-SO_3	14270	{100}	x	227
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH	19140	{100}	x	227
Xylidine Red	**CC**-2-OH-3,6-SO_3-9,11-CH_3	16150	{100}	x	227

magnesium perchlorate hexahydrate	$Mg(ClO_4)_2 \bullet 6H_2O$	*Pmn2*$_1$	*a*=7.76, *b*=13.46, *c*=5.26 Å		
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3	16150		x	333

meconic acid trihydrate	**H** • $3H_2O$	*C2/c*	*a*=12.2591, *b*=9.8938, *c*=16.2499 Å, *β*=95.791°		
Mordant Orange 10	**AAA**-3-CO_2-4-OH-5-CH_3-4'-SO_3	26560	{001}	d	277,430

meconic acid trihydrate	**H** • $3H_2O$	*Pbca*	*a*=15.9821, *b*=6.3658, *c*=19.6955 Å		
	BB-3-CO_2-4-OH-4'-NH_2		{101},{101}	d	167,168
	BB-3-SO_3-4-N($CH_3)_2$-4'-SO_3CH_3		{101},{101}	d	167,168
Acridine Orange	**G**-2,7-N($CH_3)_2$-(X=CH)	46005	{110},{101}	d	277,430
Acridine Yellow 6	**G**-2,7-NH_2-3,6-CH_3-(X=CH)	46025	{110},{101}	d	277,430
Alizarin	**E**-1,2-OH	58000	{110},{101}	d	130,277,430
Alizarin Yellow 2G	**BB**-3-CO_2-4-OH-3'-NO_2	14025	{101},{101}	d	167,168
Alizarin Yellow 5G	**BB**-3-CO_2-4-OH-4'-OEt	14080	{101},{101}	d	167,168
Alkali Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph-*p*-SO_3)-(X=NH(Ph))	42750		d	130
Aminoanthraquinone	**E**-(1 or 2)-NH_2		{101},{101}	d	167,168
Aminoazobenzene	**BB**-4-NH_2		{101},{101}	d	167,168
Aminoazobenzenedisulfonate	**BB**-3,4'-SO_3-4-NH_2		{101},{101}	d	167,168
Aminoazobenzenesulfonate	**BB**-4-NH_2-4'-SO_3		{110},{101}	d	167,168
Aminoazoebenzenetrisulfonate	**BB**-2,3',4-SO_3-4'-NH_2		{110},{101}	d	167,168
Aminodimethylazoebenzene	**BB**-2',3-CH_3-4-NH_2		{110},{101}	d	167,168
Aminomethylanthraquinone	**E**-1-NH_2-2-CH_3		{101},{101}	d	167,168
Antharobin			{110},{101}	d	167,168
Anthragallol	**E**-1,2,3-OH	58200		d	130
Anthraquinone Methylamine	**E**-1-$NHCH_3$		{110},{101}	d	167,168
Aurine	**S**-9,9'-OH-(X=O)	43800		d	130,143
Azophenine (xvii)	**D**-2,5-NHPh-(X,Y=NPh)	50400		d	130
Basic Fuchsin	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510	{110},{101}	d	277,430
Biebrich Scarlet	**MM**-2-OH-9,15-SO_3	26905		d	143
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000		d	143
Bismarck Brown R	**TT**-2,2'-NH_3Cl-4,4'-NH_2-5,5',7-CH_3-(X=N)	21010	{101},{101}	d	277,430
Bismarck Brown Y	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000	{101},{101}	d	277,430
Brilliant Green	**S**-9-N($Et)_2$-(X=N($Et)_2$)	42040		d	143

(xvii) Intermediate in preparation of 860(1).

Table 1 (Continued)

Carminic Acid	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3	75470	{101},{101}	d	167,168
Chrysaniline	**U**-3,8-NH_2-(X=N,Y=C)(HNO_3)	46045		d	130
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl	11270		d	130,143
Chrysoidin Basic	**BB**-2-NH_2-4-NH_2	11270	{101},{101}	d	130
Crystal Violet	**S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)	42555	{110},{101}	d	277,430
Diaminoanthraquinone	**E**-1,(2 or 4 or 5 or 8)-NH_2		{101},{101}	d	167,168
Diaminoanthraquinone	**E**-2,(3 or 6)-NH_2		{110},{101}	d	167,168
Diaminoanthraquinonesulfonate	**E**-1,4-NH_2-3-SO_3		{101},{101}	d	167,168
Diaminoanthraquinonesulfonate	**E**-1,5-NH_2-2-SO_3		{101},{101}	d	167,168
Diaminomethylazobenzene	**BB**-2-CH_3-4,4'-NH_2		{101},{101}	d	167,168
Diazoamidobenzol	**Q**		{101},{101}	d	167,168
Dibromoaminoanthraquinone	**E**-1-NH_2-$(Br)_2$		{101},{101}	d	167,168
Dicinnamenylvinlketon				d	130
Dihydroxyanthraquinone	**E**-1,(2 or 3 or 4 or 5 or 8)-OH		{101},{101}	d	167,168
Dihydroxyanthraquinone	**E**-2,(6 or 7)-OH		{101},{101}	d	167,168
Dihydroxyanthraquinonesulfonate	**E**-1,2-OH-3-SO_3		{110},{101}	d	167,168
Dihydroxyanthraquinonesulfonate	**E**-1,4-OH-6-SO_3		{101},{101}	d	167,168
Dimethoxyanthraquinone	**E**-1,5-OCH_3		{101},{101}	d	167,168
Dimethylaminoazobenzene	**BB**-4-$N(CH_3)_2$		{110},{101}	d	167,168
Ethyl Violet	**S**-9,9'-$N(Et)_2$-(X=$N(Et)_2Cl$)	42600	{110},{101}	d	277,430
Eucanthinsäure				d	130
Frangulinsäure				d	130
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)	42500		d	130
Gentian Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2Cl$)	42535		d	143
	& **S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$ & dextrin	42555			
Granatbraun	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl	42775		d	130
Helianthin	**BB**-4-$N(CH_3)_2$-4'-SO_3	13025	{110},{101}	d	167,168
Hematein	**Y**-1,2,6-OH	75290		d	143
Hexahydroxyanthraquinone	**E**-1,2,3,5,6,7-OH		{101},{101}	d	167,168
Hexahydroxyanthraquinone	**E**-1,2,4,5,6,8-OH		{110},{101}	d	167,168
Hofmann's Violet	**S**-8-CH_3-9,9'-NH(Et)-(X=NH(Et)Cl)	42530		d	130
Hydroxyanthraquinone	**E**-(1 or 2)-OH		{110},{101}	d	167,168
Hydroxyazobenzene	**BB**-4-OH		{101},{101}	d	167,168
Indulin	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & $(-SO_3)_x$	50405		d	130
Isatin	**AA**			d	130
Karthaminsäure				d	130
Magdala Red	**W**-2-NH_2-(X=N,Y=N(α-**B**))Cl	50375		d	130
	& **W**-2,2'-NH_2-(X=N,Y=N(α-**B**))Cl (mixture)				
Malachite Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) • ZnCl	42000		d	130
Marine Blue	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)	42000		d	130
	& **S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) (mixture)	42535			
Methoxyanthraquinone	**E**-1-OCH_3		{101},{101}	d	167,168
Methyl Green	**S**-9-$N(CH_3)_2$-9'-$N(CH_3)_3Cl$-(X=$N(CH_3)_2Cl$)	42585		d	130
	& **S**-9-$N(CH_3)_2$-9'-$N(CH_3)_2$(Et)Br-(X=$N(CH_3)_2Cl$)	42590			
Methyl Orange	**BB**-4-$N(CH_3)_2$-4'-SO_3	13025		d	130
Methyl Red	**BB**-2-CO_2-4'-$N(CH_3)_2$	13020	{110},{101}	d	167,168
Methyl Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2Cl$)	42535		d	130I,143
Methyl Yellow	**BB**-4-$N(CH_3)_2$	11020	{110},{101}	d	277,430
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)	52015	{110},{101}	d	129,130,143,277,430
m-Nitro-*p*-toluidine	**A**-1-NH_2-3-NO_2-4-CH_3			d	130
Mode Braun				d	130
Mordant Orange 10	**AAA**-3-CO_2-4-OH-5-CH_3-4'-SO_3	26560	{101},{101}	d	277,430
Mordant Orange 6	**AAA**-3-CO_2-4-OH-4'-SO_3	26520	{101},{101}	d	277,430
Nigrosin (ix)		50420		d	130
Nile Red	**X**-3-$N(Et)_2$		{110},{101}	d	277,430PI
Nitrosonaphthalenesulfonate	**B**-1-NO-2-OH		{110},{101}	d	130
N-Me-pyridylporphrin			{101}	d	277,430
Pentahydroxyanthraquinone	**E**-1,2,4,5,8-OH		{101},{101}	d	167,168
Phenyl Blue				d	130
Picramic Acid				d	130
Picric Acid	**A**-1-OH-2,4,6-NO_2			d	143
Prontosil Rubrum	**BB**-2,4-NH_2-4'-SO_3NH_2		{110},{101}	d	167,168
Purpurin	**E**-1,2,4-OH	58205		d	143
Roccelline	**FF**-2-OH-4'-SO_3	15620		d	130
Rothe Fettfarbe				d	130
Safranin	**U**-1-CH_3-8,11-CH_3-7,12-NH_2-(X,Y=N)	50240	{110},{101}	d	130,277,430
	& (**U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)				

Table 1 (Continued)

Santalin (xviii)	$C_{24}H_{22}O_8$		1245		d	130
St. Denis Red (xii)			604		d	143
Tetraaminoanthraquinone	**E**-1,4,5,8-NH_2			{110},{101}	d	167,168
Tetrahydroxyanthraquinone	**E**-1,2,5,8-OH			{101},{101}	d	167,168
Tetrahydroxyanthraquinone	**E**-1,3,5,7-OH			{101},{101}	d	167,168
Trihydroxyanthraquinone	**E**-1,2,(3 or 4 or 5 or 6 or 7 or 8)-OH			{101},{101}	d	167,168
Trihydroxyanthraquinone	**E**-1,4,5-OH			{110},{101}	d	167,168
Trihydroxyanthraquinonesulfonate	**E**-1,2,4-OH-3-SO_3			{110},{101}	d	167,168
Tropäoline O	**BB**-2,4-OH-4'-SO_3		14270	{101},{101}	d	130,167,168
Vesuvine	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		d	130
Violette Fettfarbe					d	130
methotrexate tetrahydrate	**III** • 4 H_2O	$P4_12_12$	a=10.343, b=10.343, c=45.521 Å			
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185		x	469
Methyl Orange	**BB**-4-$N(CH_3)_2$-4'-SO_3		13025		x	469
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	469
morphine	$C_{17}H_{20}N_1O_3$	$P2_12_12_1$	a=7.408, b=13.713, c=14.781 Å			
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	153
oxalic acid	$C_2H_2O_4$		Polymorph not specified.			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		x	129
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015	{110}	d	135P
Mode Braun					d	129
Rhodamine B	**T**-1-CO_2-8-$N(Et)_2$-(X=O,Y=$N(Et)_2$)		45170		x	399
2-oxaloate-3-hydroxy-5-carboxyfuran dihydrate	**M** • 2 H_2O	$P2_1/n$	a=6.554, b=16.730, c=9.633 Å, β=106.0°			
Methyl Yellow	**BB**-4-$N(CH_3)_2$		11020		d	277,430
2-oxaloate-3-hydroxy-5-carboxyfuran monohydrate	**M** • H_2O	$P2_1/c$	a=10.3391, b=12.8377, c=14.0874 Å, β=101.05°			
Alizarin	**E**-1,2-OH		58000		d	277,430
phlorizine dihydrate	$C_{21}H_{24}O_{10}$	$P2_12_12$	a=23.275, b=19.109, c=4.9094 Å			
Bleu de Coupier	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & $(-SO_3)_x$		861		n	140,156,157
Hematein	**Y**-1,2,6-OH		75290		n	140,156,157
Hofmann's Violet	**S**-8-CH_3-9,9'-NH(Et),(X=NH(Et)Cl)		42530		n	140,156,157
Methyl Red	**BB**-2-CO_2-4'-$N(CH_3)_2$		13020		n	140,156,157
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		n	140,156,157
Methylene Violet 2RA	**U**-7-$N(CH_3)_2$-12-NH_2		50205		n	140,156,157
phloroglucinol	**A**-1,3,5-OH	$P2_12_12_1$	a=4.83, b=9.37, c=12.56 Å			
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)		42500		x	158
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	158
phthalic acid	**A**-1,2-COOH	$C2/c$	a=5.03, b=14.30, c=9.59 Å, β=93.2°			
	BB-3-CO_2-4-OH-4'-NH_2			{021}	d	167,168
	BB-3-SO_3-4-$N(CH_3)_2$-4'-SO_3CH_3			{021}	d	167,168
Acridine Orange	**G**-2,7-$N(CH_3)_2$-(X=CH)		46005	{021}	d	431
Alizarin Yellow 2G	**BB**-3-CO_2-4-OH-3'-NO_2		14025	{021}	d	167,168
Alizarin Yellow 5G	**BB**-3-CO_2-4-OH-4'OEt		14080	{021}	d	167,168
Alkanna	root of *Anchusa tinctoria*				d	130
Aloësäure					d	130
Aminoazobenzene	**BB**-4-NH_2			{021}	d	167,168
Aminoazobenzenedisulfonate	**BB**-3,4'-SO_3-4-NH_2			{021}	d	167,168
Aminoazobenzenesulfonate	**BB**-4-NH_2-4'-SO_3			{021}	d	167,168
Aminoazobenzenetrisulfonate	**BB**-2,3'-4-SO_3-4'-NH_2			{021}	d	167,168
Aminodimethylazobenzene	**BB**-2',3-CH_3-4-NH_2			{021}	d	167,168
Aminonaphthalenesulfonate	**B**-1-NH_2-(6 or 7)-SO_3^- (mixture)				x	17

(xviii) Powdered wood of *Pterocarpus santalinus* (Sandalwood) and indicus. Component of natural red 22 (75540). Stucture unknown.

Table 1 (Continued)

Aniline Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl	42775		d	130,129
Aurine (xix)	**S**-9,9'-OH-(X=O)	43800	{021}	d	130,136,274
Azobenzene	**BB**			d	130
Basic Fuchsin	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510	{021}	d	200,277,431
Biebrich Scarlet	**MM**-2-OH-9,15-SO_3	26905	{021}	d	136,274
Bismarck Brown (xx)	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000	{021}	d	17,129,130,136,142,274
Bordeaux Roth				d	130
Carmine	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3 (Al,Ca)	1239		d	130
Chrysaniline	**U**-3,8-NH_2-(X=N,Y=C)(HNO_3)	46045		d	130
Chrysoidin	**BB**-2,NH_2-4-NH_3Cl	11270	{021}	d	130,129,136,274,277
Chrysoidin Basic	**BB**-2-NH_2-4-NH_2	11270	{021}	d	130
Coomassie Brilliant Blue G	**PP**	42660	{021}	d	431
Crystal Violet	**S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2$Cl)	42555	{021}	d	136,200,274,277,431
Diaminomethylazobenzene	**BB**-2-CH_3-4,4'-NH_2		{021}	d	167,168
Diazoamidobenzol	**Q**		{021}	d	130,167,168
Dimethylaminoazobenzene	**BB**-4-$N(CH_3)_2$		{021}	d	167,168
Dimethylaminomethylazobenzene	**BB**-2-CH_3-4-$N(CH_3)_2$		{021}	d	277
Diphenylamine Blue	**S**-9,9'-NHPh-(X=NHPh)Cl	42760	{021}	d	136,274
Drachenblut (xv)	Sanguis draconis	75200		d	130
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)	45380		d	129,130
Erythrosin	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)	45430		d	129,130
Ethyl Red	**BB**-2-CO_2-4'-$N(Et)_2$		{021},{010}	d	277
Ethyl Violet	**S**-9,9'-$N(Et)_2$-(X=$N(Et)_2$Cl)	42600	{021}	d	200,277,431
Fluorescein or Uranin	**T**-1-CO_2-11-OH-(X,Y=O)	45350		d	17,130
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)	42500	{021}	d	130,136,142,274
Gentian Violet (xvi)	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2$Cl) & **S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2$Cl & dextrin	42535 42555	{021}	d	130,129,136,274
Gentiana Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl	42775		d	130
Gummigutt	Gum resin of *Garcinia morella* (Gambogium)			d	130
Helianthin	**BB**-4-$N(CH_3)_2$-4'-SO_3	13025	{021}	d	167,168
Hofmann's Violet	**S**-8-CH_3-9,9'-NH(Et),(X=NH(Et)Cl)	42530		d	129,130
Hydroxyazobenzene	**BB**-4-OH		{021}	d	167,168
Indulin	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & $(-SO_3)_x$	861	{021}	d	130,136,274
Isatin	**AA**			d	130
Jaune de Diphénylamine			{021}	d	136,274
Karthaminsäure				d	129,130
Magdala Red	**W**-2-NH_2-(X=N,Y=N(α-**B**))Cl & **W**-2,2'-NH_2-(X=N,Y=N(α-**B**))Cl	50375		d	130
Magenta	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510		d	17
Malachite Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2$Cl) • ZnCl	42000	{021}	d	136,142,274,431
Methyl Blue (x)	**S**-9,9'-NH($PhSO_3$)-(X=NHPh)	42770	{021}	d	136,274
Methyl Green	**S**-9-$N(CH_3)_2$-9'-$N(CH_3)_2$(Et)Br-(X=$N(CH_3)_2$Cl) & **S**-9-$N(CH_3)_2$-9'-$N(CH_3)_3$Cl-(X=$N(CH_3)_2$Cl)	42585 42590		d	130
Methyl Orange	**BB**-4-$N(CH_3)_2$-4'-SO_3	13025	{021}	d	130,277
Methyl Red	**BB**-2-CO_2-4'-$N(CH_3)_2$	13020	{021},{010}	d	142,163,164,167,168,217,277
Methyl Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2$Cl)	42535	{021}	d	130,136,274
Methyl Yellow	**BB**-4-$N(CH_3)_2$	11020	{021},{010}	d	277
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)	52015	{021}	d	130,136,138,139,142,164,217,431P
m-Nitro-*p*-toluidine	**A**-1-NH_2-3-NO_2-4-CH_3			d	130
Mode Braun				d	129,130
Nigrosin (ix)		50420		d	129,130
Nile Red	**X**-3-$N(Et)_2$		{021},{010}	d	277
Phenylblau				d	130
Picraminic Acid	$C_6H_2(NO_2)_2(NH_2)OH$			d	130
Prontosil Rubrum	**BB**-2,4-NH_2-4'SO_3NH_2		{021}	d	167,168
Purpurin	**E**-1,2,4-OH	58205		d	130
Rhodamine			{021}	x	142
Rhodamine B	**T**-1-CO_2-8-$N(Et)_2$-(X=O,Y=$N(Et)_2$)	45170		x	17
Rosaniline	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510	{021}	d	136,274
Safranin	**U**-1-CH_3 -8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)	50240	{021}	d	129,130,136,142,274
Santalin (xviii)	$C_{24}H_{22}O_8$	1245		d	130
Tropäoline O	**BB**-2,4-OH-4'-SO_3	14270	{021}	d	167,168

(xix) Also pararosolic acid and rosolsäure.
(xx) Also vesuvin.

Table 1 (Continued)

Turmeric	**RR**-3,3'-OCH_3-4,4'-OH	75300		d	130
Victoria Blue	**QQ**-9-$N(CH_3)_2$-9'-NHPh-(X=$N(CH_3)_2$	44045	{021}	d	136
Violette Fettfarbe				d	130

poppy acid (see meconic acid)

potassium alum	$KAlSO_4 \cdot 12\ H_2O$	$Pa\bar{3}$	a=12.158 Å			
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{100}	d	202
Bismarck Brown (G)	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{100}	x	77, 78,179,202,219, 225,226I,263,233
Bismarck Brown R	**TT**-2,2'-NH_3Cl-4,4'-NH_2-5,5',7-CH_3-(X=N)		21010		x	76
Croceine Scarlet 3B	**MM**-2-OH-8,15-SO_3		27155	{100}	x	399
Crystal Violet	**S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)		42555	{100}	x	233
Diamine Sky Blue FF (iv)	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410	{100}	x	17,219I,222,225,226, 228,235P, 330,399I
Metanil Yellow (xxi)	**BB**-3-SO_3-4'-NHPh		13065	{100}	x	202,221,226,233
Methyl Red	**BB**-2-CO_2-4'-$N(CH_3)_2$		13020		x	179
Methyl Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2Cl$)		42535	{111}	x	399
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015	{100}	x	233,235P
Oxamine Blue B	**YY**-1,1'-OH-3,4'-SO_3-5-NH_2-9,9'-OCH_3		24170	{100}	x	226
Pontamine Blue BBF	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2		22610	{100}	x	230
Quinoline Yellow	**MMM**-1,2-SO_3		47005		x	75
Safranin	**U**-1-CH_3 -8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)		50240		x	179I

potassium bromate	$KBrO_3$	$R3m$	a=4.413 Å, α=85.8°			
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180		x	296
Ponceau G (xxii)	**CC**-2-OH-3,6-SO_3		16100		x	296

potassium bromide	KBr	$Fm\bar{3}\,m$	a=6.600 Å			
Acid Fuchsin	**DD**-1-OH-3,6-SO_3-8-NH_2		17200	{100}	x	227
Alizarin Red S	**E**-1,2-OH-3-SO_3		58005	{100}	x	227
Brilliant Crocein 9B	**KK**-2-OH-(3 or 8),6,17,19-SO_3-9-CH_3		27300	{111}	x	227
Brilliant Yellow R	**BB**-4-NHPh-4'-SO_3 & $(-SO_3)_1$		13085	{100}	x	227
Chromotrope 2R	**DD**-1,8-OH-3,6-SO_3		16570	{100}	x	227
Chromotrope 6B	**DD**-1,8-OH-3,6-SO_3-11-$NHC(O)CH_3$		16600	{100}	x	227
Chrysoidin R	**BB**-2-NH_2-4-NH_3Cl-5-CH_3		11320	{100}	x	227
Columbia Blue G	**YY**-1,1'-OH-3,5',8-SO_3-8'-NH_2-9,9'-CH_3		23740	{100}	x	227
Croceine Orange	**CC**-2-OH-6-SO_3		15970	{100}	x	227
Cyanol Extra	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NH(Et)		43535	{100}	x	227
Fast Yellow G	**BB**-3,4'-SO_3-4-NH_2		13015	{100}	x	227
Formyl Violet S4B	**S**-9,9'-N(Et)(**P**)-(X=$N(Et)_2$)		42650	{100}	x	227
Methylene Violet 2RA	**U**-7-$N(CH_3)_2$-12-NH_2		50205	{100}	x	227
Naphthol Black 3B	**JJ**-2-OH-3,6,19,21-SO_3		27260	{100}	x	227
Naphthol Green B	(**J**-6-SO_3-(X=NO,Y=O))$_3$Fe		10020	{100}	x	227
Orange IV	**BB**-4-NHPh-4'-SO_3		13080	{100}	x	227
Patent Blue	**S**-7,9-SO_3-9'-$N(Et)_2$-10-OH-(X=$N(Et)_2$)		42051	{100}	x	227
Pontacyl Carmine 2G	**DD**-1-OH-3,6-SO_3-8-$NHCOCH_3$		18050	{100}	x	227
Pontacyl Carmine 6B	**DD**-1-OH-3,6-SO_3-8,11-$NHC(O)CH_3$		18055	{100}	x	227
Solochrome Black	**DD**-1,5,9-OH-12-SO_3		16500	{100}	x	227
Superchrome Yellow RN	**DD**-6,8-SO_3-10-CO_2-11-OH		14110	{100}	x	227

potassium chlorate	$KClO_3$	$P2_1m$	a=4.6569, b=5.5909, c=7.099 Å, β=109.65°			
Biebrich Scarlet	**MM**-2-OH-9,15-SO_3		26905		x	212
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180		x	296
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3		16150		x	297,333
Ponceau G (xxii)	**CC**-2-OH-3,6-SO_3		16100		x	296
St. Denis Red (xii)			604		x	212
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH		19140		x	212
Trypan Red	**XX**-2,2'-NH_2-3,3',6,6',9-SO_3		22850		x	17,184

potassium chloride	KCl	$Fm\bar{3}\,m$	a=6.29294 Å

(xxi) Also France Dye #11.
(xxii) Parent structure for ponceau G is given. May have additional (9,11-CH_3) substituents.

