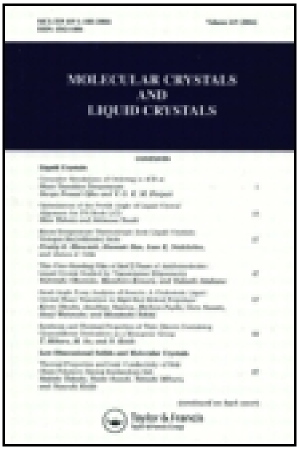

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CRITICAL EVALUATION OF DYES AS CRYSTAL GROWTH INHIBITORS

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ABSTRACT. Between 1933 and 1951, H. E. Buckley conducted an extensive investigation of the manner in which commercial dyes modify the habits of simple salt crystals. While he and others reasonably assumed that the mechanism by which dyes inhibited the growth of crystal surfaces involved the substitution of anionic functionalities for anion position in the lattice, the stereochemical details of these processes were never articulated. In light of the recent explanation, by Davey and coworkers,[1] of the inhibition of alkaline earth sulfate growth by the stereospecific two-point attachment of diphosphonates, we felt that the time was ripe for a reinvestigation of Buckley's data. A conformational analysis, using the AM1 Hamiltonian, was carried out on nine constitutionally isomeric azo dyes whose habit modifying effects for five salts were recorded by Buckley. No stereochemical relationships were found which could explain the stated data. We argue that the action of unspecified impurities, often comprising 50% of commercial dye samples, may render a structural interpretation of Buckley's data virtually unattainable.

Keywords: Habit modification, Crystal growth inhibition, Dyes

HISTORICAL INTRODUCTION

The realization that impurities can impart striking effects on the habits of growing crystals can be credited to several scientists working at the turn of the Nineteenth Century, including de Lisle, LeBlanc, and Beudant.[2] Surprisingly, it was not until very recent times that crystallographers were able to explain the habit modifying effects of particular impurities in molecular terms. This was accomplished by a group of crystallographers at the Weizmann Institute by carefully correlating tailor-made habit modifying impurities with likely growth surface structures. Addadi and coworkers showed that habit modification phenomena were powerfully-suited to studying intermolecular interactions.[3]

In the years separating de Lisle and LeBlanc from Lahav and Leiserowitz,[2] the problem of controlling crystallization with the use of suitable impurities was attacked sporadically. Unquestionably, one of the most bizarre, compelling, and heroic studies to come out of this "dark age" of habit modification is Harold Buckley's extended investigation of the manner in which commercial dyes affect simple salt habits. Buckley, a crystallographer who worked in Manchester, was one of the first twentieth century scientists to seriously study habit modification.[4] Between 1930 and 1932 he wrote a series of papers describing the habit modification of simple salts[5] such as $NaClO_3$[4b], $Ba(NO_3)_2$[4c], and K_2SO_4[4e] when these crystals were grown in the presence of simple ionic impurities. In 1933, Buckley changed his tack; he started using organic dyes as his habit modifying agents.[6] Manchester was - and still is - a great textile and dyeing center. Buckley had access to thousands of commercial dyes. During the next ten years he recorded the results of 16,000 crystallizations of salts in the presence of dyes.[7] This database is a unique record. It is unlikely that another massive set of observations of this nature soon will be recorded.

Buckley's data presumably contains structural information about the interaction of organic dyes with growing crystal surfaces; as we have stated habit modification can underscore molecular recognition. Buckley appreciated this, but the nature of the information was not extracted easily. In 1934, 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."[8]

For 18 years Buckley tried in vain to make chemical sense of his monumental study. In a summary of his work in the *Proceedings of the Manchester Literary and Philosophical Society* he wrote, "The idea behind the author's (probably incomplete) speculations has been to stimulate some organic chemist to act similarly, but with more telling effect, the author being an indifferent organic chemist."[7] We were stimulated and chose to be *that organic chemist.* Equipped with more that a half century of developments in structural chemistry and crystallography, as well as modern tools of computational organic chemistry, we set out comprehend Buckley's habit modification data. Our attempt is discussed herein.

BUCKLEY'S METHODOLOGY

Buckley ranked dyes in order of the efficacy with which they exacted a particular morphological change on simple salt crystals. For example, K_2SO_4 has the natural form represented in the left of Figure 1 when crystallized rapidly from water by evaporation. Buckley would include enough of a dye in the solution of the crystals such that the {010} faces increased in relative area by a specified amount with respect to a reference form, {021} in this case. When the ordinarily "vestigial" {010} became equal in area to {021} the *standard effect* was achieved. For example, it required only 5.3 x 10^{-5} moles of methyl orange to produce the standard {010} effect on 1.0 gram of K_2SO_4 while 3.5 x 10^{-3} moles of Eosamine B produced the same change. One hundred other dyes produced intermediate results.[8]

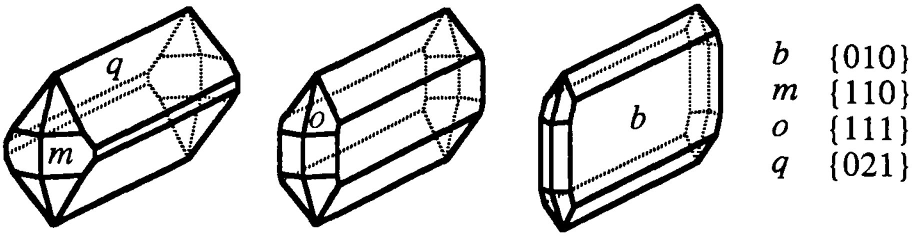

FIGURE 1 Habit modification of K_2SO_4 (after Buckley[8]). (a) Habit of crystals grown rapidly from H_2O at room temperature. (b) Standard effect on {010} for crystals grown in the presence of particular habit modifying dyes. (c) 2-3 times standard effect on {010}. Indices of faces for this salt and most other reported by Buckley follow the axial ratios given in Groth's *Chemische Krystallographie*.[9]

Buckley recognized that the habit modification of simple salts by impurity dyes is not qualitatively different from the effects exerted by inorganic ions. However, many dyes would produce the effect in much smaller quantities than would be required of inorganic ions. Since many of the dyes were sulfonates, Buckley was lead to presume that the principal interaction of the dyes on the crystal surfaces was a substitution of the $-SO_3^-$ tripods with anion positions in the lattice occupied by tetrahedral ions such as SO_4^{2-}. Multiple interactions of di- and trisulfonates, where stereochemically feasible, presumably would have augmented the crystal growth inhibition by increasing the electrostatic