Table 1 (Continued)

Acid Violet 4BN	**S**-2,8-SO_3-9-$N(CH_3)_2$-9'-$N(CH_3)$(**P**)-(X=$N(CH_3)_2$)		42561	{100}	x	227
Alizarin Blue Black B	**E**-1-OH-(2 or 3),4-NH($PhSO_3$) (mixture)		63615	{111}	x	227
Alizarin Red S	**E**-1,2-OH-3-SO_3		58005	{100}	x	227
Anthraquinone Green GX	**E**-1-NH(Ph-SO_3)-4-NH(Ph)-6-SO_3		1081	{100}	x	227
Azorubin	**EE**-1-OH-4,4'-SO_3		14720	{100}	x	227
Brilliant Crocein 9B	**KK**-2-OH-(3 or 8),6,17,19-SO_3-9-CH_3 (mixture)		27300	{111}	x	227
Brilliant Scarlet	**FF**-2-OH-4',6,8-SO_3		16255	{100}	x	227
Brilliant Yellow R	**BB**-4-NHPh-4'-SO_3 & $(-SO_3)_1$		13085	{100}	x	227
Chicago Blue BX	**YY**-1,1'-OH-5,5'-SO_3-8,8'-NH_2-9,9'-CH_3		23830	{100}	x	227
Chicago Blue RW	**VV**-2,17-OH-9,14-OCH_3-20,22-SO_3-23-NH_2		24280	{100}	x	227
Chromotrope 2R	**DD**-1,8-OH-3,6-SO_3		16570	{100}	x	227
Chrysoidin R	**BB**-2-NH_2-4-NH_3Cl-5-CH_3		11320	{100}	x	227
Columbia Blue G	**YY**-1,1'-OH-3,5',8-SO_3-8'-NH_2-9,9'-CH_3		23740	{100}	x	227
Croceine Orange	**CC**-2-OH-6-SO_3		15970	{100}	x	227
Croceine Scarlet 3B	**MM**-2-OH-8,15-SO_3		27155	{100}	x	227
Croceine Scarlet 7B	**MM**-2-OH-8,15-SO_3-9,13-CH_3		27165	{100}	x	227
Cyanol Extra	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NHEt)		43535	{100}	x	227
Diamine Blue 6G	**JJ**-2-OH-9-OEt-19,21-SO_3		26980	{100}	x	227
Diamine Blue BX	**YY**-1,1'-OH-3,4',6-SO_3-8-NH_2-9,9'-CH_3		23710	{100}	x	227
Diaminogen Blue NA	**II**-2-OH-6,(19 or 20)-SO_3-17-NH_2 (mixture)		27095	{100}	x	227
Diphenyl Citronine G	**WW**-8,8'-SO_3		40045	{100}	x	227
Direct Deep Black E Extra	**NNN**-1,17,19-NH_2-3,6-SO_3-8-OH-20-CH_3		30245	{100}	x	227
Direct Orange G (xii)	Stilbene derivative (undetermined structure)		40015	{100}	x	227
Eboli Blue 6A	**YY**-1,1'-OH-4,4',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3		475	{100}	x	227
Erythrosin	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)		45430	{100}	x	227
Fast Red A	**FF**-2-OH-4'-SO_3		15620	{100}	x	227
Fast Red VR	**EE**-1-OH-4',5-SO_3		14835	{100}	x	227
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350	{100}	x	227
Formyl Violet S4B	**S**-9,9'-N(Et)(**P**)-(X=$N(Et)_2$)		42650	{100}	x	227
Metanil Yellow	**BB**-3-SO_3-4-NHPh		13065	{100}	x	227
Methyl Violet	**S**-9-$N(CH_3)_2$-9'-$NHCH_3$-(X=$N(CH_3)_2Cl$)		42535	{100}	x	227
Methylene Violet 2RA	U-7-$N(CH_3)_2$-12-NH_2		50205	{100}	x	227
Murexide	**GGG**				x	163
Naphthol Black 3B	**JJ**-2-OH-3,6,19,21-SO_3		27260	{100}	x	227
Naphthol Black 6B	**II**-4,(6 or 7),16,19-SO_3-15-OH (mixture)		27240	{111}	x	227
Naphthol Green B	(**J**-6-SO_3-(X=NO,Y=O))$_3$Fe		10020	{100}	x	227
Naphthyl Blue Black N	**II**-4,(6 or 7)-SO_3-16-OEt-17-NH_2 (mixture)		310	{100}	x	227
Napthol Yellow S	**B**-1-OH-2,4-NO_2-7-SO_3		10316	{100}	x	227
Newport Direct Blue 3B	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3		23850	{100}	x	227
Orange I	**CC**-4-OH-11-SO_3		14600	{100}	x	227
Orange III	**BB**-4-$N(CH_3)_2$-4'-SO_3		13025	{100}	x	227
Palatine Scarlet	**DD**-1-OH-3,6-SO_3-9,11-CH_3		14900	{100}	x	227
Phloxine	**T**-1-CO_2-2,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)		45405	{100}	x	227
Pontachrome Yellow 3RN	**BB**-3-CO_2-4-OH-4'-NO_2 (mordant dyestuff)		14030	{111}	x	227
Pontacyl Carmine 2G	**DD**-1-OH-3,6-SO_3-8-$NHCOCH_3$		18050	{100}	x	227
Pontamine Blue BBF	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2		22610	{111}	x	227
Pontamine Fast Pink BL	**HH**-2,2'-NH_2-6,6',9,9'-SO_3-8,8'-OH		25380	{100}	x	227
Pontamine Yellow XSG	**WW**-2,2',7,7'-SO_3-4,4'-NO_2		40006	{100}	x	227
Quinoline Yellow	**MMM**-1,2-SO_3		47005	{100}	x	227
Resorcin Yellow	**BB**-2,4-OH-4'-SO_3		14270	{100}	x	227
Rhodamine B	**T**-1-CO_2-8-$N(Et)_2$-(X=O,Y=$N(Et)_2$)		45170	{100}	x	227,411
Rose Bengal	**T**-1-CO_2-2,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)		45435	{100}	x	227
Rose Bengal 3B	**T**-1-CO_2-2,3,4,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)		45440	{100}	x	227
Safranin A	**U**-1-CH_3 -8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)		50240	{100}	x	227
Superchrome Yellow RN	**DD**-6,8-SO_3-10-CO_2-11-OH		14110	{111}	x	227
potassium dichromate	$K_2Cr_2O_7$	*C2/c*	*a*=12.99, *b*=7.368, *c*=7.48 Å, *β*=91.92°			
Chinolin Säuregelb					n	87,174
potassium dihydrogen phosphate	KH_2PO_4	$I\bar{4}\,2d$	*a*=7.448, *c*=6.977 Å			
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{101}	d	247P,354I,355P,359
Chicago Sky Blue (iv)	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410	{101}	d	247P,355P
Direct Blue 15	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3		24400	{101}	d	354I,355
Fast Red Extra	**FF**-2-OH-4',6-SO_3		16045	{101}	d	247,354I
Hematein	**Y**-1,2,6-OH		75290	{010}	d	112,120,247,284,355
Phthalocyaninetetrasulfonate-Co	**N**-$(SO_3)_4$-(M^+=Co)			{101}	d	247P
Phthalocyaninetetrasulfonate-Zn	**N**-$(SO_3)_4$-(M^+=Zn)			{101}	d	247P

Table 1 (Continued)

Stilbene-420	**WW**-6,6'-SO_3		{101}	d	247P
Sunset Yellow	**CC**-2-OH-6,11-SO_3	15985	{101}	d	247P
Trypan Blue	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3	23850	{101}	d	247P,354I,355
University of Washington Dye	**O**		{100}	x	247P,354I,355
University of Washington Dye	**R**		{101}	x	247P,354I,355
University of Washington Dye	**CC**-2-OH-6-SO_3-11-AsO_3		{101}	d	247P
University of Washington Dye	**DD**-1-OH-5,7-SO_3-8-NH_2-9-Cl		{101}	d	247
University of Washington Dye	**DD**-1-OH-5,7-SO_3-8-NH_2-9-Cl-12-OCH_3		{101}	d	247

potassium hydrogen tartrate	$KHC_6H_4O_6$	$P2_12_12_1$	a=7.64, b=10.62, c=7.75 Å		
Acid Magenta	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3	42685	{010}	d	187
Azogrenadine L	**CC**-2-OH-3,6-SO_3-11-NHC(O)CH_3	16130	{010}	d	17,187
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000	{010}	d	187
Chlorazol Fast Orange D (xii)	Stilbene derivative (undetermined structure)	40015	{010}	d	187
Diamine Sky Blue A	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3	24400	{010}	d	187
Diamine Sky Blue FF	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3	24410	{010}	d	187
Diphenyl Citronine G	**WW**-8,8'-SO_3	40045	{010}	d	187
Magenta (xxiii)	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510	{010}	d	187
Metanil Yellow	**BB**-3-SO_3-4'-NHPh	13065	{010}	d	187
Methyl Violet	**S**-9-N(CH_3)$_2$-9'-$NHCH_3$-(X=N(CH_3)$_2$Cl)	42535	{010}	d	187
Naphthalene Black 12B	**BBB**-1-NH_2-3,6-SO_3-8-OH-11-NO_2	20470	{010}	d	187
Orange I	**CC**-4-OH-11-SO_3	14600	{010}	d	187
Orange II	**CC**-2-OH-11-SO_3	15510	{010}	d	187
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3	16150	{010}	d	17
Ponceau 4GB	**CC**-2-OH-6-SO_3	15970	{010}	d	187
Solochrome Brown RH	**BB**-2,4-NH_2-2'-OH-5-SO_3-5'-NO_2	13250	{010}	d	17,187
Solochrome Violet R	**CC**-2,9-OH-12-SO_3	15670	{010}	d	187
Wool Scarlet R	**DD**-1-OH-4,8-SO_3-9,11-CH_3	15010	{010}	d	187

potassium iodate	KIO_3	$R3m$	a=4.410 Å, α=89.42°		
Bordeaux B	**FF**-2-OH-3,6-SO_3	16180		x	296
Ponceau G (xxii)	**CC**-2-OH-3,6-SO_3	16100		x	296

potassium iodide	KI	$Fm\bar{3}m$	a=7.0655		
Acid Fuchsin	**DD**-1-OH-3,6-SO_3-8-NH_2	17200	{111}	x	227
Alizarin Red S	**E**-1,2-OH-3-SO_3	58005	{100}	x	227
Brilliant Crocein 9B	**KK**-2-OH-(3 or 8),6,17,19-SO_3-9-CH_3 (mixture)	27300	{100}	x	227
Brilliant Yellow R	**BB**-4-NHPh-4'-SO_3 & (-SO_3)$_1$	13085	{111}	x	227
Chicago Blue RW	**VV**-2,17-OH-9,14-OCH_3-20,22-SO_3-23-NH_2	24280	{100}	x	227
Chromotrope 2R	**DD**-1,8-OH-3,6-SO_3	16570	{100}	x	227
Chromotrope 6B	**DD**-1,8-OH-3,6-SO_3-11-NHC(O)CH_3	16600	{100}	x	227
Chrysoidin R	**BB**-2-NH_2-4-NH_3Cl-5-CH_3	11320	{100}	x	227
Croceine Orange	**CC**-2-OH-6-SO_3	15970	{100}	x	227
Cyanol Extra	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NHEt)	43535	{100}	x	227
Fast Yellow G	**BB**-3,4'-SO_3-4-NH_2	13015	{100}	x	227
Formyl Violet S4B	**S**-9,9'-N(Et)(**P**)-(X=N($Et)_2$)	42650	{100}	x	227
Methylene Violet 2RA	**U**-7-N(CH_3)$_2$-12-NH_2	50205	{100}	x	227
Patent Blue	**S**-7,9-SO_3-9'-N(Et)$_2$-10-OH-(X=N(Et)$_2$)	42051	{100}	x	227
Pontacyl Carmine 2G	**DD**-1-OH-3,6-SO_3-8-$NHCOCH_3$	18050	{100}	x	227
Superchrome Yellow RN	**DD**-6,8-SO_3-10-CO_2-11-OH	14110	{100}	x	227

potassium nitrate	KNO_3	$R\bar{3}c$	a=7.542 Å, α=42.02°		
Acid Alizarin Blue	**E**-1,3,4,5,7,8-OH-2,6-SO_3	58610		d	377
Amaranth	**FF**-2-OH-3,4',6-SO_3	16185	{010}	d	208,209,377
Bordeaux B	**FF**-2-OH-3,6-SO_3	16180		x	296
Diaminoanthraquinone	**E**-1,4-NH_2		{100}	x	190
Diaminoanthraquinonesulfonate	**E**-1,4-NH_2-2-SO_3		{100}	d	190,197,377
Fast Red E	**FF**-2-OH-6,4'-SO_3			d	377
Naphthol Red S (viii)	**FF**-2-OH-3,4',6-SO_3	16185		d	197
Nigrosin (ix)		50420		n	126
Ponceau G (xxii)	**CC**-2-OH-3,6-SO_3	16100		x	296
Tetraaminoanthraquinone	**E**-1,4,5,8-NH_2		{100}	x	190
Trypan Red	**XX**-2-2'-NH_2-3,3',6,6',9-SO_3	22850		d	197
Whetstone Dye	**CC**-2-OH-6,11-SO_3			d	377

(xxiii) Parent structure given. Dye may have additional (2,8,8'-CH_3) substituents.

Table 1 (Continued)

Whetstone Dye (viii)	**FF**-2-NH_2-3,6,4'-SO_3				d	197
Whetstone Dye (viii)	**FF**-2-NH_2-6,4'-SO_3				d	197
potassium oxalate	$K_2C_2O_4$	*Pbam*	*a*=10.916, *b*=6.120, *c*=3.441 Å			
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3		16150		d	17
potassium perchlorate	$KClO_4$	*Pnma*	*a*=8.834, *b*=5.650, *c*=7.240 Å			
Azofuchsin B (xxiv)	**DD**-1,8-OH-4-SO_3-11-CH_3		16550	{011}	x	17,185,263P,369P
Methyl Blue (x)	**S**-9,9'-NH($PhSO_3$)-(X=NHPh)		42770		x	212
Methylene Blue	**G**-3,6-N(CH_3)$_2$-(X=S)		52015		x	212
St. Denis Red (xii)			604		x	212
potassium selenate	K_2SeO_4	*Pmcn*	*a*=6.00, *b*=10.47, *c*=7.66 Å			
Acid Fuchsin	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3-(X=NH_2)		42685	{110}	d	202
potassium sulfate	K_2SO_4	*Pmcn*	*a*=5.772, *b*=10.072, *c*=7.483 Å			
	K-1,3,6-SO_3-8-$OCH_2C(O)OCH_3$			{010}	d	389I
Acetylpyrenetrisulfonate	**K**-1,3,6-SO_3-8-$C(O)CH_3$			{010}	d	389I
Acid Fuchsin	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3-(X=NH_2)		42685	{110}	d	17P,183,198,201,202P 263P,264,276,354I 367P,382,389I
Acid Magenta N.D.	**S**-2,8,8'-SO_3-6,10,10'-CH_3-9,9'-NH_2-(X=NH_2)		42520	{110}	d	201P,383,389I
Algosol Blue 04B	5,5',7,7'-tetrabromoindigo leuco sulfuric ester, Na				x	269
Alizarin Red S	**E**-1,2-OH-3-SO_3		58005	{110}	x	17,263P
Alizarin Yellow 2G (H^+ or ^-OH)	**BB**-3-CO_2-4-OH-3'-NO_2		14025	{100}	x	379
Alizarin Yellow 5G (H^+ or ^-OH)	**BB**-3-CO_2-4-OH-4'-OEt		14080	{100}	x	17PI,379I
Alizarin Yellow R	**BB**-3-CO_2-4-OH-4'-NO_2		14030	{100}	x	379
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{110}	d	202, 264
Aminonaphthalenedisulfonate	**B**-1,5-SO_3-2-NH_2			{110},{021}	d	264,270,354I,419PI
Aminonaphthalenedisulfonate	**B**-2-NH_2-6,8-SO_3			{021}	d	274
Aminonaphthalenedisulfonate	**B**-3-NH_2-1,5-SO_3			{021}	d	274
Aminonaphthalenedisulfonate	**B**-4-NH_2-1,5-SO_3			{110}	d	274
Aminonaphthalenedisulfonate	**B**-2-NH_2-3,6-SO_3			{010},{110}	d	274
Aminonaphthalenesulfonate	**B**-1-SO_3-2-NH_2			{110},{021}	d	264,270,274,419PI
Aminonaphthalenesulfonate	**B**-1-NH_2-4-SO_3			{*hkl*}	d	274
Aminonaphthalenesulfonate	**B**-2-NH_2-5-SO_3			{021}	d	274
Aminonaphthalenesulfonate	**B**-2-NH_2-6-SO_3			{*hkl*}	d	274
Aminonaphthalenesulfonate	**B**-1-NH_2-6-SO_3			{110}	d	274
Aminonaphthalenesulfonate	**B**-1-NH_2-7-SO_3			{*hkl*}	d	274
Aminonaphtholdisulfonate	**B**-1-OH-2-NH_2-5,7-SO_3			{110}	d	274
Aminonaphtholdisulfonate	**B**-1-OH-3,6-SO_3-8-NH_2			{010},{110}	d	274
Aminonaphtholdisulfonate	**B**-1-NH_2-2-OH-3,6-SO_3				x	269
Aminonaphtholsulfonate	**B**-1-NH_2-2-OH-4-SO_3				x	269
Aminopyrenetrisulfonate	**K**-1,3,6-SO_3-8-NH_2			{010}	d	389I
Aminotoluenesulfonate	**A**-1-NH_2-2-SO_3-4-CH_3			{021},{011} {110},{111} {001}	d	270
Aniline-2-sulfonate	**A**-1-NH_2-2-SO_3			{021},{011} {110},{111} {001}	d	264,270PI,359
Aniline-3-sulfonate	**A**-1-NH_2-3-SO_3			{021},{011} {110},{001}	d	270
Aniline-4-sulfonate	**A**-1-NH_2-4-SO_3			{021},{011} {110},{001}	d	270
Anthrasol Brown IBR					x	269
Anthrasol Printing Blue IGG					x	269
Azo Orseille R	**DD**-1-OH-3,6-SO_3-7-NH_2		17160	{110}	x	17,263P
Azofuchsin B	**DD**-1,8-OH-4-SO_3-11-CH_3		16550		d	187
Azofuchsin G	**DD**-1,8-OH-4,11-SO_3		16540		x	17P,269
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		d	126,154,174,175I
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180		x	183,296
Brilliant Congo R	**XX**-2,2'-NH_2-3,6,6'-SO_3-9,9'-CH_3		23570	{111}	x	17,263P
Bromopyrenetrisulfonate	**K**-1,3,6-SO_3-8-Br			{010}	d	389I
Carboxypyrenetrisulfonate	**K**-1,3,6-SO_3-8-CO_2			{010}	d	389I

(xxiv) Misnamed biebrich scarlet.

Table 1 (Continued)

Carmoisine L9156K	**EE**-1-OH-4',5-SO_3	14835		x	183
Chinolin Säuregelb				d	87,174
Chromazol Yellow	**UU**-3,3'-CO_2-4,4'-OH-8,8'-SO_3	22880		x	269
Chromotrope 2B	**DD**-1,8-OH-3,6-SO_3-11-NO_2	16575	{010}	d	17,182,264
Columbia Green B	**NNN**-1,19-OH-3,6-SO_3-8-NH_2-24-NO_2	30295	{010}	x	17,186
Coomassie Scarlet 9012K	**OO**-1-OH-4,6'-SO_3	14730		x	183
Croceine Scarlet 3BX	**FF**-2-OH-4',8-SO_3	16050	{021}	x	17,183,263P
Crystal Ponceau (xxv)	**FF**-2-OH-6,8-SO_3	16250	{001}	d	126,154,161I,163, 174,175I
Diamine Sky Blue A	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3	24400	{111}	x	263
Diamine Sky.Blue FF (iv)	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3	24410	{111}	x	263,269
Dihydroxynaphthalenedisulfonate	**B**-1,8-OH-3,6-SO_3		{010},{110}	d	274
Disulphine Blue AS	**S**-7,9-SO_3-9'-N(Et)(CH_2Ph)-10-OH-(X=N(Et)(CH_2Ph))	42052		x	269
Disulphine Blue V	**S**-7,9-SO_3-9'-N(Et)$_2$-10-OH-(X=N(Et)$_2$)	42051		x	269
Edicol Amaranth	**XX**-2,2'-NH_2-3,3',6,6',9-SO_3			x	269
Eriochrome Black TS	**EE**-1,2'-OH-4'-SO_3-5'-NO_2	14645		x	269
Evans Blue	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-CH_3	23860	{110},{111}	d	264
Fast Light Yellow	**CC**-1,8-OH-4,11-SO_3	16540		x	269
Fast Red Extra	**FF**-2-OH-4',6-SO_3	16045		x	183
Fast Yellow	**BB**-3,4'-SO_3-4-NH_2	13015		x	269
France Dye: A-β-NH_2-(6 or 7)	**CC**-2-NH_2-(6 or 7)-SO_3		{110},{010}	x	234,238
France Dye: A-α-NH_2-5	**DD**-1-OH-5-SO_3		uniform	x	234,238
France Dye: A-β-NH_2-5	**CC**-2-NH_2-5-SO_3		{111},{110}	x	234,238
France Dye: A-α-OH-5	**DD**-1-OH-5-SO_3		{110},{010}	x	234,238
France Dye: M-β-NH_2	**CC**-2-NH_2-10-SO_3		{111},{110} {010}	x	234,238
France Dye: M-α-NH_2-(2or7or8)	**DD**-1-NH_2-(2 or 7 or 8),10-SO_3		{110}	x	234,238
France Dye: M-α-NH_2-4	**DD**-1-NH_2-4,10-SO_3		uniform	x	234,238
France Dye: M-α-NH_2-6	**DD**-1-NH_2-6,10-SO_3		{111},{110}	x	234,238
France Dye: M-β-NH_2-7	**CC**-2-NH_2-7,10-SO_3		uniform	x	234,238
France Dye: M-α-OH	**DD**-1-OH-10-SO_3		{110},	x	234,238
France Dye: M-β-OH	**CC**-2-OH-10-SO_3		uniform	x	234,238
France Dye: M-β-OH-(6 or 7)	**CC**-2-OH-(6 or 7),10-SO_3		{111},{110}	x	234,238
France Dye: M-α-OH-3	**DD**-1-OH-3,10-SO_3		{110}	x	234,238
France Dye: M-β-OH-3:6	**CC**-2-OH-3,6,10-SO_3			x	234,238
France Dye: M-α-OH-3:8	**DD**-1-OH-3,8,10-SO_3		uniform	x	234,238
France Dye: M-α-OH-4	**DD**-1-OH-4,10-SO_3		uniform	x	234,238
France Dye: M-β-OH-7	**CC**-2-OH-7,10-SO_3		{111},{110}	x	234,238
France Dye: O-α-NH_2-2	**DD**-1-NH_2-2,9-SO_3		{110}	x	234,238
France Dye: O-β-OH-(6 or 7)	**CC**-2-OH-(6 or 7),9-SO_3		{110},{010}	x	202,234,238
France Dye: O-α-OH-3:8	**DD**-1-OH-3,8,9-SO_3		uniform	x	234,238
France Dye: P-α-NH_2	**DD**-1-NH_2-11-SO_3		{110}	x	234,238
France Dye: P-β-NH_2	**CC**-2-NH_2-11-SO_3		{111},{110}	x	234,238
France Dye: P-α-NH_2-(7 or 8)	**DD**-1-NH_2-(7 or 8),11-SO_3		{111},{110}	x	234,238
France Dye: P-α-OH	**DD**-1-OH-11-SO_3		{110}	x	234,238
France Dye: P-β-OH	**CC**-2-OH-11-SO_3	15510	{111},{110} {010}	x	234,238
France Dye: P-β-OH-6:8	**CC**-2-OH-6,8,11-SO_3		{111},{110}	x	234,238
France Dye: P-β-OH-7	**CC**-2-OH-7,11-SO_3		{111},{110}	x	234,238
Hematein	**Y**-1,2,6-OH	75290		d	174
Hydroxynaphthalenedisulfonate	**B**-2-OH-6,8-SO_3		{110}	d	274
Hydroxynaphthalenedisulfonate	**B**-1-OH-3,6-SO_3		{010}	d	274
Hydroxynaphthalenedisulfonate	**B**-2-OH-3,6-SO_3		{010},{110}	d	274
Indigosol Yellow I2G	**HHH**-4,11-SO_3-7-CO_2-8-OH	19140		x	269
Lissamine Fast Yellow	**BB**-2,3'-CH_3-4'-NH_2-4,5'-SO_3	13135		x	269
Mars Red G Carmoisine	**EE**-1-OH-4,4'-SO_3	14720		x	183
Methoxypyrenetrisulfonate	**K**-1,3,6-SO_3-8-OCH_3		{010}	d	389I
Mode Braun				d	126
Naphthalene Fast Orange				x	269
Naphthalenedisulfonate	**B**-1,5-SO_3		{*hkl*}	d	274
Naphthol Green	(**J**-6-SO_3-(X=NO,Y=O))$_3$Fe	10020	{001}	x	17,184,202,263,269, 354I
Naphthol Red S	**FF**-2-OH-3,4',6-SO_3	16185		d	17
National Fast Wool Blue B	**FF**-3,5',6-SO_3-4'-NH(Ph-*p*-CH_3)-8-OH	13405		d	17
Palatine Red A	**EE**-1-OH-3,6-SO_3	14910		x	183
Palatine Scarlet 3R	**OO**-1-OH-3,6-SO_3	14920		x	183

(xxv) Also ponceau red.

Table 1 (Continued)

Patent Blue	**S**-7,9-SO_3-9'-N(Et)$_2$-10-OH-(X=N(Et)$_2$)	42051		d	174
Phosphine	**U**-3,8-NH_2-(X=N,Y=C)(HNO_3)	46045	{001}	x	154
Ponceau 2R	**CC**-2-OH-3,6-SO_3-9,11-CH_3	16150		d	17
Ponceau 3R	**EE**-1,2'-OH-3,8'-SO_3-7-NH_2	17110	{021}	x	17,263
Ponceau 6R	**FF**-2-OH-3,4',6,8-SO_3	16290		x	269
Ponceau G (xxii)	**CC**-2-OH-3,6-SO_3	16100		x	296
Pyranine	**K**-1,3,6-SO_3-8-OH	59040	{010}	d	276,354I,367P,389I
Pyranine (Basic)	**K**-1,3,6-SO_3-8-O	59040	{110},{010}	d	201P,264,383
Pyrenetetrasulfonate	**K**-1,3,6,8-SO_3		{010}	d	389I
Pyrenetrisulfonatecarboxaldehyde	**K**-1,3,6-SO_3-8-CHO		{010}	d	389I
Quinoline Yellow	**MMM**-1,2-SO_3	47005	{021},{*hkl*}	x	17,202,263
Quinolinic Acid	**I**-2,3-CO_2			d	175I
Safranin	**U**-1-CH_3 -8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)	50240	{001}	x	154
Solochrome Brown RH	**BB**-2,4-NH_2-2'-OH-5-SO_3-5'-NO_2	13250		d	17,187
Sulforhodamine 101	**V**-1,3-SO_3		{110}	d	264
Sulforhodamine B	**T**-1,3-SO_3-11-N(Et)$_2$-(X=O,Y=N(Et)$_2$)	45100	{110}	d	264,354I,389I
Sunset Yellow	**CC**-2-OH-6,11-SO_3	15985	{110},{010} {111}	x	202,234,238
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH	19140		x	269
Trisulfonated Pararosaniline	**S**-2,8,8'-SO_3-9,9'-NH_2-(X=NH_2)	42500	{110}	d	201,389I
Trypan Blue	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3	23850	{010},{111}	d	264
Trypan Red	**XX**-2,2'-NH_2-3,3',6,6',9-SO_3	22850		x	269
Wool Scarlet R	**DD**-1-OH-4,8-SO_3-9,11-CH_3	15010		d	187
Xylene Cyanol FF	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NH(Et)	43535		x	269

protocatechuic acid monohydrate	**A**-1-COOH-3,4-OH • H_2O	Polymorph not specified			
Alizarin	**E**-1,2-OH	58000		d	129
Alkali Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph-*p*-SO_3)-(X=NH(Ph))	42750		d	129
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)	21000		d	129
Carmine	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3 (Al,Ca)	75470		d	129
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl	11270		d	129
Curcuma	**RR**-3,3'-OCH_3-4,4'-OH	75300		x	129
Drachenblut (xv)	Sanguis draconis	75200		d	129
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)	45380		d	129
Erythrosin	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)	45430		d	129
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)	45350		d	129
Gentian Violet	**S**-9-N(CH_3)$_2$-9'-NHCH_3-(X=N(CH_3)$_2$Cl)	42535		d	129
	& **S**-9,9'-N(CH_3)$_2$-(X=N(CH_3)$_2$Cl & dextrin	42555			
Gentiana Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl	42775		d	129
Karthaminsäure				d	129
Methyl Violet	**S**-9-N(CH_3)$_2$-9'-NHCH_3-(X=N(CH_3)$_2$Cl)	42535		d	129
Mode Braun				d	129
Nigrosin (ix)		50420		d	129
Phenylblau				d	129
Purpurin	**E**-1,2,4-OH	58205		d	129
Tropäolin	**BB**-2,4-OH-4'-SO_3	14270		d	129
Water Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-SO_3)$_3$	42755		d	129

quinine sulfate dihydrate	$C_{40}H_{50}N_4O_8$ • 2 H_2O	*C*2	*a*=15.49, *b*=6.74, *c*=20.02Å, *β*=110.98°		
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	d	130
Chrysoidin	**BB**-2-NH_2-4-NH_3Cl		11270	d	130
Mode Braun				d	130

rubidium sulfate	Rb_2SO_4	*Pnma*	*a*=7.801, *b*=5.965, *c*=10.416 Å		
Acid Fuchsin	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3-(X=NH_2)		42685	{110}	d	264
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{110}	d	264
Aminonaphthalenedisulfonate	**B**-1,5-SO_3-2-NH_2			{021}	d	264
Aminonaphthalenesulfonate	**B**-1-SO_3-2-NH_2			{021}	d	264
Aniline-2-sulfonate	**A**-1-NH_2-2-SO_3			{001}	d	264
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{001}	x	154
Chromotrope 2B	**DD**-1,8-OH-3,6-SO_3-11-NO_2		16575	{010}	d	264
Phosphine	**U**-3,8-NH_2-(X=N,Y=C)(HNO_3)		46045	{001}	x	154
Ponceau Red	**FF**-2-OH-6,8-SO_3		16250	{001}	x	154
Pyranine	**K**-1,3,6-SO_3-8-OH		59040	{010}	d	354
Pyranine (Basic)	**K**-1,3,6-SO_3-8-O		59040	{110},{010}	d	264
Safranin	**U**-1-CH_3 -8,11-CH_3-7,12-NH_2-(X,Y=N)		50240	{001}	x	154

Table 1 (Continued)

	& **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)					
Sulforhodamine 101	**V**-1,3-SO_3			{110}	d	264
Sulforhodamine B	**T**-1,3-SO_3-11-$N(Et)_2$-(X=O,Y=$N(Et)_2$)		45100	{110}	d	264
Trypan Blue	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3		23850	{010}{111}	d	264
saccharin (*o*-sulfobenzoimide)	$C_7H_5N_1O_3S$	$P2_1/c$	a=9.552, b=6.919, c=11.803 Å, β=103.9°			
Indigo	**L**		73000	(102) xxvi	x	376
salicylic acid	**A**-1-CO_2-2-OH	$P2_1/a$	a=11.52, b=11.21, c=4.92 Å, β=90.83°			
Fluorescein or Uranin	**T**-1-CO_2-11-OH-(X,Y=O)		45350		x	17
silver bromide	AgBr	$Fm\bar{3}\,m$	a=5.7745 Å			
Maskasky Dye: A	**CCC**-(X=$(CH_2)_2SO_3$)-(Y=CH_3)			{111}	x	407
Maskasky Dye: B	**CCC**-(X=$(CH_2)_2SO_3$)-(Y=H)				x	407
Maskasky Dye: C	**LLL**-(X,Y=CH_3)				x	407
Maskasky Dye: D	**LLL**-(X=CH_3)-(Y=H)				x	407
Maskasky Dye: E	**CCC**-(X=$(CH_2)CO_2$)-(Y=H)				x	407
Maskasky Dye: F	**CCC**-(X=H)-(Y=H)				x	407
Maskasky Dye: G	**DDD**			{111}	x	407
Maskasky Dye: H	**FFF**				x	407
Maskasky Dye: I	**EEE**			{100},{111}	x	407
Maskasky Dye: J	**JJJ**				x	407
Methyl Blue (x)	**S**-9,9'-NH($PhSO_3$)-(X=NHPh)		42770		x	212
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	212
silver chloride	AgCl	$Fm\bar{3}\,m$	a=5.547 Å			
Acid Violet	**S**-9,9'-N(Et)(**P**)-(X=$N(Et)_2$)		42650	{111}	x	213P,214P,215
Benzoazurin	**YY**-1,1'-OH-4,4'-SO_3-9,9'-OCH_3		24140	{111}	x	213P,214P,215
	or **YY**-1,1'-OH-5,5'-SO_3-9,9'-OCH_3		24205			
	or **YY**-1,1'-OH-3,4'-SO_3-6-NH_2-9,9'-CH_3		23705			
Benzopurpurin				{111}	x	213P,214P,215
Brilliant Congo	**XX**-2,2'-NH_2-3,6,6'-SO_3		22160	{111}	x	213P,214P,215
	or **XX**-2,2'-NH_2-3,6,7'-SO_3-9,9'-CH_3		23585			
	or **XX**-2,2'-NH_2-3,6,6'-SO_3-9,9'-CH_3		23570			
Chrome Violet	**CC**-2,9-OH-12-SO_3		15670	{111}	x	213P,214P,215
Chrysophenine	**WW**-4,4'-OEt-8,8'-SO_3		24895		x	213P,214P,215
Congo Corinth	**YY**-1-OH-1'-NH_2-4,4'-SO_3		22145		x	213P,214P,215
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3		22120		x	213P,214P,215
Delta Purpurin	**XX**-2,2'-NH_2-6,7'-SO_3-9,9'-CH_3		23565	{111}	x	213P,214P,215
	or **XX**-2,2'-NH_2-7,7'-SO_3-9,9'-CH_3		23580			
Diamond Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) • ZnCl		42000		x	213P,214P,215
Erythrosin A	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)		45430	{111}	x	213P,214P,215
Indulin	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & $(-SO_3)_x$		861	{111}	x	213P,214P,215
Kiton Green				{111}	x	213P,214P,215
Kiton Violet				{111}	x	213P,214P,215
Marine Blue	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)		42000		x	213P,214P,215
	& **S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) (mixture)		42535			
Methyl Blue (x)	**S**-9,9'-NH($PhSO_3$)-(X=NHPh)		42770		x	212
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	212,213P,214P,215
Orseille Brown	coloring matter from lichen, *Roccella tincoria*		1242	{111}	x	213P,214P,215
Phloxin O	**T**-1-CO_2-2,3,4,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)		45405	{111}	x	213P,214P,215
	& **T**-1-CO_2-2,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)					
Quinoline Yellow	**MMM**-1,2-SO_3		47005	{111}	x	213P,214P,215
Roccelline	**FF**-2-OH-4'-SO_3		15620	{111}	x	213P,214P,215
Rose Bengal	**T**-1-CO_2-2,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)		45435	{111}	x	213P,214P,215
Toluylene Orange	**UU**-2,6-NH_2-3,3',7,7'-CH_3-4'-OH-5-SO_3-5'-CO_2		23370	{111}	x	213P,214P,215
	or **UU**-2,2',6,6'-NH_2-3,3',7,7'-CH_3-5,5'-SO_3		23380			
	or **SS**-2,2'-NH_2-10-SO_3-11-CH_3		21515			
***trans*-sinapic acid**	$C_{11}H_{12}O_5$	$P2_1/n$	a=4.760, b=15.686, c=14.185 Å, β=90.30°			
Acridine Orange	**G**-2,7-$N(CH_3)_2$-(X=CH)		46005	{021}	d	431
Coomassie Brilliant Blue G	**PP**		42660	{021}	d	431
Crystal Violet	**S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)		42555	{021}	d	136,274,431

(xxvi) Dye incorporated at the twin interface.

Table 1 (Continued)

Malachite Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) • ZnCl		42000	{021}	d	136,274,431
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015	{021}	d	431P
sodium acetate trihydrate	$NaOAc \cdot 3H_2O$	*C2/c*	*a*=12.341, *b*=111.65, *c*=10.408 Å, *β*=111.65°			
4-aminobenzoic acid	**A**-1-CO_2-4-NH_2			{001}	d	419PI
sodium chlorate	$NaClO_3$	$P2_13$	*a*=6.5756 Å			
Croceine Scarlet 3B	**MM**-2-OH-8,15-SO_3		27155		x	399
Extra China Blue (xxvii)					x	292P
France Dye: P-β-OH-7	**CC**-2-OH-7,11-SO_3			{100}	x	235P,293
Phloxine	**T**-1-CO_2-2,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)		45405		x	399
Sunset Yellow	**CC**-2-OH-7,11-SO_3		15985	{100}	x	235P,293
sodium chloride	NaCl	$Fm\bar{3}m$	*a*=5.64056 Å			
France Dye: M-α-NH_2-5	**DD**-1-NH_2-5,10-SO_3			{100}	x	234
Murexide	**GGG**			{111}	x	145,163
sodium fluoride	NaF	$Fm\bar{3}m$	*a*=4.620 Å			
Aceko Fast Red	**FF**-2-OH-4',6-SO_3		16045	{100}	x	227
Acid Anthracene	**XX**-2,2'-OH-10,10'-SO_3		22890	{100}	x	227
Acid Blue GR	**L**-2,4,5,7-SO_3		73015	{100}	x	227
Acid Fuchsin	**S**-2,8,8'-SO_3-9,9'-NH_2-10-CH_3-(X=NH_2)		42685	{100}	x	227
Acid Violet 4BN	**S**-2,8-SO_3-9-$N(CH_3)_2$-9'-$N(CH_3)$(**P**)-(X=$N(CH_3)_2$)		42561	{100}	x	227
Alizarin Blue Black B	**E**-1-OH-(2 or 3),4-NH($PhSO_3$) (mixture)		63615	{100}	x	227
Alizarin Cyanol EF	**E**-1-NH_2-2-Br-4-NH($PhSO_3$)-(5or8)-SO_3 (mixture)		62060	{100}	x	227
Alizarin NAC	**E**-1,2-OH		58000	{100}	x	227
Alizarin Red S	**E**-1,2-OH-3-SO_3		58005	{111}	x	227
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{100}	x	227
Anthraquinone Blue SR	**E**-1,5-NH_2-2,6-Br-4,8-NH($PhSO_3$)		64515	{100}	d	227
Anthraquinone Green GX	**E**-1-NH-($PhSO_3$)-4-NH(Ph)-6-SO_3		1081	{100}	d	227
Azo Blue	**YY**-1,1'-OH-4,4'-SO_3-9,9'-CH_3		23680	{100}	x	227
Azo Red A	**EE**-1-OH-3,4',6-SO_3		14915	{100}	x	227
Azorubin	**EE**-1-OH-4,4'-SO_3		14720	{100}	x	227
Basic Fuchsin	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)		42510	{100}	x	227
Benzopurpurin 4B	**YY**-1,1'-NH_2-4,4'-SO_3-9,9'-CH_3		23500	{100}	x	227
Benzopurpurin 6B	**YY**-1,1'-NH_2-5,5'-SO_3-9,9'-CH_3		23530	{100}	x	227
Biebrich Scarlet	**MM**-2-OH-9,15-SO_3		26905	{100}	x	227
Bordeaux B	**FF**-2-OH-3,6-SO_3		16180	{100}	d	227
Brilliant Crocein 9B	**KK**-2-OH-(3 or 8),6,17,19-SO_3-9-CH_3 (mixture)		27300	{100}	x	227
Brilliant Scarlet	**FF**-2-OH-4',6,8-SO_3		16255	{100}	x	227
Brilliant Yellow R	**BB**-4-NHPh-4'-SO_3 & $(-SO_3)_1$		13085	{100}	x	227
Chicago Blue BX	**YY**-1,1'-OH-5,5'-SO_3-8,8'-NH_2-9,9'-CH_3		23830	{100}	x	227
Chicago Blue RW	**VV**-2,17-OH-9,14-OCH_3-20,22-SO_3-23-NH_2		24280	{100}	x	227
Chrome Brown R	**BB**-2,4-NH_2-5-SO_3-2'-OH-5-NO_2		13250	{100}	x	227
Chrome F	**DD**-1,9-OH-3,6-SO_3-8-NH_2-12-NO_2		17225	{100}	x	227
Chromotrope 2R	**DD**-1,8-OH-3,6-SO_3		16570	{100}	x	227
Chromotrope 6B	**DD**-1,8-OH-3,6-SO_3-11-NHC(O)CH_3		16600	{100}	x	227
Chromotrope 8B	**EE**-1,8-OH-3,4',6-SO_3		16645	{100}	x	227
Chrysamine R	**UU**-3,3'-CO_2-4,4'-OH-7,7'-CH_3		23640	{100}	x	227
Chrysoidin R	**BB**-2-NH_2-4-NH_3Cl-5-CH_3		11320	{100}	x	227
Cochineal	**E**-1,3,4,6-OH-2-($C_6H_{11}O_5$)-5-CO_2-8-CH_3		75470	{100}	x	227
Columbia Blue G	**YY**-1,1'-OH-3,5',8-SO_3-8'-NH_2-9,9'-CH_3		23740	{100}	d	227
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3		22120	{100}	x	227
Coomassie Fast Black B	**II**-5,18-SO_3-17-NHPh		26370	{100}	x	236
Croceine Orange	**CC**-2-OH-6-SO_3		15970	{111}	d	227
Croceine Scarlet 3B	**MM**-2-OH-8,15-SO_3		27155	{100}	x	227
Croceine Scarlet 7B	**MM**-2-OH-8,15-SO_3-9,13-CH_3		27165	{100}	x	227
Croceine Scarlet N Extra	**MM**-2-OH-6,8-SO_3		27290	{100}	x	227
Crystal Ponceau	**FF**-2-OH-6,8-SO_3		16250	{100}	x	227
Crystal Violet	**S**-9,9'N$(CH_3)_2$-(X=$N(CH_3)_2Cl$)		42555	{100}	x	227
Cyanol Extra	**S**-2,8'-CH_3-7,9-SO_3-9'-NH(Et)-10-OH-(X=NH(Et)		43535	{100}	x	227
Diamine Blue 6G	**JJ**-2-OH-9-OEt-19,21-SO_3		26980	{100}	d	227
Diamine Blue BX	**YY**-1,1'-OH-3,4',6-SO_3-8-NH_2-9,9'-CH_3		23710	{100}	d	227
Diamine Sky Blue A	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3		24400	{100}	x	227

(xxvii) Perhaps triphenyltri-*p*-aminodi(tri-)phenyltolylbarbinoldi(mono)sulfonate

Table 1 (Continued)

Diaminogen Blue NA	**II**-2-OH-6,(19 or 20)-SO_3-17-NH_2 (mixture)	27095	{100}	x	227
Dianil Azurine	**YY**-1,1'-OH-3,4'-SO_3-6-NH_2-9,9'-CH_3	23705	{100}	d	227
Diphenyl Citronine G	**WW**-8,8'-SO_3	40045	{100}	x	227
Direct Deep Black E Extra	**NNN**-1,17,19-NH_2-3,6-SO_3-8-OH-20-CH_3	30245	{100}	x	227
Direct Orange G (xii)	Stilbene derivative (undetermined structure)	40015	{100}	x	227
Disulphine Blue A	**S**-7,9-SO_3-9'-N(Et)(CH_2Ph)-10-OH-(X=N(Et)(CH_2Ph))	42052	{100}	x	236
Eboli Blue 6A	**YY**-1,1'-OH-4,4',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3	475	{100}	d	227
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)	45380	{100}	x	227
Erythrosin	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)	45430	{100}	x	227
Fast Red A	**FF**-2-OH-4'-SO_3	15620	{100}	x	227
Fast Red VR	**EE**-1-OH-4',5-SO_3	14835	{100}	x	227
Fast Yellow G	**BB**-3,4'-SO_3-4-NH_2	13015	{100}	x	227
Formyl Violet S4B	**S**-9,9'-N(Et)(**P**)-(X=N($Et)_2$)	42650	{100}	x	227
Gentian Violet (xvi)	**S**-9-N($CH_3)_2$-9'-NHCH_3-(X=N($CH_3)_2$Cl) & **S**-9,9'-N$(CH_3)_2$-(X=N($CH_3)_2$Cl & dextrin	42535 42555	{100}	x	227
Hematein	**Y**-1,2,6-OH	75290	{111}	x	227
Indulin	**U**-7,8,11,12-NH(Ph)-(X,Y=N) & (-$SO_3)_x$	50405	{100}	d	227
Light Green SF Yellowish	**S**-9-SO_3-9'-N(Et)(**P**)-(X=N(Et)(**P**))	42095	{100}	x	227
Magenta (xxiii)	**S**-8-CH_3-9,9'-NH_2-(X=NH_2Cl)	42510	{111}	x	236
Martius Yellow	**B**-1-OH-2,4-NO_2	10315	{100}	x	227
Metanil Yellow	**BB**-3-SO_3-4'-NHPh	13065	{100}	x	227
Methyl Alkali Blue	**S**-9-NH(Ph)-9'-NH(Ph-*p*-SO_3)-(X=NH(Ph))	42765	{100}	x	227
Methyl Violet	**S**-9-N$(CH_3)_2$-9'-NHCH_3-(X=N($CH_3)_2$Cl)	42535	{100},{111}	x	227,236
Methylene Blue	**G**-3,6-N$(CH_3)_2$-(X=S)	52015	{100}	x	227
Methylene Violet 2RA	**U**-7-N$(CH_3)_2$-12-NH_2	50205	{100}	x	227
Naphthol Black 12B	**BBB**-1-NH_2-3,6-SO_3-8-OH-11-NO_2	20470	{100}	x	236
Naphthol Black 3B	**JJ**-2-OH-3,6,19,21-SO_3	27260	{100}	d	227
Naphthol Black 6B	**II**-4,(6 or 7),16,19-SO_3-15-OH (mixture)	27240	{100}	x	227
Naphthol Green B	(**J**-6-SO_3-(X=NO,Y=O))$_3$Fe	10020	{100}	x	227
Naphthol Yellow S	**B**-1-OH-2,4-NO_2-7-SO_3	10316	{100}	x	227
Napthyl Blue Black N	**II**-4,(6 or 7)-SO_3-16-OEt-17-NH_2 (mixture)	310	{100}	x	227
Newport Croceine Scarlet	**FF**-2-OH-4',8-SO_3	16050	{100}	x	227
Newport Direct Blue 3B	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-CH_3	23850	{100}	x	227
Nigrosin WSB (ix)		50420	{100}	x	227
Orange G	**CC**-2-OH-6,8-SO_3	16230	{100}	x	227
Orange GT	**CC**-2-OH-6-SO_3-11-CH_3	16010	{100}	x	227
Orange I	**CC**-4-OH-11-SO_3	14600	{100}	x	227
Orange II	**CC**-2-OH-11-SO_3	15510	{100}	x	227
Orange III	**BB**-4-N$(CH_3)_2$-4'-SO_3	13025	{100}	x	227
Orange IV	**BB**-4-NHPh-4'-SO_3	13080	{100}	x	227
Orange RO	**CC**-2-OH-9-CH_3-11-SO_3	15575	{100}	x	227
Palatine Scarlet	**DD**-1-OH-3,6-SO_3-9,11-CH_3	14900	{100}	x	227
Patent Blue	**S**-7,9-SO_3-9'-N$(Et)_2$-10-OH-(X=N($Et)_2$)	42051	{100}	x	227
Phloxine	**T**-1-CO_2-2,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)	45405	{100}	x	227
Ponceau 3R	**CC**-2-OH-3,6-SO_3-9,11,12-CH_3	16155	{100}	x	227
Ponceau 6R	**FF**-2-OH-3,4',6,8-SO_3	16290	{100}	x	227
Pontachrome Black K	**EE**-1,2'-OH-4-SO_3-5'-NO_2	14645	{100}	x	227
Pontachrome Yellow 3RN	**BB**-3-CO_2-4-OH-4'-NO_2 (mordant dyestuff)	14030	{100}	x	227
Pontacyl Carmine 2G	**DD**-1-OH-3,6-SO_3-8-NHCOCH_3	18050	{100}	x	227
Pontacyl Carmine 6B	**DD**-1-OH-3,6-SO_3-8,11-NHC(O)CH_3	18055	{100}	x	227
Pontamine Blue BBF	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2	22610	{100}	x	227
Pontamine Fast Pink BL	**HH**-2,2'-NH_2-6,6',9,9'-SO_3-8,8'-OH	25380	{100}	d	227
Pontamine Yellow XSG	**WW**-2,2',7,7'-SO_3-4,4'-NO_2	40006	{100}	x	227
Quinoline Yellow	**MMM**-1,2-SO_3	47005	{100}	x	227
Resorcin Yellow	**BB**-2,4-OH-4'-SO_3	14270	{100}	x	227
Rhodamine B	**T**-1-CO_2-8-N$(Et)_2$-(X=O,Y=N($Et)_2$)	45170	{100}	x	227
Rose Bengal	**T**-1-CO_2-2,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)	45435	{100}	x	227
Rose Bengal 3B	**T**-1-CO_2-2,3,4,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)	45440	{100}	x	227
Safranin A	**U**-1-CH_3-8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)	50240	{100}	x	227
Solochrome Black	**DD**-1,5,9-OH-12-SO_3	16500	{111}	x	227
Solochrome Black A	**FF**-2,2'-4-SO_3-5-NO_2	15710	{100}	x	227
Soluble Blue	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-$SO_3)_3$	42755	{100}	x	227
Soluble Blue 3M	**S**-8-CH_3-9-NH_2-9'-NH(Ph)-(X=NH(Ph)) & (-$SO_3)_3$	42755	{100}	x	236
Superchrome Yellow RN	**DD**-6,8-SO_3-10-CO_2-11-OH	14110	{100}	x	227
Tartrazin	**HHH**-4,11-SO_3-7-CO_2-8-OH	19140	{100}	x	227
Turmeric	**RR**-3,3'-OCH_3-4,4'-OH	75300	{100}	x	227
Uranin	**T**-1-CO_2-11-OH-(X,Y=O)	45350	{100}	x	227
Xylidine Red	**CC**-2-OH-3,6-SO_3-9,11-CH_3	16150	{100}	x	227

Table 1 (Continued)

sodium nitrate	$NaNO_3$	*Im2m*	*a*=3.569, *b*=5.563, *c*=5.384 Å			
Bismarck Brown G	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{111}	x	193,235
France Dye #4	**LL**-4-NH_2-13,17-SO_3			{111}	x	193,231,235
France Dye #5	**DD**-1-NH_2-3,6-SO_3-8-OH-11-NO_2			{111}	x	193,231,235
France Dye: M-α-OH-3	**DD**-1-OH-3,10-SO_3			uniform	x	235
France Dye: P-β-NH_2-5	**CC**-2-NH_2-5,11-SO_3			uniform	x	235
France Dye: P-β-NH_2-(6 or 7)	**CC**-2-NH_2-(6 or 7),11-SO_3			{111}	x	235
Quinoline Yellow	**MMM**-1,2-SO_3		47005	{111}	x	193,231,235
Sunset Yellow	**CC**-2-OH-6,11-SO_3			{111}	x	235
sodium potassium tartrate	$KNaC_6H_4O_6 \cdot 4H_2O$	$P2_12_12_1$	*a*=11.93, *b*=14.30, *c*=6.17 Å			
Acid Green G	**S**-9-$N(CH_3)_2$-9'-SO_3-(X=$N(CH_3)_2Cl$)		42020	{010}{210}	x	399I,400
	or **S**-9-$N(CH_3)$(**P**)-9'-SO_3-(X-$N(CH_3)$(**P**))		42075			
Amaranth	**FF**-2-OH-3,4',6-SO_3		16185	{100}	d	400P
Croceine Scarlet 3B (xxviii)	**MM**-2-OH-8,15-SO_3		27155	{010}	x	399I,400
Chlorazol Sky Blue FF (iv)	**YY**-1,1'-OH-5,5',7,7'-SO_3-8,8'-NH_2-9,9'-OCH_3		24410	{010}	n	399I,400,402
Direct Blue 15	**YY**-1,1'-OH-3,3',6,6'-SO_3-8,8'-NH_2-9,9'-OCH_3		24400	{010}	d	400
Phloxine	**T**-1-CO_2-2,5-Cl-7,9,10,12-Br-11-OH-(X,Y=O)		45405	{001}	x	399I,400
Rose Bengal (xxix)	**T**-1-CO_2-2,5-Cl-7,9,10,12-I-11-OH-(X,Y=O)		45435	{001}	x	399I,400
strontium nitrate	$Sr(NO_3)_2$					
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015	{100}	d	146,153,312,321
strontium nitrate tetrahydrate	$Sr(NO_3)_2 \cdot 4\ H_2O$	$Pa\bar{3}$	*a*=7.7798 Å			
Fernambuk Farbstoff	**Y**-2,6-OH				x	109,110,111,115
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)		42500		d	114
Hematein	**Y**-1,2,6-OH		75290	{001}	d	109,110,111,115,123
Safranin	**U**-1-CH_3-8,11-CH_3-7,12-NH_2-(X,Y=N)		50240		d	109,110,111,115
	& **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)					
Turmeric	**RR**-3,3'-OCH_3-4,4'-OH		75300		d	109,110,111,115
succinamide	$NH_2C(O)CH_2CH_2C(O)NH_2$	*C2/c*	*a*=6.932, *b*=7.994, *c*=9.878 Å, *β*=102.47°			
Alizarin	**E**-1,2-OH		58000		x	129
Isatin	**AA**				x	129
succinic acid	$HOOCCH_2CH_2COOH$	$P2_1/a$	*a*=5.126, *b*=8.880, *c*=7.619 Å, *β*=133.60°			
Alizarin	**E**-1,2-OH		58000		d	130
Aloësäure					d	130
Aurine	**S**-9,9'-OH-(X=O)		43800		d	130
Chrysamine Acid (xiv)	**UU**-3,3'-CO_2-4,4'-OH		22250		d	130
Curcuma	**RR**-3,3'-OCH_3-4,4'-OH		75300		d	130
Drachenblut (xv)	Sanguis draconis		75200		d	130
Eosin	**T**-1-CO_2-7,9,10,12-Br-11-OH-(X,Y=O)		45380		d	129,130
Erythrosin	**T**-1-CO_2-7,9,10,12-I-11-OH-(X,Y=O)		45430		d	129,130
Fluorescein	**T**-1-CO_2-11-OH-(X,Y=O)		45350		d	130
Gentiana Blue	**S**-8-CH_3-9-NH_2-9'-NHPh-(X=NHPh)Cl		42775		d	130
Karthaminsäure					d	129,130
Marine Blue	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$)		42000		d	129,130
	& **S**-9,9'-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) (mixture)		42535			
Methyl Orange	**BB**-4-$N(CH_3)_2$-4'-SO_3		13025		d	130
Mode Braun					d	129,130
Nigrosin (ix)			50420		d	129,130
Purpurin	**E**-1,2,4-OH		58205		d	130
Rothe Fettfarbe					d	130
Safranin	**U**-1-CH_3 8,11-CH_3-7,12-NH_2-(X,Y=N)		50240		d	130
	& **U**-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)					
Santalin (xviii)	$C_{24}H_{22}O_8$		1245		d	130
Tropäolin	**BB**-2,4-OH-4'-SO_3		14270		d	129,130

(xxviii) The structure given by Milligan does not match that for croceine scarlet 3B in the 1st edition Colour Index. Milligan's structure is **B**-3-OH-6,8-SO_3. This also was incorrectly identified as brilliant crocein MOO (27290), **B**-2-OH-6,8-SO_3.

(xxix) The structure in ref. 400 is for rose bengal 3B and not rose bengal of the 1st edition Color Index. Rose bengal 3B has two extra Cl atoms in positions 3 and 4.

Table 1 (Continued)

sucrose	$C_6H_6O_6$	$P2_1$	a=10.863, b=8.7044, c=7.7624 Å, β=102.938°			
Congo Red	**YY**-1,1'-NH_2-4,4'-SO_3		22120		d	122
***d*-tartaric acid**	$HO_2CHOH(CHOH)_2CO_2H$	$P2_1$	a=7.72, b=6.00, c=6.20 Å, β=100.17°			
France Dye: M-α-NH_2-5	**DD**-1-NH_2-5,10-SO_3			{111}	x	234
France Dye: P-α-NH_2-2	**DD**-1-NH_2-2,11-SO_3			{111}	x	234
thallium sulfate	Tl_2SO_4	*Pmcn*	a=5.929, b=10.665, c=7.808 Å			
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000	{001}	x	154
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		d	153
Phosphine	**U**-3,8-NH_2-(X=N,Y=C)(HNO_3)		46045	{001}	x	154
Ponceau Red	**FF**-2-OH-6,8-SO_3		16250	{001}	x	154
Safranin	U-1-CH_3-8,11-CH_3-7,12-NH_2-(X,Y=N) & U-8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)		50240	{001}	x	154
thiourea	$NH_2C(S)NH_2$	*Pnma*	a=7.695, b=8.537, c=5.520 Å			
Malachite Green	**S**-9-$N(CH_3)_2$-(X=$N(CH_3)_2Cl$) • ZnCl		42000		x	129
thymol	**A**-1-OH-2-$CH(CH_3)_2$-5-CH_3	*R3*	a=14.73, b=14.73, c=23.115 Å, γ=120°			
Purpurin	**E**-1,2,4-OH		58205		x	146
triglycine sulfate	$(H_2NCH_2COOH)_3H_2SO_4$	$P2_1$	a=9.417, b=12.643, c=5.735 Å, β=100.38°			
Aniline	**A**-1-NH_2				x	387,403,404
2-Aminobenzoic Acid	**A**-1-CO_2-2-NH_2				x	387,403,404
3-Aminobenzoic Acid	**A**-1-CO_2-3-NH_2				x	387,403,404
Aniline-4-sulfonate	**A**-1-NH_2-4-SO_3				x	387,403,404
Aniline-4-nitrate	**A**-1-NH_2-4-NO_2				x	387,403,404
Dicyand amide					x	387,403,404
Rhodamine 6G	**T**-1-CO_2Et-11-NH(Et)-(X=O,Y=NH(Et))Cl		45160		x	387,403,404
Rhodamine S	**T**-1-CO_2-11-$N(CH_3)_2$-(X=O,Y=$N(CH_3)_2Cl$)		75050		x	387,403,404
urea nitrate	$(H_2NC(O)NH_2)HNO_3$	$P2_1/c$	a=9.527, b=8.203, c=7.523 Å, β=124.37°			
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015	{001}	d	140,305,306
Picramique					d	306,
Picric acid	**A**-1-OH-2,4,6-NO_2				d	306,
Tetrazine				{001}	n	305
urea oxalate	$(H_2NC(O)NH_2)$ $(C_2O_4H_2)$	$P2_1/c$	a=5.13, b=12.40, c=11.58 Å, β=143.0°			
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015		x	140
uric acid dihydrate	$C_5H_4N_4O_3$ • 2 H_2O	*Pnab*	a=7.409, b=17.549, c=6.332 Å			
Beet Root Extract (Betanin)						437,438,439,440
Bismarck Brown	**TT**-2,2'-NH_3Cl-4,4'-NH_2-(X=N)		21000		d	159
Fuchsin (xi)	**S**-9,9'-NH_2-(X=NH_2Cl)		42500		d	159
Methylene Blue	**G**-3,6-$N(CH_3)_2$-(X=S)		52015			437,439,440,441
Methylene Violet	**U**-7-$N(CH_3)_2$-12-NH_2		50205		d	159
Rouge Neutre					d	159
Safranin	**U**-8,11-CH_3-7,12-NH_2-(X,Y=N) & **U**-1,8,11-CH_3-7,12-NH_2-(X,Y=N) (mixture)		50240		d	159
Urosein						439,440

recognition must be available. In some cases, qualification is by no means obvious given the available descriptions in the literature. We have relied on our judgment and experience, erring on the inclusive side.

The table is organized according to host, as in Ny'vlt and Ulrich's *Admixtures in Crystallization*.[253] While inorganic admixtures are specified in the valuable, aforementioned compendium, dyes are listed with a single generic appellation, "organic dyes". Table 1 may be considered the organic partner of *Admixtures in Crystallization*.

Dyes are classified according to their parent skeletons in Scheme 1. Their substituents are specified in Table 1. We have made our most informed judgments when assigning constitution. In cases where we are uncertain, we give names only, as they appeared in the original source.

We have tried to trace indices (*hkl*) of relevant growth sectors in older papers back to the crystal systems in Groth,[254] thereby enabling a transformation to contemporary standard settings. In other cases, we have maintained nonstandard settings used commonly. In either case, cell parameters are given. Unless otherwise specified, space groups and lattice constants were taken from Wyckoff,[255] the Cambridge Structural Database,[256] or Structure Reports.[257]

The presence or absence of dichroism and/or the availability of a photograph or illustration are indicated. In cases where the 3rd edition CI numbers are not available, 1st edition numbers are provided. Biopolymeric dyes were not tabulated. Descriptions of these are confined to sections IV.D.1.b, IV.E, and V.A.

IV. Recent Studies

A. Chemical Selectivity

1. Intersectoral Zoning

Additives interacting with growing crystals must discriminate between faces that are not symmetry related. Consequently, mixed crystals exhibiting more than one form will invariably display chemical zoning, the partitioning of impurities from one growth sector to another. While countless examples of such phenomena exist in mineralogy[258,259] as well as in the literature on dyeing crystals, a molecular level understanding was first provided by Lahav, Leiserowitz, and their colleagues in a sweeping revision of the structure of solid solutions,[260−262] In our work, we explicitly designate this phenomenon *intersectoral zoning* to distinguish it from *temporal or concentric zoning*, compositional changes that come about as a function of crystal growth history, and from *intrasectoral zoning*, the subject of section IV.B.2.

Following Buckley,[263] Bastin and Kahr prepared more than 100 intersectorally zoned K_2SO_4 DICs containing sulfonated synthetic dyes.[264] A typical example shown in Figure 16 is K_2SO_4 containing sulforhodamine B in the {110} growth sectors. Their detailed study of 13 examples included at least one dye for each of the principal growth sectors of K_2SO_4: {010}, {001}, {110}, {021}, and {111} (Figure 17). The electronic transition dipole moments of the dyes were determined relative to the host lattice through measurements of linear dichroism on cut and polished thin crystal sections. Theoretical transition moments of the dyes were computed using the INDO/S-CI method.[265,266] The angles between the experimental and theoretical transition moments were calculated after the $-SO_3^-$ ions in the minimum energy dye structures were least-squares fit to the SO_4^{2-} ions in the host lattice (Figure 18). The average angular deviation between experimental and theoretical transition moments was 9°, but this number should be considered with a number of assumptions

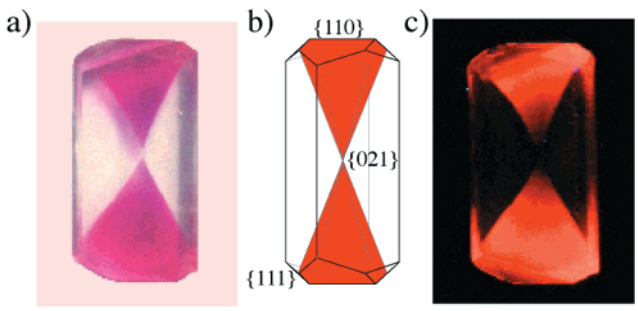


Figure 16. (a) Photograph of sulforhodamine B in the {110} sectors of K_2SO_4. (b) Idealized representation of the habit. (c) Fluorescence from the same crystal. Height = 6 mm. Photos by L. Bastin.

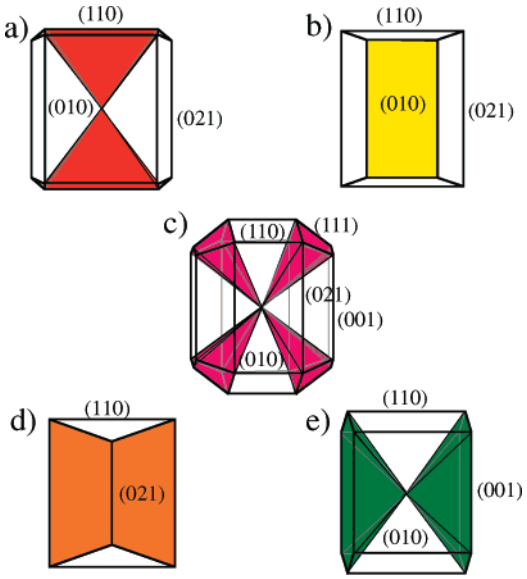


Figure 17. K_2SO_4 crystals can be selectively dyed in each of the principal growth sectors. Examples include the following: (a) acid fuchsin (Figure 25), (b) pyranine (Figure 40), (c) Evan's blue (Figure 11b), (d) orange 2, (e) naphthol green (Figure 25).[264] (Adapted with permission from ref 264. Copyright 2000 Elsevier Science.)

and caveats discussed in the cited paper but too numerous to list here. Moreover, there are intrinsic ambiguities in determining the sign of the linear dichroism with respect to the extinction angle of a crystal plate. The near parallelism nevertheless suggests that there is merit in Buckley's and France's proposals of sulfonate−sulfate substitution during DIC formation in many cases. This substitution of anions for anionic functionalities has also gained credence in the context of the recent work of Davey and co-workers on the inhibition of $BaSO_4$ crystal growth by diphosphonates.[267,268]

Boeglin described a procedure for identifying K_2SO_4, a premium fertilizer component that included the precipitation of K_2SO_4 particles from solutions that contained sulfonated dyes.[269] Face-specific recognition processes that are to be expected when cocrystallizing sulfonated dyes with K_2SO_4 were not described; however, Boeglin clearly stated that the process is effective only when sulfonated dyes are employed and that some work better than others, in support of the stereospecificity of the inclusion phenomena.

2. Janus Guests

A number of dyes exhibit more than one spectroscopic signature in a given crystal. If the varied photophysical characteristics are specific to particular growth sectors, DICs can be multicolored. In this section we illustrate dyes that show sector-specific conformations, states of protonation, and solvatochromism.

a. Conformations. Crystal faces that are not related to one another by symmetry must express different affinities for the conformations of adsorbates in equilibrium in solution. Crystals of K_2SO_4 incorporating *o*-aminobenzenesulfonate showed an astonishing range of photophysical responses in different

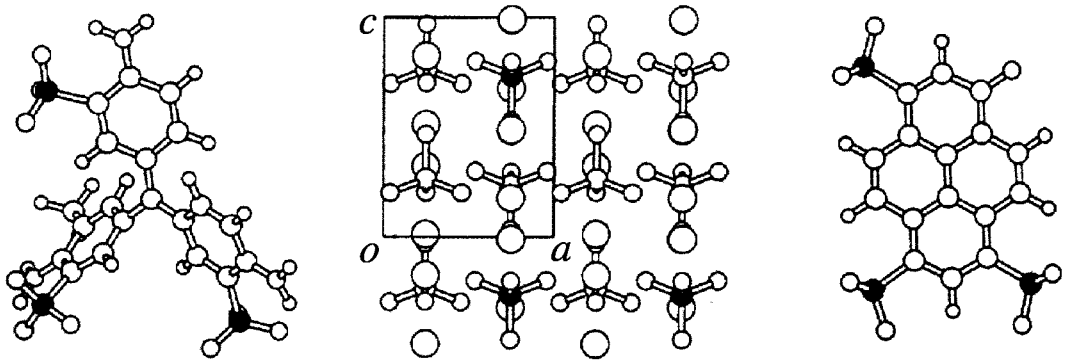


Figure 18. Acid fuchsin (left) and pyranine (right) drawn to the same scale as K_2SO_4 (center). Filled sulfur atoms define substituting sulfate (SO_4^{2-}) and sulfonate ($-SO_3^-$) groups.[201]

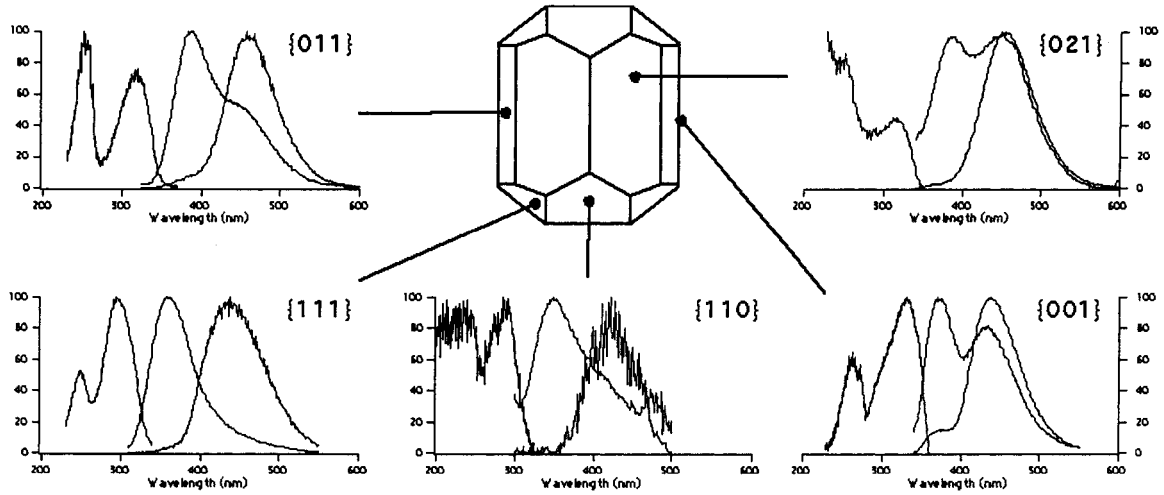


Figure 19. Growth sector specific photophysics of *o*-aminobenzenesulfonate in single crystals of K_2SO_4. Excitation, fluorescence, and phosphorescence spectra are shown for light collected from each of the developed facets. The vertical scale represents normalized intensities.[270]

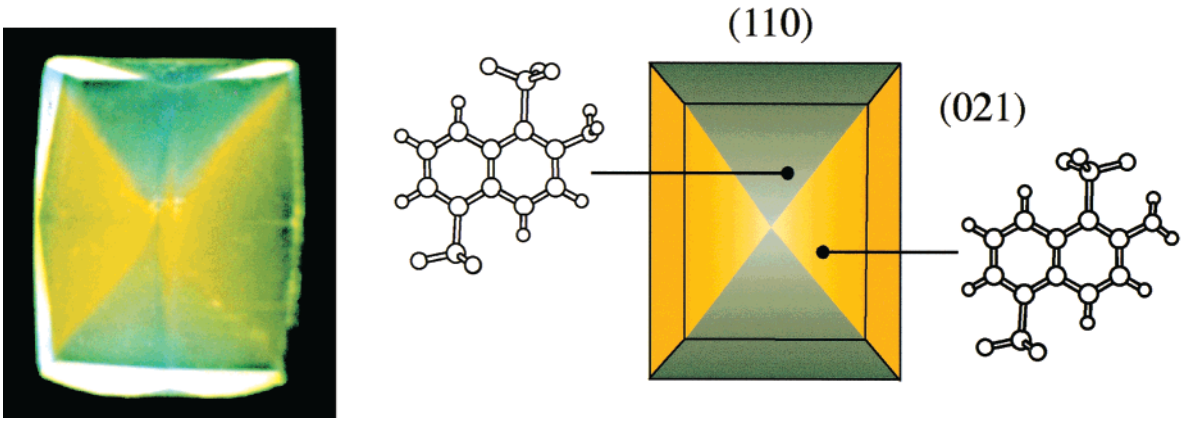


Figure 20. Photograph of dual luminescence of K_2SO_4/2-amino-1,5-naphthalenedisulfonate single crystal ($7 \times 5 \times 2$ mm^3) and schematic representation.[270] Conformations of guest in adjacent sectors are shown as ball-and-stick figures.

growth sectors (Figure 19).[270] The luminescence energies and lifetimes were inversely correlated; the more energetic the emission, the shorter the lifetime.[271] Such a correlation suggests that the differences among the molecules in the sectors are a consequence of a progressive rotation of the $-NH_2$ lone electron pair out of conjugation with the π system.[272,273]

Similar observations were obtained for a variety of *o*-aminoarenesulfonates.[274] Specifically, K_2SO_4 containing 2-aminonaphthalene-1,5-disulfonate had unique optical and magnetic properties in the {021} and {110} growth sectors (Figure 20). Polarized optical spectroscopy coupled with single-crystal electron paramagnetic resonance measurements of guest photoexcited triplet states allowed detailed conformational analyses. Both techniques indicated that the species in the {021} and {110} had the $-NH_2$ group in and out of conjugation with the π-system, respectively.

b. Acids and Bases. Pyranine, a guest that colors the {010} and {110} growth sectors of K_2SO_4 and Rb_2SO_4 crystals, is widely used as a pH probe.[275] The

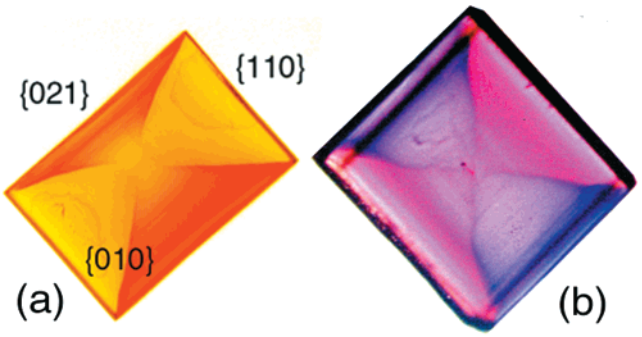


Figure 21. (a) Crystal of phthalic acid grown in the presence of acid−base indicator methyl red. Phthalic acid incorporates protonated and neutral dye molecules in the {010} and {021} growth sectors, respectively.[286] Crystal length ~0.5 mm. (b) Phthalic acid crystal grown in the presence of solvatochromic dye Nile red. Orientation and size of crystal are as in part a.[277] Photo by S. Lovell.

rate of excited-state deprotonation competes with the fluorescence lifetime. Therefore, a dual luminescence is observed and the relative proportion depends on the basicity of the environment. Either the acidic and/or basic form of the ground state was found in K_2SO_4 and Rb_2SO_4 depending on the pH of the crystallizing solution. However, the relative proportions of the two peaks in the fluorescence spectra of the acid form were different in {010} and {110} despite the fact that pyranine had the same polarization in either sector. The deprotonation of the excited state was favored in {110} as compared to {010} and the luminescence was of higher energy.[276] In other words, for similarly oriented dyes, the {110} sectors were more "basic".

Lovell found that a variety of acid/base indicators, most often simple azo dyes, could be oriented in specific growth sectors of aromatic acid crystals in various protonation states.[277] Moreover, adjacent growth sectors showed selectivity toward particular states of protonation. Specifically, methyl red was found within both the {021} and the {010} growth sectors of phthalic acid (Figure 21a). Methyl red has complex acid−base equilibria in solution due to the presence of a carboxylic acid group immediately adjacent to the azo bridge. Protonated, deprotonated, neutral, and zwitterionic forms have been spectroscopically differentiated in solution.[278] Phthalic acid crystals selectively incorporate the yellow, neutral form in the {010} sectors, while {021} includes the red azo N-protonated species.

c. Solvatochromism. Dyes in crystals sometimes show host-induced solvatochromism. In K_2SO_4,[389] dye absorption energies are not distinguished from solution. On the other hand, dyes in KH_2PO_4 show persistent blue shifts,[355] whereas dyes in phthalic acid show characteristic red shifts.[431] This is most likely due to H-bonding raising the energy of transitions with some $n \rightarrow \pi^*$ character in the former case and the formation of charge transfer absorption in the latter case. Nile red is a highly solvatochromic dye[279] that shows different colors in phthalic acid depending upon the face through which it had adsorbed (Figure 21b). Surprisingly, Nile red has the same polarizations in either growth sector; therefore, the orientations (presuming the molecular transition moments are not much altered) are the same even though the molecule is found in more than one environment.

Nile red can actually be encapsulated in a variety of crystallographic environments. Figure 44 shows Nile red in poppy acid. Figure 22a shows the luminescence of Nile red in benzamide, a prototypical substance for habit modification studies.[280,281] The dye is in the $\{10\bar{2}\}$ sectors only. The horizontal polarization of the excitation is consistent with the hydrogen bonding of Nile red to three benzamide molecules in a linear crystal chain (Figure 22 b,c). However, this model, while suggestive, is provisional at this time and subject to a closer analysis. The luminescence energy, also consistent with H-bonding, is characteristic of that found in polar protic solvents where the $-NEt_2$ group has turned out of plane giving rise to a twisted intermolecular charge-transfer state.[282,283]

3. Enantioselectivity

Despite the fact that Retgers[126] failed to dye growing KH_2PO_4, Blattner et al. reported in a brief note in 1946 that solutions of hematein stained the {100} growth sectors and depressed the ferroelectric transition temperature.[284] Since these researchers were principally concerned with the effects of impurities on the phase transition temperature, they did not describe the morphological or optical properties of their mixed crystals, although they did publish a photograph. Recent reinvestigation of their work revealed that hematein stains *every other* prism face. Hematein, the colored component of logwood extract, is chiral.[285] Adjacent prism faces of KH_2PO_4 are related by mirror symmetry in the D_{2d} point group. Therefore, hematein must have recognized the KH_2PO_4 faces enantiospecifically.

From these experiments we can deduce that Seherr-Thoss (section II.A.2) was referring to $(NH_4)H_2PO_4$, an isomorph of KH_2PO_4, when he reported that *phosphorsaurem Ammoniak* was stained by logwood extract. In 1879, he could have partitioned the prismatic faces from different crystals into mirror image sets merely by judging the color of their associated growth sectors. However, it would have been astonishing had he recognized the meaning of this Pasteur-like resolution by color; while individual faces of $(NH_4)H_2PO_4$ are handed, whole crystals are not.

Recently, Kurimoto et al. observed a visible blue luminescence localized in the pyramidal {101} growth sectors of KH_2PO_4 grown from a solution containing adenosine triphosphate (ATP).[286] This is a common pattern of zoning of anionic dyes in KH_2PO_4 (section IV.B.2). Comparisons of the luminescence viewed through the *a* and *b* faces revealed that the (011) sector was considerably brighter than the (101) sector (Figure 23). As these sectors are mirror images of one another in the space group $I\bar{4}\,2d$, the chiral nucleotides must have recognized these faces enantioselectively, as we previously observed with hematein and KH_2PO_4 in the prismatic {100} sectors. Under the conditions of crystal growth, ATP must undergo some hydrolysis. Therefore, the experiment was

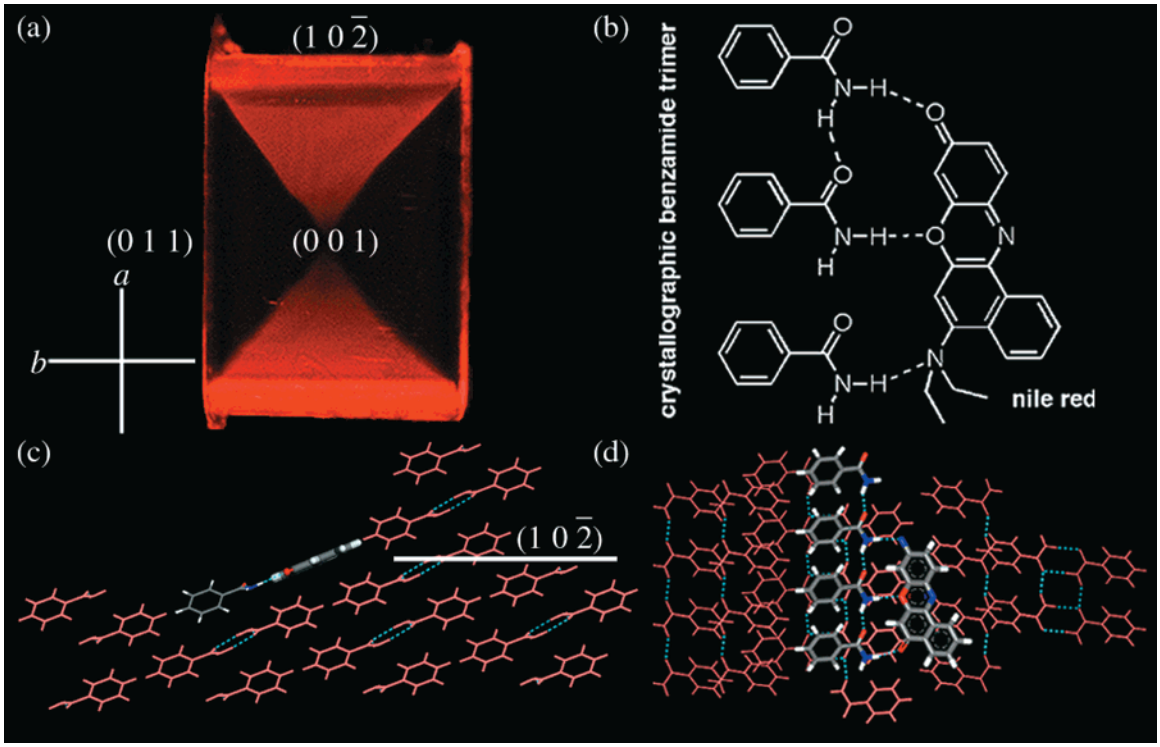


Figure 22. (a) Benzamide crystal containing luminescent Nile red in the {10$\bar{2}$} growth sectors. (b) Proposed structure of Nile red on (10$\bar{2}$) face of benzamide that is consistent with the linear dichroism and energy of the solvatochromic dye. Ethyls have been omitted for clarity. (c,d) Model of possible (benzamide)$_3$·Nile red complex in the crystal. Crystal grown and photographed by M. Kurimoto.

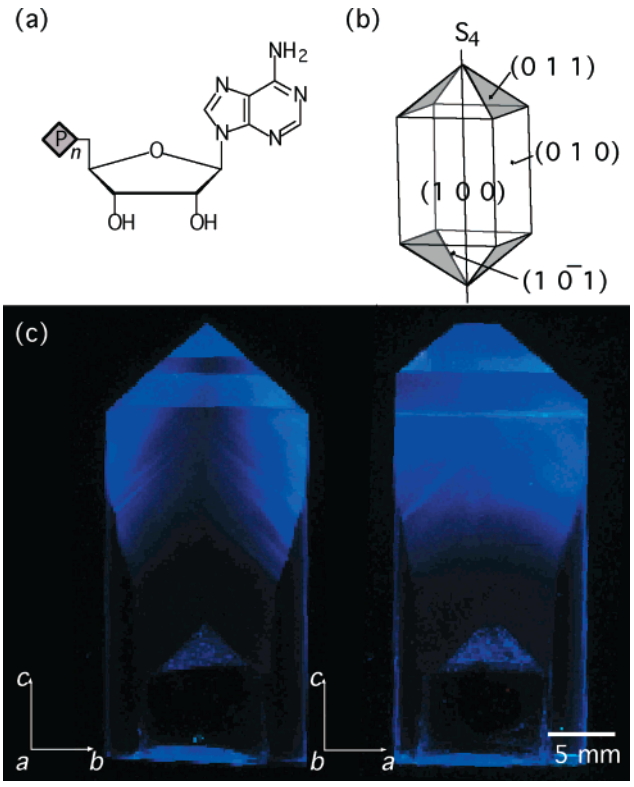


Figure 23. (a) Adenosine phosphate. (b) Schematic diagram of KH_2PO_4 indicating the enantiomorphous (101) and (011) (blue) faces. (c) Fluorescence from KH_2PO_4 containing adenosine phosphates, viewed normal to the enantiomorphous (100) (left) and (010) (right) faces.[286] Seed crystal is visible at the base. (Reprinted with permission from ref 286. Copyright 2001 Materials Research Society.)

repeated with adenosine monophosphate. Similar results were obtained.

Sodium chlorate ($NaClO_3$) and sodium bromate ($NaBrO_3$) are the prototypical chiral salt crystals.[287−289] Chiral dyes that selectively stain enantiomorphous crystals would affect a visual resolution on the basis of color. Previous attempts to resolve enantiomers with homochiral halate crystals were unsuccessful.[290] However, it was just reported that a suspension of $NaClO_3$ could bring about the asymmetric reduction of an aldehyde.[291] Perucca[292] discovered the first dye, *extra China blue*, in $NaClO_3$. Milligan produced "spotty" crystals of $NaClO_3$ with phloxine B and croceine scarlet 3B. On the other hand, France reported "beautifully opalescent" crystals of $NaClO_3$ with two azo dyes, sunset yellow and *p*-*β*-OH-7.[293,294] We observed that sunset yellow induced a cross-hatched microtexture in $NaClO_3$ that in reflected light might to some observers resemble opalescence. At lesser dye concentrations the crystals took on an irregular pattern of color and a nearly complete linear dichroism but with no apparent dependence on the sector structure of the crystals.[295]

Though not chiral, $KClO_3$ and $KBrO_3$ showed up on Retgers list of salts that could not be stained.[126] KIO_3 was sometimes colored but never pleochroic. Kirkova and Draganova reported that some achiral sulfonated dyes, particularly acid red 26, stained $KClO_3$, $KBrO_3$, and KIO_3.[296,297]

Prior to the recent determination of absolute configuration by inspection using scanning probe microscopies,[298,299] only a very small number of ways of assigning absolute stereochemistry had been invented.[300,301] The interpretations by Addadi et al. of additive-induced habit changes in terms of the ste-

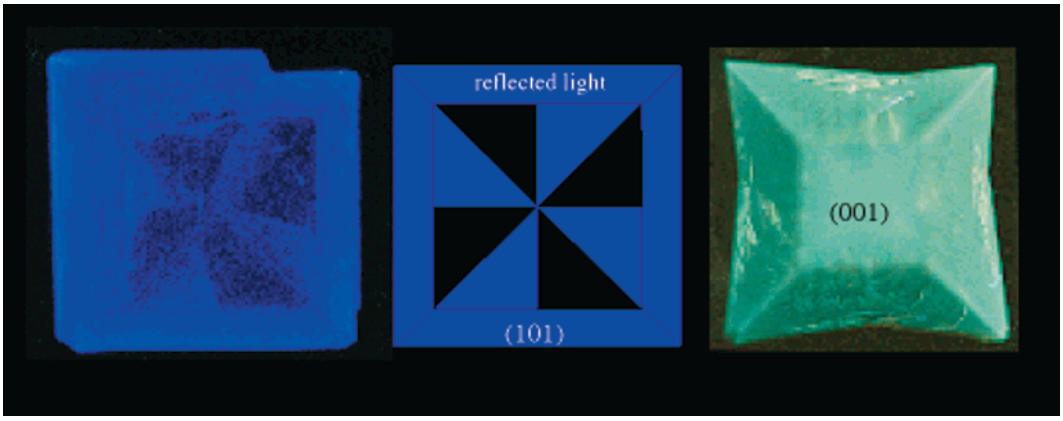


Figure 24. (Left) Pinwheel of luminescence from *p*-aminobenzoate in barium acetate. Crystal dimension $1 \times 1 \times 1$ cm^3.[270] (Center) Schematic representation. (Right) Habit of barium acetate crystal during early growth with *m*-aminobenzoate. The reentrant angles define the luminescent pinwheels.[270]

reospecific interactions at crystal interfaces[302] is most relevant for our discussion. In this way they determined the absolute growth directions of glycine crystals from solutions containing other amino acids.[303] Gurney et al. assigned absolute growth directions to an achiral salt crystal, anhydrous barium acetate, using growth additives in a manner that is conceptually akin to the aforementioned example, although the assignment was based on patterns of light emitted by benzene derivatives. Barium acetate crystals fall to the bottom of dishes on their (001) or ($00\bar{1}$) faces and therefore grow in the $+c$ or the enantiomorphous $-c$ direction with equal probability. However, when crystals grown in the presence of *m*-aminobenzoic acid or *p*-aminobenzoic acid were irradiated with UV light, "luminescent pinwheel" structures within the crystals emerged, "spinning" clockwise or counterclockwise (Figure 24). This observation partitioned the crystals into two sets having grown in one direction or the other, a Pasteur-like resolution and determination of absolute hand using luminescence. The pinwheels were defined by reentrant angles that bisected the lateral edges during early, rapid growth.

4. Separations

In principle, dyes that recognize different faces of a growing crystal can be separated from one another. Lehmann first grew succinic acid crystals in the presence of a mixture of dyes but was solely interested in the combined effect of dyes that alone were ineffective as habit modifiers.[130] Gaubert later discovered that urea nitrate crystals grown from solutions containing methylene blue and picric acid had adjacent yellow and blue growth sectors.[304−306] Paine produced bicolored $Pb(NO_3)_2$ and $Ba(NO_3)_2$ crystals in the presence of methylene blue and Bismarck brown.[232] The cube faces were blue, and the octahedral faces were brown.

We affected several separations in this way with K_2SO_4. Crystals grown from muddy-brown aqueous saturated K_2SO_4 solutions containing acid fuchsin and naphthol green had alternately red {110} and green {001} growth sectors (Figure 25). Visible absorption spectra of individual sectors as compared with the growth solution showed that the dyes were sectorally exclusive. In other words, crystal growth served as a kind of chromatography. Similar results

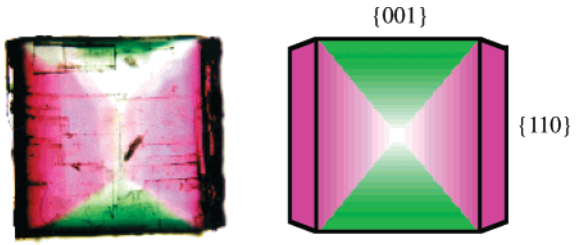


Figure 25. Photograph of crystal ($4 \times 4 \times 1$ mm^3) grown from a brown solution containing acid fuchsin and naphthol green B compared with schematic representation. The process of crystal growth from solution partitions the dye molecules in respective sectors.[264]

were obtained with naphthol green B and amaranth and without a doubt can be applied to a variety of mixtures given an appropriate host.

B. Crystal Growth

1. Desymmetrization

It is now well established that solid solutions routinely have lower symmetries than their pure counterparts.[260,262,307,308] This is because the vast majority of growing crystallographic surfaces have lower symmetries than the bulk, thereby distributing guest molecules nonstatistically among the sites that are not related to one another by symmetry *on the surface*. DICs often display linear dichroism that is inconsistent with the symmetry of the host crystals. This is most often apparent when the host is cubic (section II.D.2.). Any observation of linear dichroism in a cubic host is an apparent violation of the symmetry principle.[309] For example, France and Davis observed anomalous linear dichroism in cubic alum DICs. The colors observed in polarized light indicated that the long axes of azo dyes were normal to the growth face in any sector.[233]

No dyed crystals have received more attention than the cubic alkaline-earth nitrates $Ba(NO_3)_2$ and $Pb(NO_3)_2$ stained with methylene blue and its congeners. Slavnova carried out the most extensive and informative analyses of this nitrate mixed crystal family, first identified by Gaubert. Along with Vedeneeva, she advanced our understanding with the use of spectrophotometry, a method of analysis they earlier applied to dyes adsorbed in clays (section

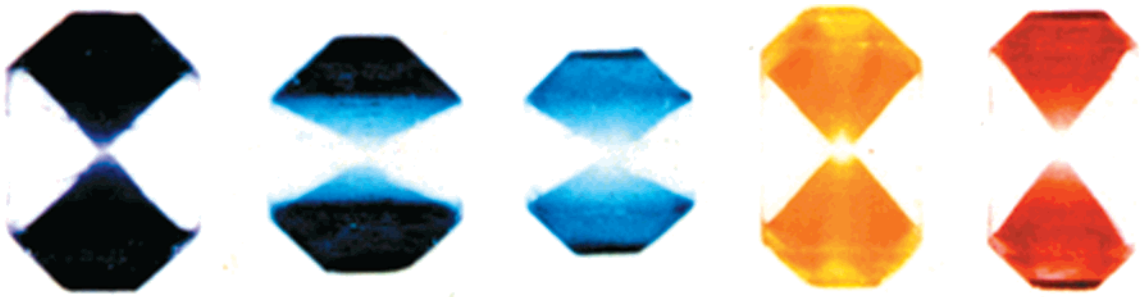


Figure 26. KH_2PO_4 crystals containing dyes in the {101} growth sectors. From left to right: Chicago sky blue, zinc phthalocyaninetetrasulfonate, cobalt phthalocyaninetetrasulfonate, sunset yellow, amaranth. Average height is 7 mm.[247,354,355] View along [100] or [010]. Crystals prepared by J. A. Subramony.

I.B).[310−312] In $Pb(NO_3)_2$, methylene blue absorbed at energies comparable to that of dilute solutions. On the other hand, the higher energy absorption in $Ba(NO_3)_2$ was characteristic of dimers or higher crystalline aggregates. At methylene blue concentrations higher than 5×10^{-3} M, $Pb(NO_3)_2$ no longer cocrystallized with the dye while dye incorporation into $Ba(NO_3)_2$ only began at concentrations greater than 3×10^{-3} M.[313,314] This puzzling behavior is further exemplified by methylene blue preferring {100} sectors of $Pb(NO_3)_2$ as opposed to {111} for $Ba(NO_3)_2$, despite that the cuboctahedral forms of the pure salts were not distinguished from one another.[315] Comparable results with $Sr(NO_3)_2$ were less definitive.[316] The $Ba(NO_3)_2$ crystals typically exhibited strong linear dichroism.[317] This work was extended to thionin blue[318,319] and Capri blue.[320] However, a clear picture of the physicochemical interactions of methylene blue with the alkaline earth nitrates on the basis of what has appeared in the literature has not formed in our minds.

Many reports emphasized the effect of the methylene blue on nitrate crystal growth rates and/or habit modification.[321−340] Since the incorporation of methylene blue in some fashion in these salts is incontrovertible, the reports are here cited even though DICs were not discussed explicitly. Other dyes that presumably can be included in $Ba(NO_3)_2$ or $Pb(NO_3)_2$ were given by Paine-Davis and France.[237]

Gaubert was the first to observe anomalous linear birefringence[341,342]—optical anisotropy inconsistent with crystalline morphology—in dyed crystals during his investigation of NaCl and murexide and NH_4Br-(Cl) and tartrazin.[145] Frondel observed anomalous linear dichroism in the cubic alkali fluorides.[227] Slavnova also detected anomalous linear birefringence in dyed alkaline earth nitrates.[320] The optical anisotropy was usually attributed to unnamed internal stresses.

2. Intrasectoral Zoning: Optical Probes of Crystal Growth Mechanisms

Optical probes are a mainstay of the biochemical scientist eager to illuminate the specificity of noncovalent interactions.[343,344] As crystal growth from solution is also governed by the specificity of noncovalent interactions, the question arises as to what extent dyes can be used to reveal noncovalent assembly during crystal growth. In this section we show how dyes have been used to image emergent, growth-active structures on crystallographic surfaces.

As discussed in section IV.A.1, impurities in crystals will distribute themselves among the symmetry distinct sectors for which they must express different affinities. In K_2SO_4, many of the crystal surfaces are active with respect to dyes, whereas KH_2PO_4 shows a strong tendency to incorporate anionic dyes only on the {101} faces (Figure 26), presumably because these faces are terminated with K^+ ions.[345] However, impurities may inhomogeneously deposit not only between growth sectors, but also *within* a single growth sector depending on the crystal's surface topography. Surfaces of crystals grown in the lower supersaturation regime often propagate through dislocations that produce growth spirals or hillocks, shallow stepped pyramids with single or multiple dislocations at the apex.[346,347] Polygonization of hillocks partitions faces into vicinal regions, each having slightly different inclinations. Impurity partitioning among vicinal slopes, *intrasectoral zoning*, results from the selective interactions of impurities with particular stepped hillock slopes. Intrasectoral zoning therefore provides more details about recognition mechanisms than intersectoral zoning because the active growth surfaces at the time of incorporation can be more highly specified. The identification of intrasectoral zoning patterns enabled the determination of the mechanism of trace element partitioning in minerals.[348−352]

Zaitseva and co-workers perfected KH_2PO_4 crystal growth conditions[353] as a prerequisite to the development of the National Ignition Facility. In their hands, amaranth, previously shown to have an exclusive affinity for the {101} surfaces of KH_2PO_4,[354,355] was both inter- and intrasectorally zoned.[356] This observation required introduction of the dye during late growth thereby coloring only a thin surface layer so that patterns of color were not confounded by moving dislocation cores. Figure 27 highlights the {101} faces of KH_2PO_4/amaranth crystals. The heterogeneities resulted from amaranth having distinguished among the **A**, **B**, and **C** slopes of the polygonized hillocks prevalent on the pyramid faces. Incorporation followed the trend **B** > **A** > **C**. On the other hand, Chicago sky blue preferred **C** as did ATP (section IV.A.3).[357] At low Chicago sky blue concentration, **B** remained colorless. The incorporation was associated with a critical temperature above which the dye was not captured. In situ interferometry[358] was used to show the influence of the dye on the surface morphology at different concentrations and KH_2PO_4 super-

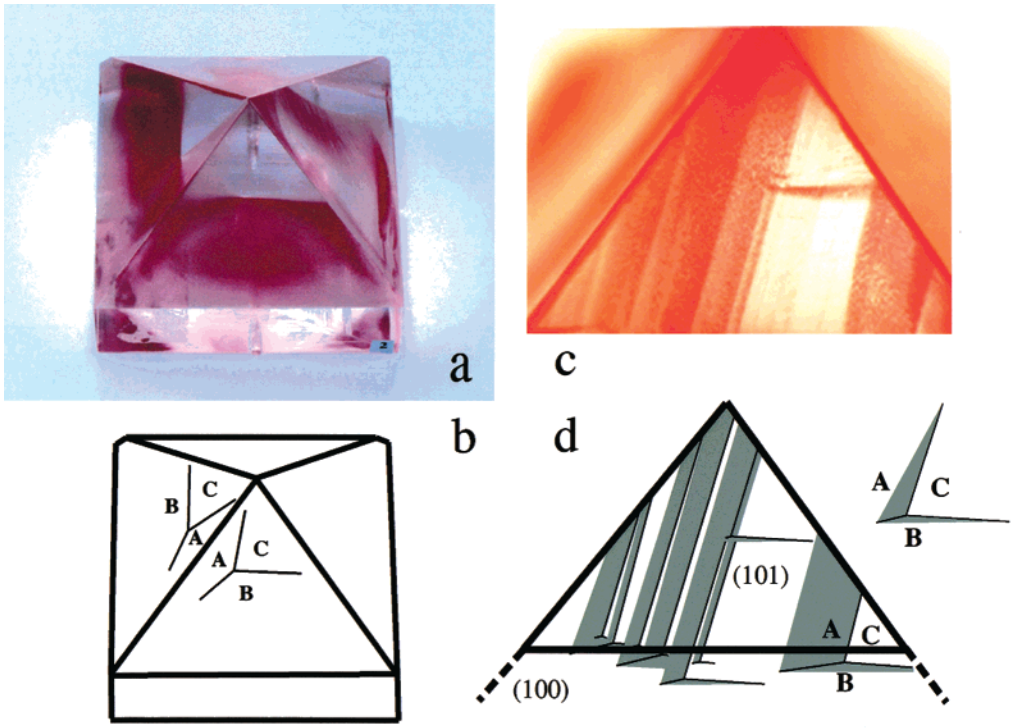


Figure 27. Intrasectoral zoning in KH_2PO_4/amaranth. (a) Photograph of KH_2PO_4/amaranth crystal grown by Zaitseva et al.[356] Width = 14 cm. (Reprinted with permission from ref 356. Copyright 1999 Elsevier Science.) (b) Idealized representation of crystal in part a, illustrating the hillocks observed on the surface. (c) The heterogeneous incorporation of amaranth in the (101) pyramidal growth sector is apparent in this closer view (width = 3.25 cm). (d) Schematic representation of part c.[359]

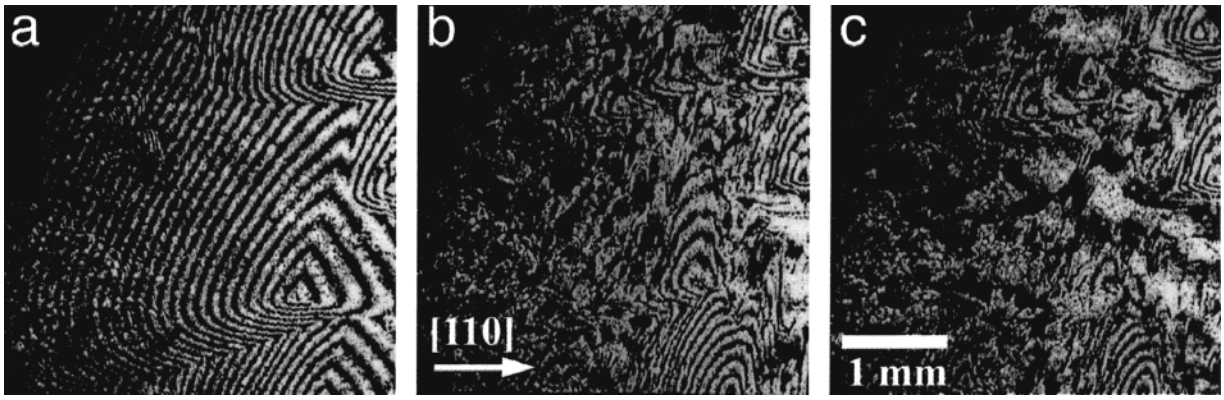


Figure 28. In-situ interferometry of the pyramid faces of KH_2PO_4 growing in the presence of Chicago sky blue recorded by Gliko et al.[357] (a) Pure solution, supersaturation = 0.022. (b) Five minutes after the introduction of 2 ppm Chicago sky blue. (c) 10 min. Time sequence shows hillock destruction. (Reprinted with permission from ref 358. Copyright 2001 Materials Research Society.)

saturations (Figure 28). A kinetic model was developed for step propagation whose parameters were characteristic of the adsorption of a mobile impurity.

The luminescence from *o*-aminobenzenesulfonate in K_2SO_4 was not always uniform in a given growth sector. Gurney et al. saw striking blue bands associated with the {021} faces (Figure 29).[359] As this crystal has macrosteps that are visible to the unaided eye, it is plain to see that the stripes correspond to the slowly advancing steps of the growth spirals; *o*-aminobenzenesulfonate only recognized the steps growing toward (001) rather than toward (010). Thus, not only did *o*-aminobenzenesulfonate select among the growing faces (section IV.A.1) of K_2SO_4, it further chose particular emergent structures on a given face. Aminoarene hydrogen bonding appears to play a role as well.

α-Lactose monohydrate crystals[360] are shaped like hatchets with a broad (010) basal plane. Crystals nucleate at the apex of the hatchet and grow unidirectionally toward $+b$ through a spiral dislocation mechanism,[361] as confirmed by the recent observation of hillocks on the (010) face by atomic force microscopy.[362,363] α-Lactose monohydrate crystals grown in the presence of green fluorescent protein (GFP) luminesced exclusively from the (010) sector (Figure 30).[364] Differential interference contrast microscopy[365] of a pure α-lactose monohydrate crystal revealed a single polygonized hillock that partitioned the (010) surface into four vicinal faces pairwise related by 2-fold symmetry. A comparison of an interference contrast micrograph with the corresponding fluorescence micrograph shows clearly that GFP only recognized the lateral slopes with the greatest step

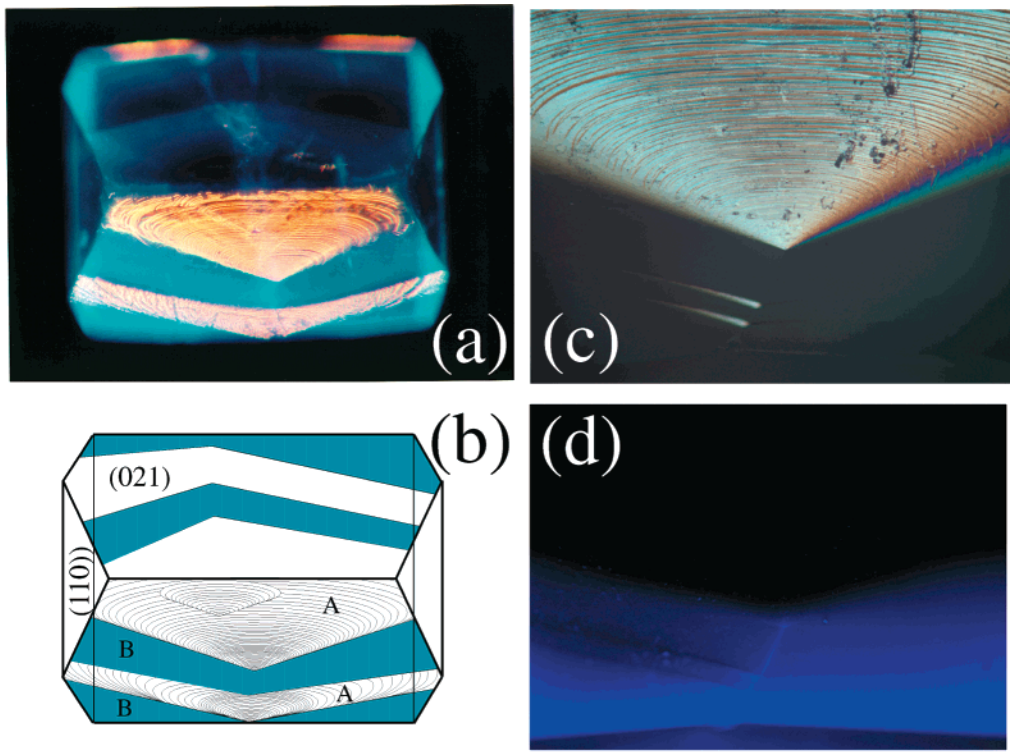


Figure 29. (a) Crystal of K_2SO_4/*o*-aminobenzenesulfonate illuminated with ultraviolet and visible light.[270] Lateral dimension 1.0 cm. Emission from *o*-aminobenzenesulfonate does not correspond to growth sector boundaries but to vicinal **B** regions on the {021} faces. (b) Idealized representation of crystal in part a. (c) Differential interference contrast image of center of hillock in part a.[359] (d) Luminescence micrograph of the region shown in part c. Luminescence of *o*-aminobenzenesulfonate is visibly confined to the steeper slopes of the hillocks. The horizontal axis is parallel to [100]. The top of the image is closer to (010) than (001).

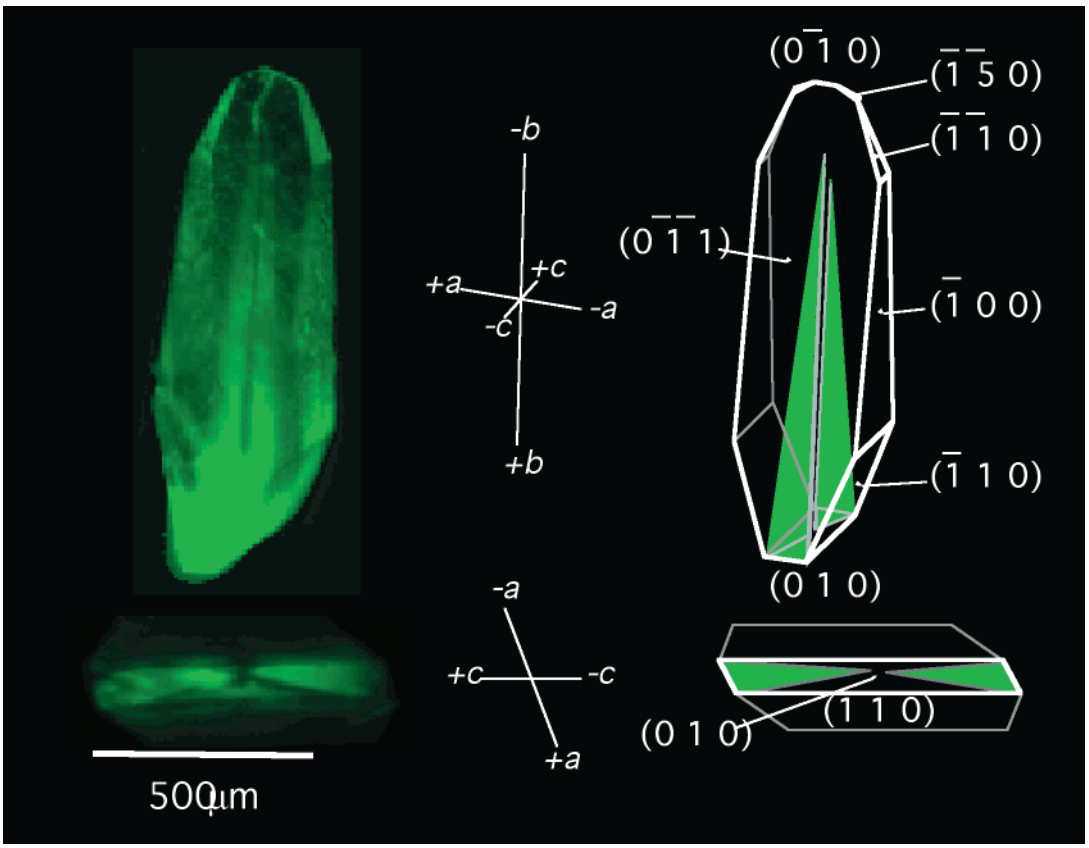


Figure 30. (Left) Fluorescence micrographs of α-lactose monohydrate/green fluorescent protein. Views through largest (0 1 $\bar{1}$) face and growth active basal plane (010). (Right) Idealized representations.[286] (Reprinted with permission from ref 286. Copyright 2001 Materials Research Society.)

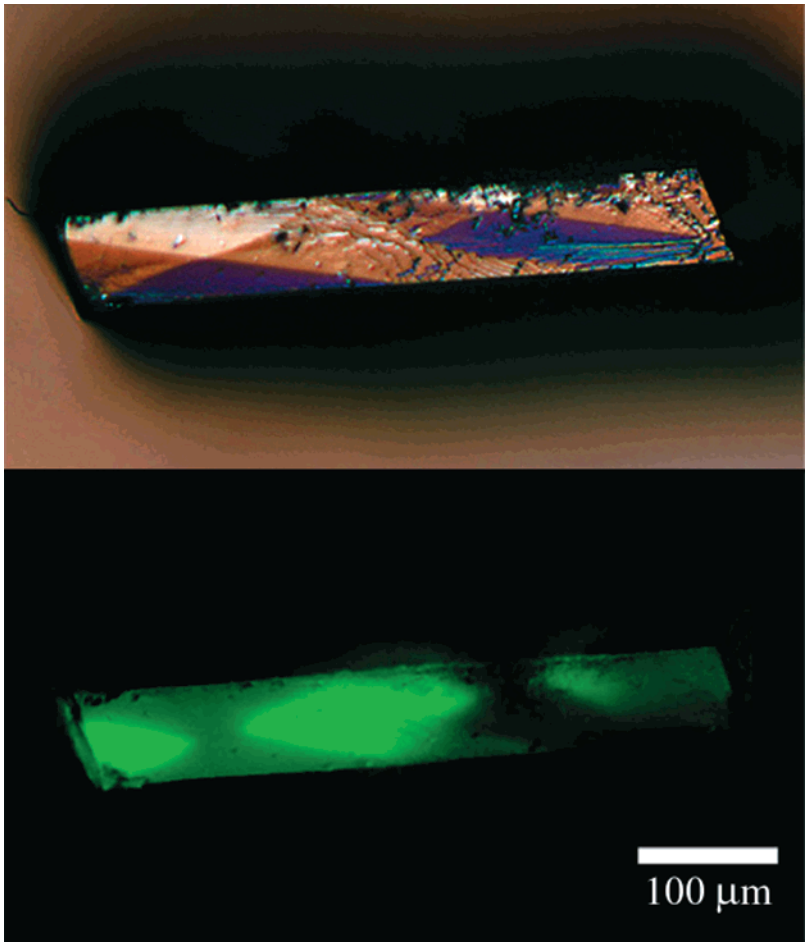


Figure 31. (Top) Differential interference contrast micrograph of α-lactose monohydrate/green fluorescent protein (010) face. (Bottom) Corresponding fluorescence micrograph.[286] Crystallographic directions as in Figure 30. (Reprinted with permission from ref 286. Copyright 2001 Materials Research Society.)

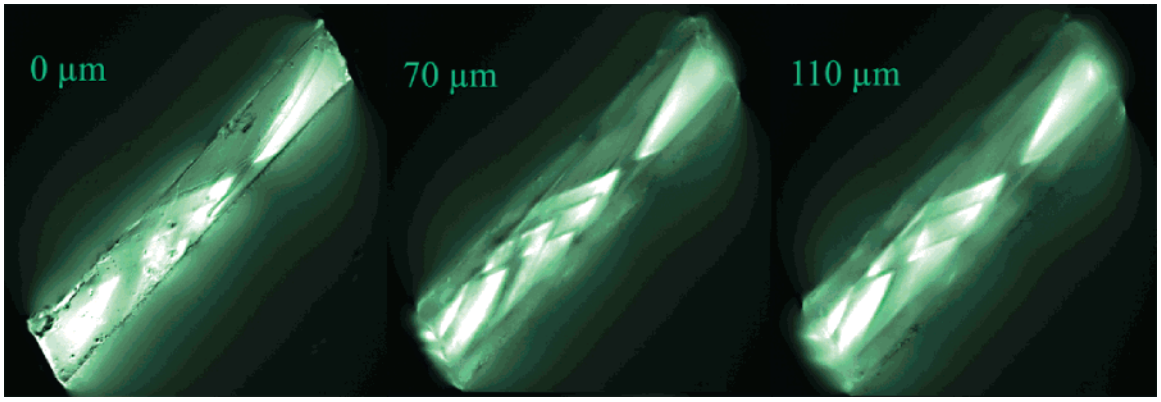


Figure 32. Fluorescence micrographs of α-lactose monohydrate/green fluorescent protein (010) face at 0, 70, and 110 μm from the surface. The fluorescence from the protein within the crystal serves to identify hillocks that were once active during the crystal's history.[286] The color in this image is false. (Reprinted with permission from ref 286. Copyright 2001 Materials Research Society.)

advancement velocity (Figure 31).[286] Figure 32 shows that by focusing through the (010) faces of α-lactose monohydrate/GFP, the sequence of active hillocks throughout the growth history can be revealed by GFP luminescence.

Carminic acid, a natural red dyestuff produced by the female Cochineal beetle (*Dactylopius coccus*),[366] recognized the (010) face of α-lactose monohydrate exclusively as did GFP. If the (0$\bar{1}$1) face of an α-lactose monohydrate/carminic acid crystal is observed obliquely, carminic acid appears partitioned within two distinct bands, suggestive of intrasectoral zoning. This partitioning was quickly interpreted when brightfield absorbance and corresponding differential interference contrast micrographs were compared (Figure 33). It was observed that carminic acid selectively interacts with the vicinal faces of the hillock as did GFP. Even though the center of the

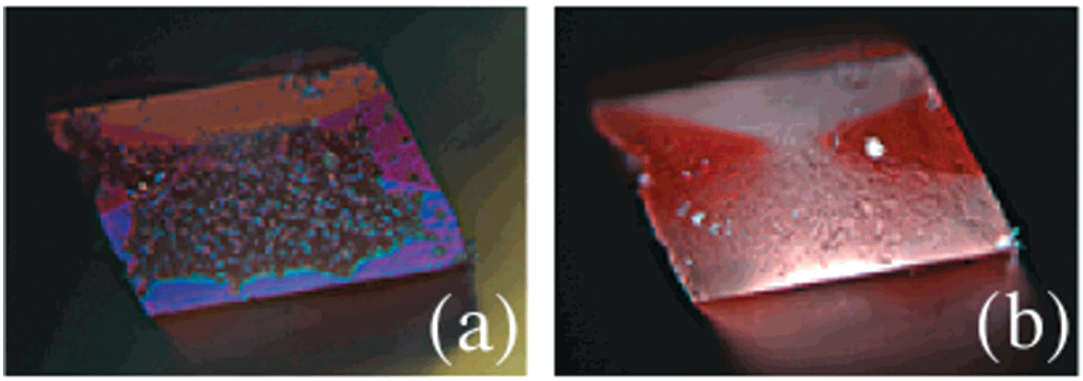


Figure 33. (a) Differential interference contrast micrograph of a pure α-lactose monohydrate crystal (010) surface. Lateral dimension is 0.6 mm. (b) Brightfield image of same crystal showing intersectoral zoning of red carminic acid.[359]

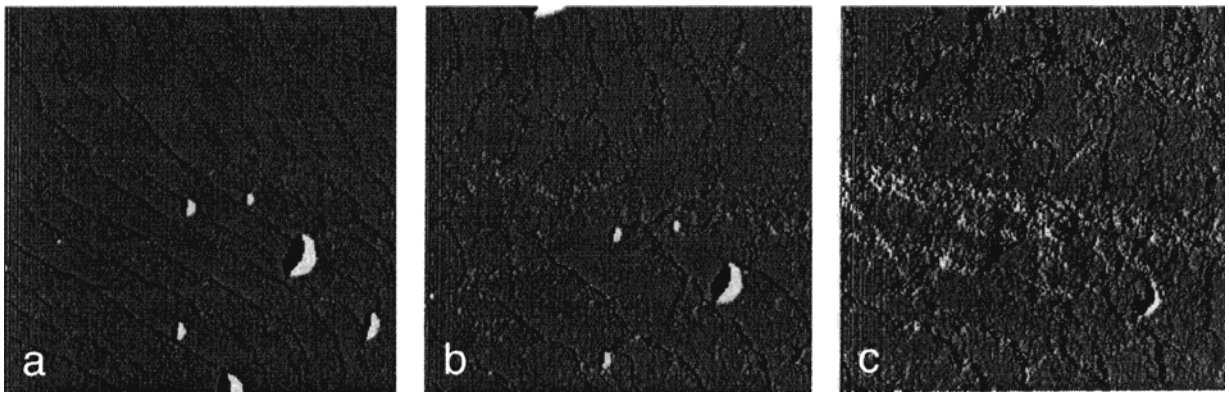


Figure 34. Mauri and Moret's AFM images of a K_2SO_4 (110) surface (45 × 45 nm^2) growing in the presence of 3 × 10^{-4} M acid fuchsin: (a) 0 s, (b) 214 s, (c) 691 s. [001] is vertical.[367] The smooth steps (a) are pinned by the dye molecules as a function of time, thereby taking on the rough contour (c). (Reprinted with permission from ref 367. Copyright 2000 Elsevier Science.)

hillock cannot be located in the differential interference contrast micrograph due to etching (Figure 33a), the dye reveals its location (Figure 33b).

Much has been learned about the surface topography of DICs using differential interference contrast microscopy but far less using scanning probe microscopies. One exception has been the work of Mauri and Moret on the in situ characterization of the growth of K_2SO_4 in the presence of acid fuchsin and pyranine.[367,368] They analyzed the changes in surface micromorphology induced by the presence of the additives on steps advancing on the (110) and (010) surfaces, respectively (Figure 34). Dye concentrations of ca. 10^{-4} M for acid fuchsin and ca. 10^{-6} M for pyranine were sufficient to pin the growing step fronts.

Buckley presented evidence for hillocks on crystals of KNO_3 grown with nigrosin and also $KClO_4$ with ponceau 2R.[369] While he did not describe intrasectoral zoning, this may be because he deposited dye throughout whole growth sectors. Moving dislocations can obscure the effect of intrasectoral zoning. Limiting dye deposition to the outer layers can be revealing.

In many cases, the macrosteps mimic the elementary steps; however, there can be differences in kinetics as shown in a recent reevaluation[370] of Cabrera and Vermilyea's "dead zone",[371] a limiting supersaturation below which the crystal does not grow due to pinning of elementary steps by impurities. Slavnova et al. investigated the $Pb(NO_3)_2$ dead zone induced by methylene blue.[372] Their results were in agreement with the theory of Cabrera and Vermilyea, although Treivus later reinvestigated the same system and found contrary evidence.[373]

C. Materials Science

1. Internal Texture

Impurities can have a profound effect on the internal texture of crystals. Aizenberg et al. showed how proteins control the size and shape of perfectly coherent domains in biominerals.[374,375] As proteins in biogenic crystals have evolved, the story of natural selection is thus writ in some form in the grain boundaries of the mineralized parts of organisms.

Davey et al. recently demonstrated that indigo binds specifically to the $(10\bar{2})$ twinning planes of saccharin crystals. For views parallel to the interface, the dye showed itself as a blue band.[376] Whetstone previously studied the effect of dyes on twinning.[377,378]

Buckley showed that crystals of K_2SO_4 grown in the presence of alizarin yellow 5G cleaved along the (100) planes due to the presence of the dye in the corresponding growth sectors. Fracture in this way is a material property nonexistent in the pure salt (Figure 35).[379] Gaubert described the cleavages induced by dyes in phloridzin.[380]

Dudley and co-workers investigated crystals of K_2SO_4 containing acid fuchsin or pyranine by synchrotron white beam X-ray topography.[381] Figure 36 shows a typical topograph made from K_2SO_4/acid fuchsin. Interference fringes, characteristic of the general quality of the crystals, are evident in topo-

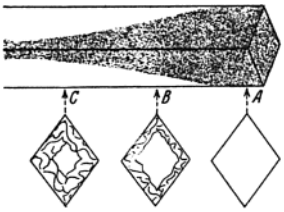


Figure 35. Induced cleavage planes in the stained regions of K_2SO_4/alizarin yellow 5G. Clear slices A, B, and C in cross section indicate perfect cleavage (A), whereas textured regions indicate coarse fracture (C).[17,379] Pure K_2SO_4 crystal does not cleave parallel to (100). (Reprinted with permission from ref 379. Copyright 1934 Oldenbourg Wissenshaftsverlag, München.)

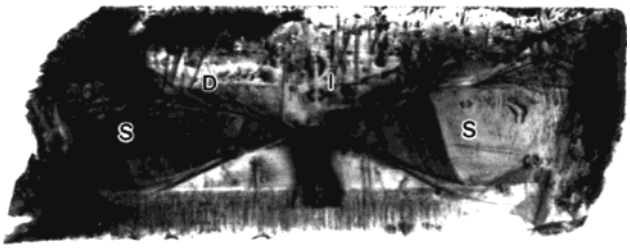


Figure 36. X-ray topograph of a K_2SO_4/acid fuchsin crystal. Regions marked *S* correspond to {110} growth sectors. Dislocations (*D*) abruptly change directions at a growth sector boundary. Large particulate inclusions (*I*) are also visible.[382] (Reprinted with permission from ref 382. Copyright 1993 Brookhaven National Laboratories Associated Universities Inc.)

graphs of some reflections. The dyed sectors (S) show through their darker contrast a higher degree of strain but this strain drops markedly farther from the site of nucleation.[382] Dislocations sharply turn direction when entering the dyed sectors. Generally speaking, however, the evident contrast indicates a surprisingly low dislocation density given the quantity (1 part in 5000) of highly offending impurities. On the other hand, crystals containing pyranine were composed of several misoriented domains of poor crystallinity.[383]

Internal crystal texture can be evidenced optically as well. Figure 37a shows the strain birefringence in the {110} sectors of K_2SO_4 grown in the presence of 3-aminonaphthalene-2,7-disulfonate. Using a new birefringence imaging technique based on the rotating polarizer method,[384,385] we have also separated the intrinsic retardation from changes in the indicatrix orientation (Figure 37g,h). This method provides much more information about the nature of differences in interference colors observed with an ordinary polarizing microscope.

The luminescence as a function of excitation polarization shows that the molecule entered both the {110} and {010} sectors in different orientations (Figure 37e,f) but that perturbations to the refractivity are much greater in the {110} sectors. A similar effect is observed in a cross section of K_2SO_4/amaranth through three growth sectors (Figure 38). The colors and azimuths indicate the directions of polarization. The colorless (021) sector shows a

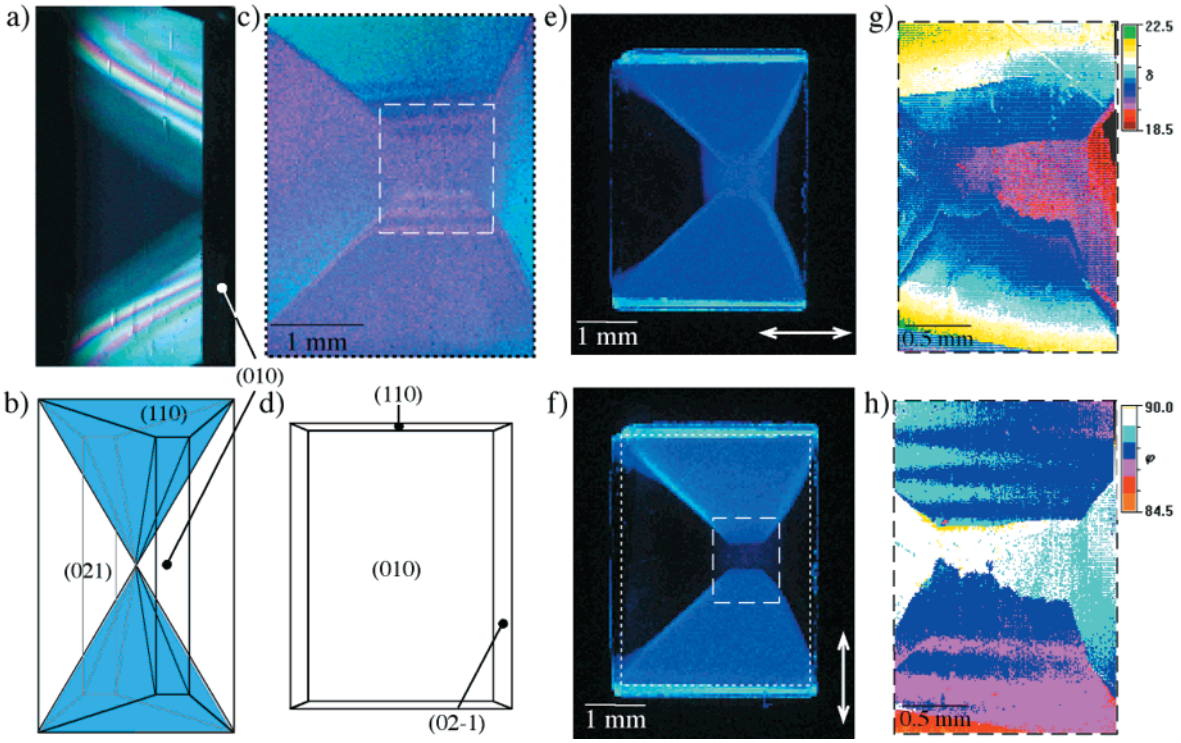


Figure 37. K_2SO_4/3-amino-2,7-naphthalenedisulfonate. (a) As grown crystal at the K_2SO_4 extinction position in crossed polarized light viewed through (021) face. Wedge-shaped {110} sectors show strain birefringence. The retardation passes through several orders as the thickness of the sector increases. (b) Idealized form with colored {110} sectors. Boxes in broken line scale subsequent images. (c) Thin section of the same crystal in crossed polarized light. View along [010]. (d) Idealized shape corresponding to part c. (e,f) Luminescence with polarized excitation indicated by double-headed arrows. The naphthalene derivative entered both the {110} and {010} sectors but in different orientations. (g) Absolute retardation ($\delta = 2\pi\Delta nL/\lambda$). (h) Indicatrix orientaion (ϕ) measured in degrees with respect to the horizontal axis. Photos by L. Bastin. Parts g and h made with Metripol system from Oxford Cryosystems.

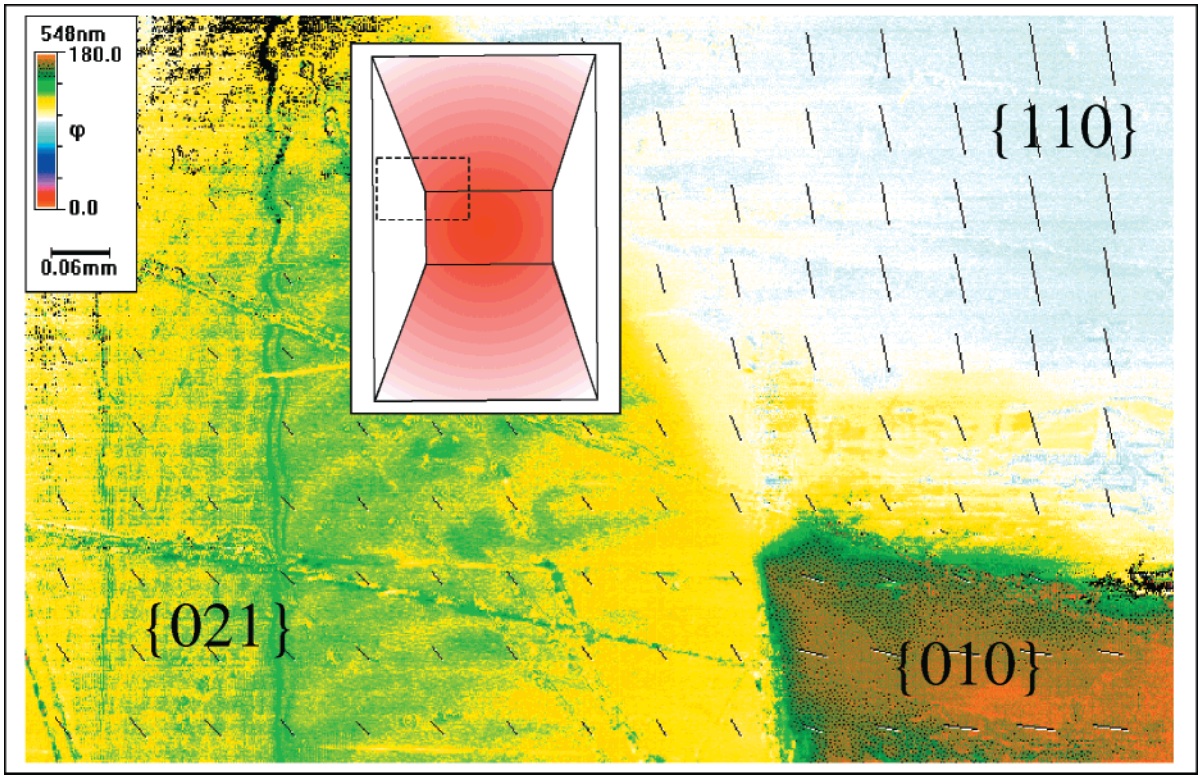


Figure 38. Metripol images (Oxford Cryosystems) of polarization directions in K_2SO_4 amaranth crystal thin section. The three regions correspond to the {010} (orange), the {110} (blue), and the {021} (yellow) sectors. Figure by L. Bastin. Inset shows a schematic representation of the as-grown K_2SO_4 crystal containing red amaranth in the {010} and {110} growth sectors but not the {021} sectors. The dashed box indicates area of analyzed cross section. The polarization (ϕ) of the absorbance, indicated by the azimuths, differs for different sectors. The 45° orientation in the {021} sector indicates no polarization, consistent with no absorption.

polarization at 45°, corresponding to the absence of linear dichroism. The red (110) and (010) sectors are polarized with respect to orthogonal axes.

2. Photonics

a. Lasers. Gaubert first described DICs containing fluorescent dyes (section II.C.1). Buckley surmised that luminescent phthalic acid crystals doped with fluorescein were "suited to anyone requiring a special effect".[17] Today a common application of dye fluorescence is in tunable lasers. Recently, materials scientists have tried to produce stable solid-state dye lasers that would obviate pumping hazardous solutions through resonant cavities as in solution dye lasers.[386] There may be distinct advantages of DICs as solid-state dye lasers as compared to doped glasses and polymers; single crystals polarize the emitted light, prevent diffusion of water or air which may react with excited states of dye molecules, and are of high optical quality and thermal conductivity.

Abubakirov and co-workers attempted to grow triglycine sulfate (TGS) in the presence of rhodamines with the intent of making new dye laser gain media.[387] While they did not make a single crystal TGS dye laser, they demonstrated that the dyes within the crystals were especially resistant to photodegradation, presumably by excluding oxygen, obviating deleterious reactions with the triplet excited states of the chromophores. More recently, dye doped zeolite lasers were demonstrated.[388]

Rifani et al. exploited the sulfonate−sulfate substitution mechanism to prepare a family of robust,

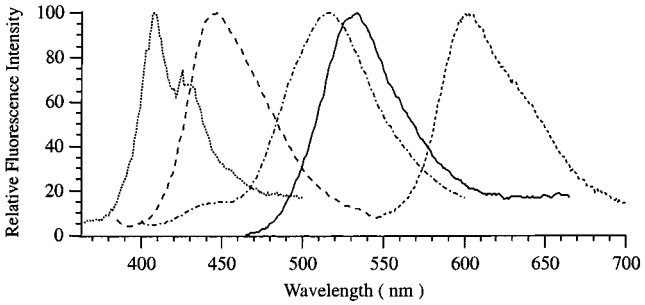


Figure 39. Emission spectra spanning the visible region in K_2SO_4 DIC lasers. From left to right: pyranine (acidic), pyranine (basic), methoxypyranine, pyranine tetrasulfonate, sulforhodamine B.[389]

inorganic, single-crystal dye lasers from K_2SO_4 doped with organic luminophores.[389−391] Pulsed lasers operating at a variety of visible wavelengths (Figure 39) were constructed by placing DICs in a Fabry−Perot configuration pumped with the harmonics of a Nd:YAG laser (Figure 40). The light produced was coherent as evidenced by speckle patterns formed by interference of scattered light. The beams were highly directional, with a few milliradian divergences. The output power displayed the standard laser threshold behavior, with a small output until the onset of lasing, followed by a rapidly linear increase with pumping.

Serra and co-workers have prepared highly luminescent lanthanide hourglasses of terbium and europium complexes within K_2SO_4.[392−394] However, the

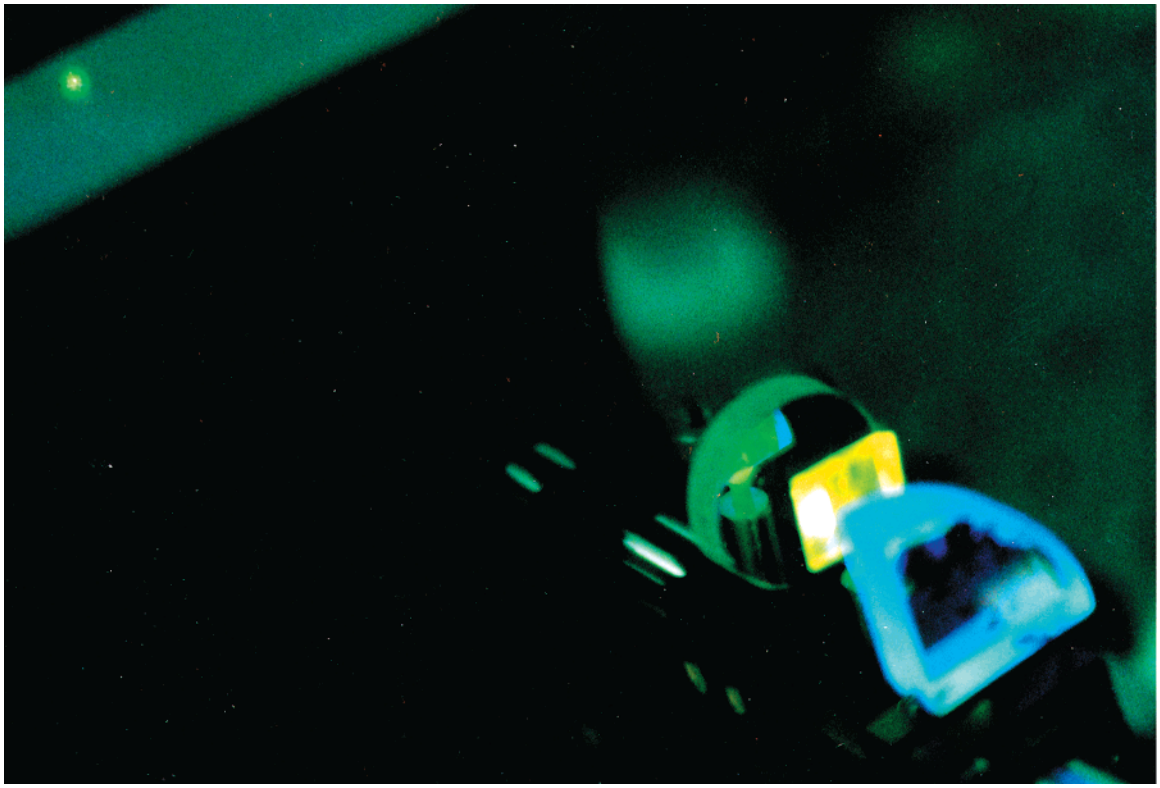


Figure 40. Single-crystal potassium sulfate dye laser. Square yellow object between blueish and greenish mirrors is the gain medium, K_2SO_4/pyranine (basic). Laser spot in upper left corner.[391]

ligand sphere of the guest ions and their relationship to the host crystals were not defined.

b. Nonlinear Optics. Subramony et al. prepared fluorescent KH_2PO_4 DICs with stilbene 3 and coumarin phosphate derivatives; efforts to couple the lasing with the nonlinear optical properties of the host are in progress.[247]

Crystal dyeing was also explored as a means of preparing photorefractive materials. Günter and coworkers doped 2-cyclooctylamino-5-nitropyridine with tetracyanoquinodimethane; however, the specificity of the growth process could not be judged in crystals grown from the melt.[395,396] A promising transparent NLO crystal, 4-aminobenzophenone, developed colored sectors when grown from solution due to an unnamed impurity.[397]

3. Phase Transitions

In principle, dye molecules inside of crystals could be used as local reporters of microscopic changes accompanying phase transformations. Ferroelectric crystals are good candidates for studies of this sort. Blattner et al. showed that hematein could be overgrown by KH_2PO_4 and $(NH_4)H_2PO_4$ crystals and had the effect of depressing the ferroelectric phase transition temperature by 2 °C.[284]

Ferroelectricity was discovered in sodium potassium tartrate tetrahydrate crystals (also known as Rochelle salt or Seignette salt).[398] Milligan[399] reported that this material selectively adsorbs and overgrows dyes on particular surfaces. Phloxine B and rose bengal colored the {010} sectors during growth. Sedarous et al. found that amaranth, Chicago sky blue, and brilliant crocein MOO also recognized the {010} faces.[400] They showed that the lifetime of the luminescence of dyes in ferroelectric crystals such as Rochelle salt and KH_2PO_4 could be used as a signature of the paraelectric → ferroelectric phase transitions. Unfortunately, the interpretation of the results is not equivocal.

Portnov and co-workers studied growth rates of the {010} faces of Rochelle salt in the presence of direct pure blue.[401,402]

Others have studied the triglycine sulfate crystals doped with aniline derivatives.[403,404] These crystals are undoubtedly luminescent. However, the authors focused their experiments not on optical properties but rather on perturbations of the spontaneous polarization and pyroelectricity.

The onset of ferroelectricity in some crystals involves the polarization of hydrogen bonds. In related experiments, the proton dynamics in ice single crystals were detected as changes in the fluorescence lifetime of 2-naphthol. The excited-state proton transfer of the fluorophore was sensitive to local fluctuations of the environment.[405,406] While comparable work of Trommsdorff and co-workers was formerly excluded from our discussion given the criteria that we established in section 1.B, we cannot help to point the reader to his elegant and extensive optical probes of H-bond dynamics.[28,29]

4. Photography

Dye inclusions in simple diatomic ionic salts are particularly attractive because of the possibility of obtaining vibrational spectra without the interference from the covalent bonds of the matrix. Recently, Maskasky[407,408] followed-up Reinders's study of dye

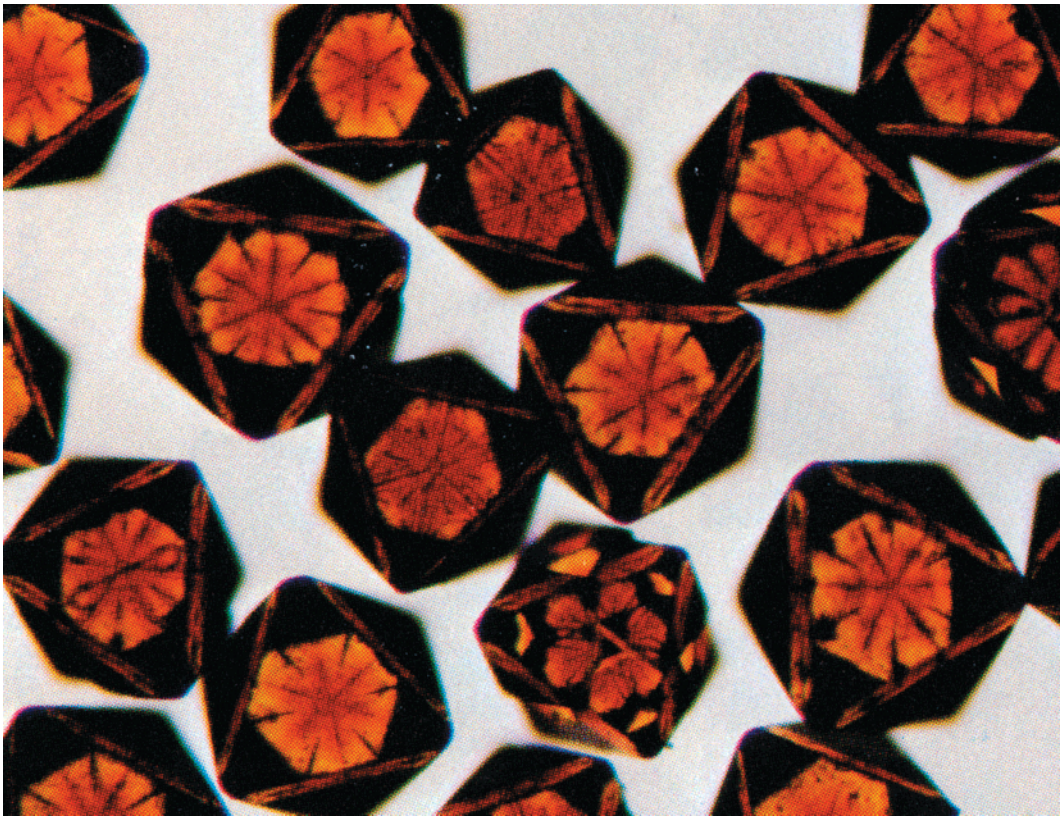


Figure 41. AgBr crystals with {111} habits dyed with Maskasky dye A.[407] Lateral dimension of crystals is ~ 0.2 mm. (Reprinted with permission from ref 407. Copyright 1984 IS&T: The Society for Imaging Science and Technology, sole copyright owners of IS&T's *Photographic Science and Engineering*.)

containing silver halide crystals (section II.E.1). He chose hundreds of colorants that were perfected for use in the photographic process[409] as guests for gel-grown AgBr crystals (Figure 41). In some cases, the dye molecules appeared to be unassociated with one another (absence of aggregate absorption bands) in the crystals, while in other cases dye particles were discerned under high optical magnification. Maskasky did not report vibrational spectra of the included dyes nor did he measure the polarization of their visible light absorption. High dye content may have been due in part to nonspecific solution inclusions.[410]

Here, we summarize other dyed diatomic salts because of their homology with the silver halides. Hoping to rationalize the ubiquity of the metastable form of $CaCO_3$, aragonite, in seashells,[227] Saylor searched for dyes that would affect the growth of NaF crystals, a surprisingly poor model for $CaCO_3$. Having observed that acid dyes tended to stain the cube faces of NaF whereas the basic dyes had no such effect, Saylor suggested that protons bound to the {100} faces had a mordanting effect.[236] Frondel also discovered many dyed NaF and LiF crystals that add to the heft of Table 1.[227]

Recently, Kanezaki reported that KCl grown in the presence of rhodamine emitted light that was characteristic of the zwitterionic form of the dye.[411]

Claassen noted in 1893 that KCl crystals grown from the extract of wormwood (*Artemisia absinthium*) took the unusual form of the cube octahedron and were "yellowish" in color.[412] However, van Gogh's yellow palette has often been interpreted as a sign of absinthe abuse.[413] Unlike Sénarmont's experiments with the extract of logwood, we are unaware of an attempt to repeat Claassen's experiments with the extract of wormwood; the United States banned absinthe in 1912.[414]

D. Single-Crystal Matrix Isolation

1. Preserving Metastable States

a. Excited States. Close-packed crystals can serve as ideal containers for the storage and stabilization of metastable molecules. For example, we have frequently observed that luminescent dyes exhibited exceptionally long phosphorescent lifetimes in simple crystal hosts, undoubtedly because the matrixes prevented the collisional deactivation of excited states (see also, sections IV.A.2a and IV.B.2).

For many years, the detection of phosphorescence from aromatic molecules was restricted to analytes in glasses at cryogenic temperatures because at room-temperature triplet excited states decay nonradiatively. This limitation was overcome when Winefordner and co-workers developed solid-surface room-temperature phosphorescence (SSRTP) as a general analytical tool.[415] Phosphorescence was routinely detected after solutions of potential phosphors were dried on a variety of solid surfaces. This sensitive method of analysis has since been used for the detection of drugs, pollutants, proteins, and polymers.[416] Yet despite the rapid growth of SSRTP and many excellent studies of the parameters that affect it, an understanding of the physical and chemical interactions required to produce SSRTP has not been fully developed. The chromophore and surface com-

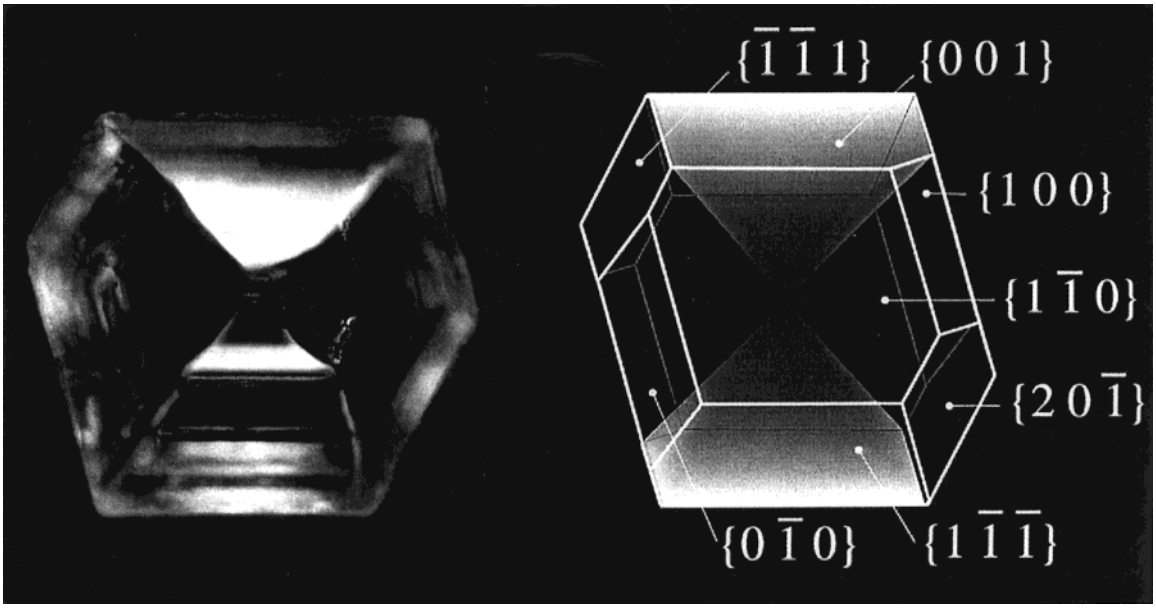


Figure 42. Luminescence photograph of a sodium acetate trihydrate/*p*-aminobenzoate crystal compared with a schematic representation.[419] Vertical dimension is 1 cm.

binations that will produce measurable phosphorescence quantum efficiencies cannot be predicted.[417]

The prototypical system for SSRTP is sodium acetate upon which solutions of *p*-aminobenzoic acid have been dried.[418] Gurney et al. found that crystals of sodium acetate trihydrate incorporated *p*-aminobenzoate in the {001} growth sectors and subsequently phosphoresced at room temperature (Figure 42).[419] The {001} faces were active presumably because they permit end-on approach of the guest carboxylate substituent that may adopt the position of acetate in the lattice by carboxylate-carboxylate substitution. Thus, it is to be expected that the formation of DICs play a large role in affecting the signature phosphorescence from a variety of molecules at room temperature. Related chemistry can perhaps be found in the influence of dyes on cupric acetate, earlier studied by France and Wolfe (see section II.E.2).[420]

The routine observation of room-temperature phosphorescence in DICs speaks to the mechanism of guest incorporation. While in some cases dyed crystals come about because of the trivial presence of fluid inclusions or dye decorated cracks and grain boundaries, this cannot be so in those systems that exhibit RTP because the triplet excited states of mobile chromophores will invariably be quenched nonradiatively by collision.

Gurney et al. studied the excited-state lifetimes and zero-field splittings of room-temperature phosphorescent *o*-aminosulfonated benzenes and naphthalenes.[270] A number of DICs show heavy atom effects. The triplet lifetime of *o*-aminobenzenesulfonate was shorter in Rb_2SO_4 as compared with K_2SO_4. Similarly, phosphorescent lifetimes of *p*-aminobenzoate were considerably shorter in barium acetate as compared to sodium acetate trihydrate. It has been demonstrated by optical detection of magnetic resonance that intersystem crossing rates for aromatic compounds are only affected by heavy atoms if they are interacting with the face of the π-system.[421,422] Thus, there is every reason to assume that cation$-\pi$ interactions are important in determining the properties of aromatic guests in ionic salt crystals.[423]

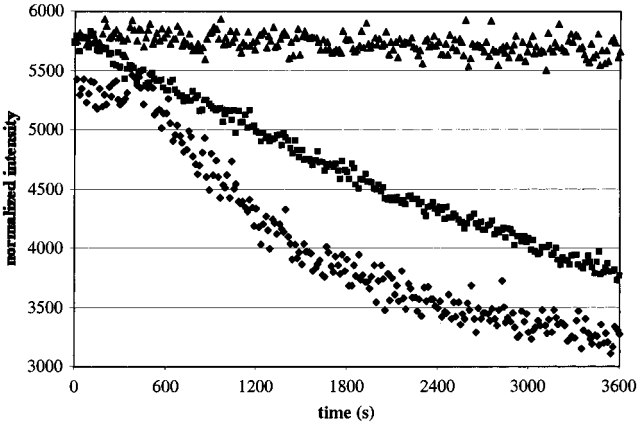


Figure 43. Decay of steady-state fluorescence of green fluorescent protein at 333 K in several environments: mixed crystal α-lactose monohydrate (▲), lyophillized α-lactose (■),saturated α-lactose solution (♦).[364]

Finally, Averyushkin and Zhevandrov used benzoflavin phosphorescence to monitor energy transfer in doped crystals of the cesium salt of *o*-sulfobenzoic acid.[424−426]

b. Proteins. In addition to excited states, Kurimoto et al. showed that biopolymers can experience significant kinetic stabilization in simple crystalline hosts.[364] The green fluorescent protein steady-state fluorescence intensity was measured as a function of time and temperature in three environments: saturated aqueous α-lactose solution, lyophilized α-lactose powder, and crystalline α-lactose monohydrate. Solution and lyophilized preparations lost nearly one-half of their fluorescence at 333 K within 1 h (Figure 43). On the other hand, the crystal showed no change at 333 K or even 343 K. It is reasonable to expect that encasing a protein in a crystal would retard the large amplitude vibrations

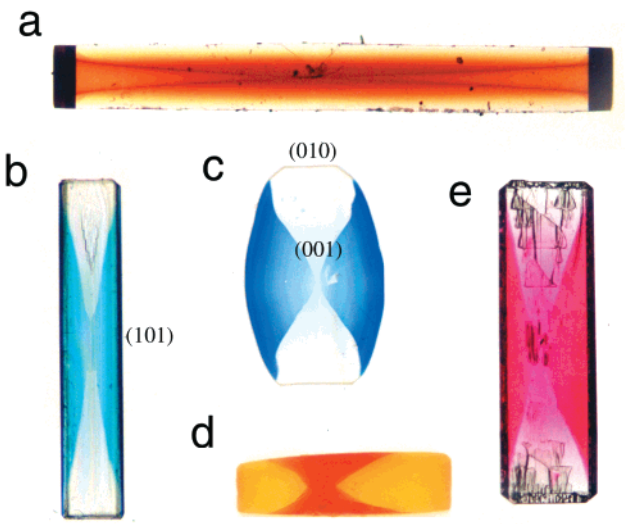


Figure 44. Poppy acid DICs with (a) tetra-*N*-methyl-4-pyridylporphine, (b) Nile red, (c) crystal violet, (d) mordant orange 10, (e) methyl yellow.[430] All crystals are viewed along [001] and similarly oriented. Length of $a = 3$ mm.

that initiate denaturation. Lactose is a common excipient used in the drug industry to store biopharmaceuticals. Another excipient that has been dyed is ascorbic acid.[427]

2. Preparing Oriented Gases

It is essential to orient molecules for the measurement of anisotropic physical properties.[428] Nevertheless, when the property to be measured is the electronic structure of a dye, molecules must not only be oriented but also isolated from one another because strong oscillators will often couple, obviating the monomolecular characteristic of interest. Unwanted intermolecular interactions of this sort have been successfully avoided by partly orienting chromophores in stretched polymer films, especially polyethylene,[429] but the analyses of these solid solutions are predicated on the proper determination of the distribution of guest orientations within the matrix. For this reason, general single-crystal hosts are highly desirable.

A review of the literature showed that some host crystals are extraordinarily general in their ability to orient and trap dyes during growth from solution. Two of the most effective are poppy acid and phthalic acid. Poppy acid is found in the latex of the opium poppy *Papaver somniferum*. Crystals of its trihydrate have served as hosts to a great variety of dyes; the resulting mixed crystals showed well-defined patterns of color and very pronounced linear dichroism. No less than five scientists, Gaubert, Lehmann, Neuhaus, Tammann, and Ruzicka, dyed poppy acid crystals (section II), however, at a time before structural organic chemistry, crystallography, and spectroscopy were sufficiently well-developed to account for the sharp polarization effects. Lovell et al. determined how the poppy acid crystals were able to serve as general hosts to such a wide variety of guests (Figure 44).[430] They solved the crystal structure of poppy acid, characterized its mixed crystals using polarization spectroscopy, and developed a model to account for the linear dichroism that is based the lamellar crystal structure of the host. The mean planes of the majority of dyes were oriented by these lamellae.

Mitchell et al., again following Gaubert, Lehmann, and Neuhaus, oriented several cationic dyes in the {021} growth sectors of phthalic acid.[431] Red shifts of the absorption maxima in the crystals and the structures of hydrogen phthalate/dye cocrystals[432] indicated charge-transfer interactions between host and guest. The linear dichroism indicated that the dyes were oriented in planes parallel to the phthalic acid rings. The free base and Zn complex of a protoporphyrin had earlier been oriented in a phthalic acid single crystal.[433] From the anisotropy of the EPR signal of the triplet excited state, the authors surmised that the planes of the porphyrins were oriented in the same direction as the H-bound layers of the phthalic acid crystals.

Chmielewski et al. grew phthalic acid crystals in the presence of luminescent heme proteins such as iron free cytochrome *c*.[476] The phthalic acid crystals showed sector-specific luminescence. Fluorescence anisotropy measurements indicated that the proteins were oriented.

E. Biology

1. Biomineralization

The dyeing of crystalline substances from which the mineralized parts of organisms are constituted originated with Kny in 1887, who reported that eosin stained growing calcium oxalate crystals, a component of kidney stones.[434] Buckley argued that the general aversion to the process of dyeing crystals could result in lost opportunities for understanding physiological crystallization.[17]

In 1964, Van't Riet and co-workers, taking Retgers's work as their point of departure,[126] studied the effect on growth inhibition and dissolution of vesical calculi of rats by the cationic and anionic dyes, methylene blue and wool violet 4 BN, respectively.[435] Boyce showed that methylene blue inhibited human renal calculi.[436] Methylene blue and beetroot extract served to identify uric acid in human renal stones and snake urine.[437−441]

Van't Riet and O'Rear later crossed several dyes with calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$) as well as $CaHPO_4$ and $MgNH_4PO_4 \cdot 6H_2O$.[442] They reported a variety of "mixed crystals"; however, the meaning of the term here is not clear as the authors described adsorption to as-grown crystals. Ponceau R appeared to have the strongest affinity for undefined facets of $CaC_2O_4 \cdot H_2O$ in vitro, measured as a ratio of adsorbed dye to dye remaining in solution. These studies spawned a small field of research unto itself that was played out mainly in the pages of urology journals. The majority of the studies focused on the dissolution and inhibition of calcium oxalate growth by methylene blue but without mention of DICs.[443−456]

Touryan et al., building on the work of Kny,[434] analyzed fluorophore and fluorophore-labeled protein G and a genetically engineered protein G mutant in

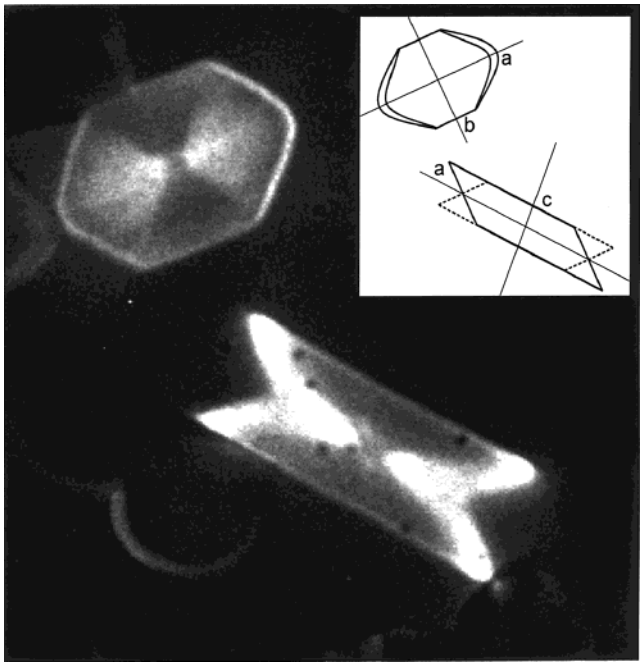


Figure 45. Calcium oxalate monohydrate grown in the presence of fluorescein labeled protein G within the {$\bar{1}$01} growth sectors. Length ~20 μm.[457] Single crystal in upper left, twin in lower right. Inset shows crystallographic directions.

calcium oxalate monohydrate.[457] They showed that eosin and fluoroscein added selectively to {101} sectors of the crystals. Both the labeled protein G and the engineered protein G labeled with rhodamine (TRITC) and fluorescein (FITC) behaved similarly (Figure 45).

Calcite ($CaCO_3$) is undoubtedly the most well studied biomineral component. However, Kohlschütter and Egg failed to dye calcite[458] as did Vater.[459] Nevertheless, they did observe that Congo red suppressed the crystallization of the aragonite form of $CaCO_3$. Kharin and Ivashina claimed that crystal violet was bound to growing nuclei of calcite, but little crystallographic information was provided.[460] Bugaenko and Kindinova studied the clarification of colored, raw cane sugar by $CaCO_3$ and concluded that the colored impurities were occluded to the salt nuclei during crystal growth.[461]

Addadi and Weiner showed that fluorecein-labeled aspartic acid rich proteins selectively recognized the {001} faces of calcite.[82,462] With Berman they grew calcite crystals in the presence of dansylated proteins isolated from the exoskeleton of a sea urchin. The crystals fluoresced even after partial dissolution, indicating that the proteins were inside.[463] Similar results were obtained for calcium dibenzoate phosphate trihydrate crystals grown in the presence of labeled mollusk shell proteins[464] and calcite with rhodamine labeled fibronectin.[465] DeOliveira and Laursen showed that an aspartic acid rich peptide labeled with fluorescein, designed to recognize the {$\bar{1}$10} faces of calcite, produced fluorescent crystals even after extensive washing.[466] Aizenberg and coworkers used the fluorophore calcein as a marker in the growth of sponge spicules, dramatic skeletal structures with luminescent tips (Figure 46).[467,468]

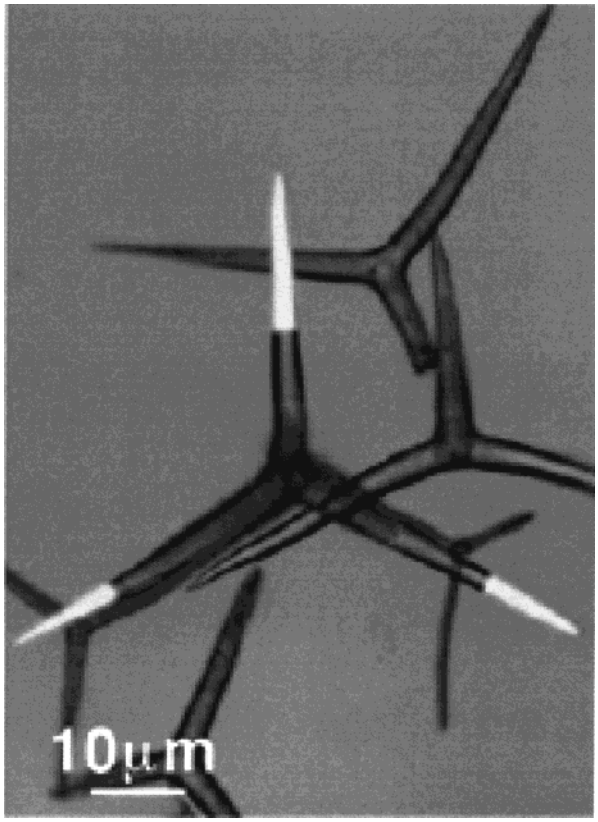


Figure 46. Triradiate calcite sponge spicule labeled with fluorescent calcein. Prepared by Aizenberg et al.[467,468]

DICs have even had application in pharmacy. Methylene blue produced green crystals of the chemotherapeutic agent methotrexate, indicating a pronounced solvatochromism.[469] Methyl orange and amaranth also stained methotrexate.

2. Matrix-Assisted Mass Spectrometry

The understanding of how and why organic molecules enter aromatic acid crystals has taken on a new urgency in light of MALDI (matrix-assisted laser desorption ionization) mass spectrometry. MALDI is a process whereby large analytes, when precipitated with a crystalline acid matrix having a large cross section for the absorption of laser light, are served-up to the gas phase, intact, and ionized upon irradiation.[470] Even when large crystals of MALDI matrixes were grown in the presence of a protein, cleaved, and irradiated on the fresh surface, the analyte signal in the spectrum was undiminished, suggesting that the protein was inside of the single crystals as well as on the surface.[471]

Recently, Beavis and Bridson designed a stimulating experiment aimed to determine how protein was included in sinapic acid, a reliable MALDI host.[472−474] They grew crystals of sinapic acid in the presence of the triarylmethyl dye coomassie brilliant blue and myoglobin which showed the characteristic hourglass pattern of blue color in the {10$\bar{3}$} growth sectors. Moreover, they reported that the crystals were strongly dichroic. Since coomassie brilliant blue is a well-known stain for myoglobin, they concluded that the proteins must have carried the dye into the crystal.

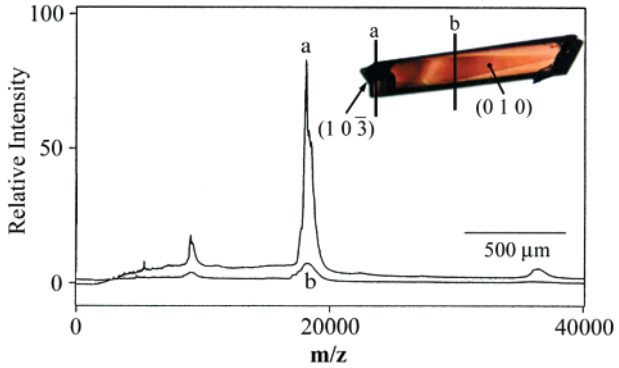


Figure 47. MALDI mass spectra of rhodamine-labeled myoglobin in a sinapic acid single crystal. The N_2 laser was focused across the crystal marked by bars *a* and *b*. Inset: Photograph of crystal stained in the (10$\bar{3}$) growth sectors.[286] (Reprinted with permission from ref 286. Copyright 2001 Materials Research Society.)

Schneider and Chait applied similar logic to oligonucleotides.[475] Acridine orange, a well-known DNA intercalator, was applied to solutions of sinapic acid containing dG18 and dT18. The resulting crystals were orange but not otherwise characterized spectroscopically or morphologically. In the absence of the oligonucleotides, the crystals did not become colored.

Mitchell et al. surmised that a simpler explanation for the hourglass pattern from coomassie brilliant blue would obviate the intermediate role of the protein.[431] They found that coomassie brilliant blue stained sinapic acid in the {10$\bar{3}$} growth sectors in the absence of protein. Their crystals resembled those that were formerly grown only when myoglobin was also present in solution.[472] Thus, covalent attachment of dyes should be requisite for the purpose of imaging guests in crystals.[476] Chmielewski et al. carried out such an experiment in which they prepared mixed crystals of sinapic acid and myoglobin labeled with rhodamine. Irradiation of the crystals in a MALDI experiment on the largest, uncolored facet (010) produced a weak protein signal that increased 20-fold when the beam spilled over the edges of the crystal associated with the colored (10$\bar{3}$) face (Figure 47).[286,476]

Li and co-workers had earlier used analytes covalently labeled with fluorophores to probe the mechanism of MALDI matrix formation.[477] They studied bovine insulin tagged with fluorocein isothiocyanate as well as a trisaccharide tagged with tetramethylrhodamine. Luminescent crystals of the well-known MALDI matrixes 2,5-dihydroxybenzoic and sinapic acids were precipitated when the labeled proteins were added to the crystallizing solutions. Their confocal luminescence micrographs revealed that the analyte was not uniformly distributed through the matrix crystals, but they could not correlate this heterogeneity with the crystal forms.

Proteins such as myoglobin, cytochrome *c*, or other hemes, already colored by an intrinsic chromophore, do produce colored crystals of 2,5-dihydroxylbenzoic and succinic acids.[478,479] There are undoubtedly countless observations of this sort in the MALDI literature, but we have chosen to list only those examples that link the color to the specificity of crystal growth.

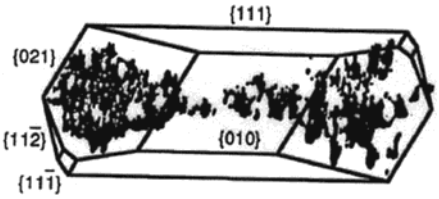


Figure 48. Autoradiograph of ^{14}C-methyl-labeled cytochrome *c* in the crystal of phthalic acid, upon which an idealized drawing of the habit has been superimposed.[476]

Chmielewski et al. further demonstrated that biological molecules can routinely be oriented in a variety of organic crystals rich in hydrogen bonds such as phthalic acid, irrespective of their activity as MALDI host matrixes.[476] By choosing biopolymers that are themselves dyes or by covalently attaching dyes to biopolymers, they prepared DICs from proteins and oligonucleotides; comparable images can be made radiographically with ^{14}C-methyl labeling (Figure 48). Fe-free cytochrome *c* also luminesces in the crystal but without a covalently attached label. The emissions are highly polarized, indicating that the molecules are oriented inside of a phthalic acid crystal. Such mixed crystals might be used to analyze anisotropic properties of biological molecules that could not otherwise be crystallized. Single-crystal matrix isolation of biopolymers should be complementary to techniques that partially orient biopolymers such as the application of electric, magnetic or flow fields, by dissolution in liquid crystals or stretched gels, and by the deposition of monolayers.[480]

Protein crystals themselves have been dyed. Ovalbumin labeled with the BODIPY FL fluorophore was incorporated into the {110} growth sectors of egg white lysozyme.[481] The effect on growth rate was measured. More ovalbumin was incorporated at high supersaturation. To the extent that the density of steps and kinks increases with increased supersaturation, it was suggested that the ovalbumin adsorbed onto these emergent surface structures. Caylor et al. used two-photon fluorescence to image labelled ovotransferrin in egg white lysozyme crystals. They observed greater fluorescence in the {101} sectors.[482,483]

V. Conclusions

A. Generalization of Single-Crystal Matrix Isolation

During the course of our research, we discovered a number of crystalline surfaces that have a remarkably general ability to orient and overgrow guest molecules bearing not size, shape, nor constitutional similarity to the host crystal molecules and ions. For instance, consider the (010) face of α-lactose monohydrate. It overgrows many proteins (Figure 49).[492] However, we have found no evidence of proteins favoring any of the other six well developed facets. The further generalization of single-crystal matrix isolation requires an understanding of the characteristics that define a highly receptive face. The most receptive surfaces including the {011} faces of KH_2PO_4 (sections IV.A.3 and IV.B.2), the {110} faces of

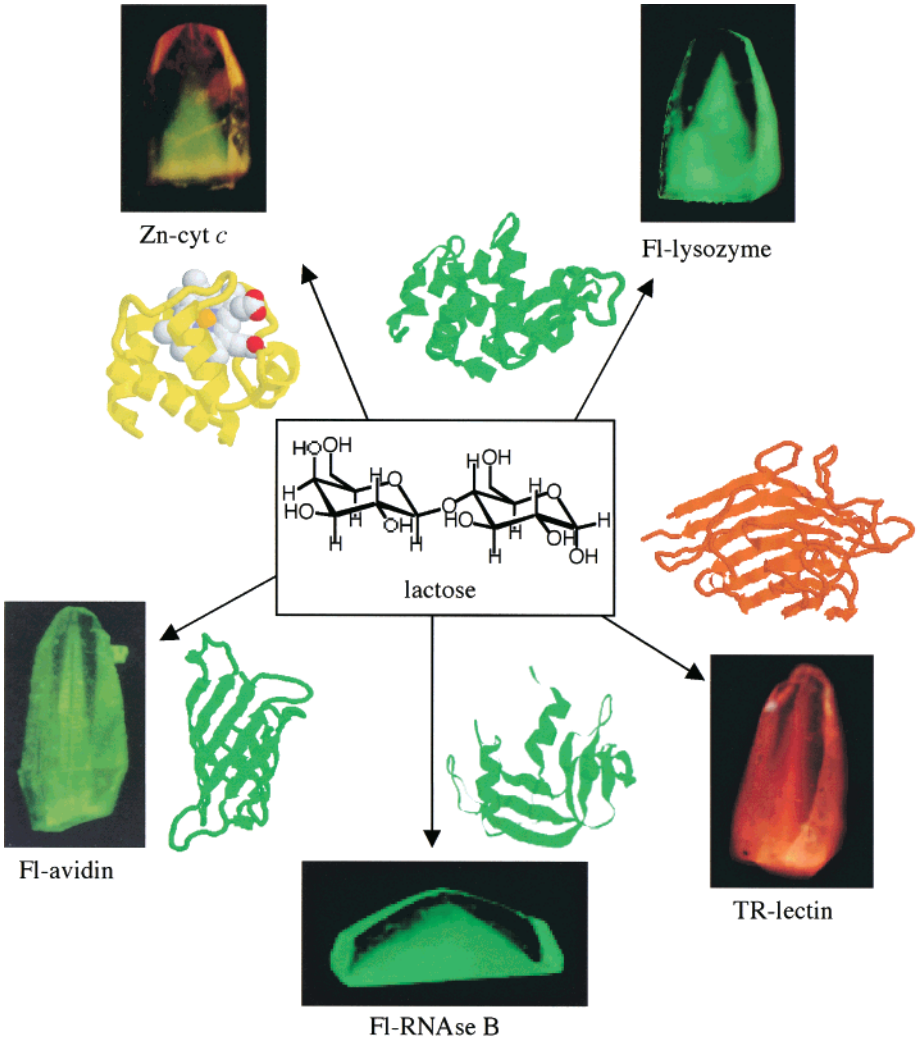


Figure 49. Crystals of α-lactose monohydrate containing a variety of proteins. Fl and TR indicate covalently attached fluorophores fluorescein and Texas red, respectively. In each case, the mixed crystal shows a characteristic fluorescence from the (010) growth sector.[492]

K_2SO_4 (sections IV.A, IV.B.2, and IV.C.1/2), and the (010) face of α-lactose monohydrate (sections IV.B.2 and IV.D.2) are decorated with macroscopic hillocks that can be observed with a reflected visible light microscope equipped with a differential interference contrast prism. Thus, we surmised that growth sectors easily doped with large guest molecules would be bounded by surfaces with bunched steps. We set out to test this supposition with phthalic acid, an extraordinarily general host crystal.

Following the paths first trod by Lehmann, Gaubert, and Neuhaus (sections II.B.2 and II.C.1/2), we found that a variety of dyes can color sectors of growing phthalic acid and measurements of linear dichroism were used to reckon mixed crystal structure.[431] A particularly stunning example, as discussed in section IV.A.2.b, is phthalic acid containing methyl red in different states of protonation in the {010} and {021} growth sectors (Figure 21). Indeed, we observed that the {021} surfaces of pure crystals were optically flat, while the addition of methyl red produced rounded, macroscopic hillocks (Figure 50). Evidence of intrasectoral zoning in phthalic acid crystals is evident with methyl green in the photograph in Figure 51.

What then is the relationship between macroscopic hillocks and mixed crystal growth? Macroscopic hillocks are typically formed through the process of step pinning by impurities and subsequent step bunching.[371] Mauri and Moret showed this process explicitly with dye adsorbates (Figure 34).[367] Accordingly, faces with macroscopic growth spirals are also likely to be those faces that have a tendency to strongly adsorb guests, either purposeful additives or adventitious impurities. As a complimentary test, we grew crystals of potassium hydrogen tartrate, known to have well-formed hillocks on the *b* face,[484] in the presence of a variety of dyes. In accord with Buckley, the dyes were indeed adsorbed and overgrown by (010)[187] and showed strong linear dichroism. The possible generalization of the supposition that macroscopic hillocks can serve to identify faces that are receptive to the incorporation of large guest molecules is currently subject to a variety of tests in our laboratories.

B. Experimental History

Why was a once vibrant area of inquiry largely abandoned before the questions that it raised were answered? The first example of a dyed crystal, from

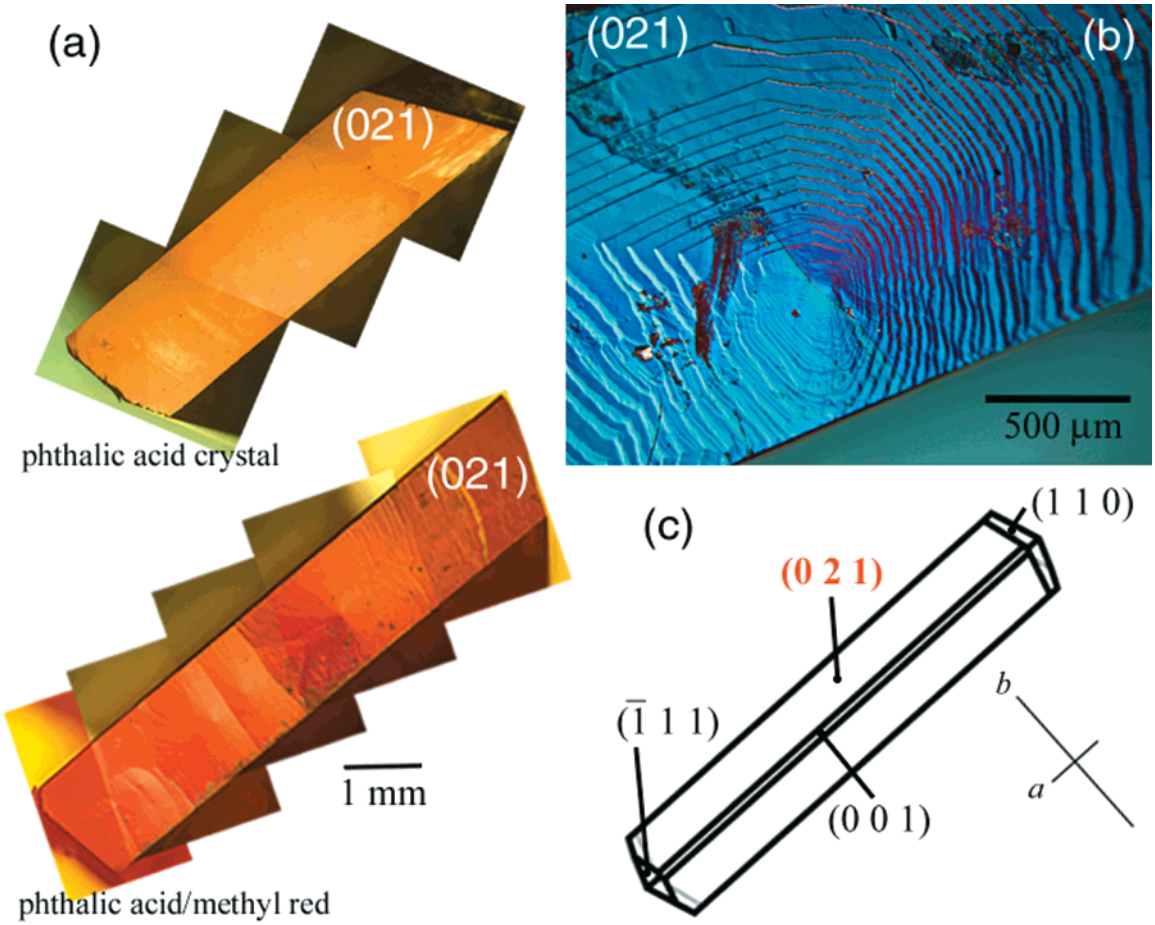


Figure 50. (a) Composite DIC micrographs of phthalic acid crystals revealing (021) surfaces. Pure (top) and doped with methyl red (bottom). (b) A polygonized macrospiral formed on the phthalic acid/methyl red (021) surface. (c) Idealized representation of habit.[286] (Reprinted with permission from ref 286. Copyright 2001 Materials Reseach Society.)

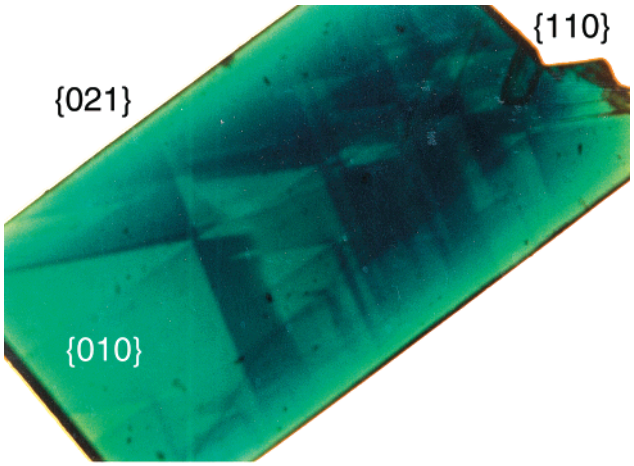


Figure 51. Phthalic acid/methyl green showing intrasectoral zoning. View is along [010]. Crystal length ~2 mm. Photo by C. Mitchell.

Sénarmont in 1854, did not quickly lead to a self-sustaining dialogue in large measure because of the difficulty in reproducing Sénarmont's salt. Retgers and Lehmann skirted this impasse at the end of the 19th century by seeking other dyed crystals. The 1930s represented a golden age as Gaubert was concluding his studies and Buckley and France began theirs. Activity slowed in the 1940s, in part as a consequence of the second world war, but never returned to its earlier high point. The 1960s saw a number of contributions in the Bulgarian and Russian languages, mostly about methylene blue and its congeners in nitrates but all underappreciated by the English speaking audience.

The demise of DIC research is due in large measure to the success of the X-ray diffraction experiment, which increased the frequency for electromagnetic radiation used in the analysis of crystals by 4 orders of magnitude from 10^{14} Hz for visible light to 10^{18} Hz for X-rays. This change was manifest in the design, execution, analysis, and interpretation of crystallographic experiments. Compare, for example, Viola's *Gründzuge der Kristallographie* (1924)[485] a study in crystal optics with Friedel's text on X-ray crystallography *Leçons de Cristallographie* (1926).[486] They seem to describe two completely different subjects. X-rays transformed the science of crystals and crystallography suddenly became central to our understanding of the structure of matter. The application of X-rays to increasing complex systems became the dominant theme in 20th century crystallography.[487] The analyses of the alkali halides in 1913 led in relatively short order to experiments with bright, pulsed X-ray sources enabling the determination of cellular substructures[488] and time-resolved dynamical processes.[489] In DICs the concentration of guest is typically about 1 part in 10^3−10^6. Such quantities, significant in visible light, will not contribute meaningfully to the scattering of X-rays.

Unfortunately, with the race to apply X-rays to each new level of complexity, crystals not amenable to X-ray analysis such as DICs and others were abandoned.[342]

In summing up his research on DICs Buckley remarked dejectedly that "...just so long as there are so many glittering prizes for the asking in other directions of scientific pursuit, so long will these and similar mysteries be left cold and unattended".[17] We would be pleased if this review convinces some that the materials described herein glitter in their own way and that they compete favorably even with some of today's hotly contested prizes because it is undeniably true that such crystals address a range of questions in contemporary chemistry. They can be used as lasers, as unique hosts in single-crystal matrix isolation experiments with metastable excited states and biopolymers, for conformational analysis, for separations, to interrogate mechanism in biomineralization and in matrix-assisted optical and mass spectrometic chemical analyses, to identify growth active surface structures on crystalline faces, and as optical reporters of phase transitions. Sénarmont and his immediate successors most concerned with understanding pleochroism and the principle of isomorphism could have foreseen none of these topics. The *raison d'être* for studying dyed crystals changed and with this change was a loss of continuity. To reestablish this connection it was necessary to carry out many of the 19th century experiments in a 20th or 21st century laboratory.

The interpretation of nature rests upon carefully planned experiments. It also must be true that our interpretation of history can benefit from experiment, especially when, according to the medical historian Belloni, past "observations and experiments are described which in arrangement and technique are as distant from our habits and mentality as the cultural climate in which the author lived". He continues, "the best and sometimes the only way of arriving at an exact interpretation of the text being considered lies in repeating the experiments...".[490,491] In this review, we have described recent efforts at recreating the lost art and science of dyeing crystals in the laboratory.

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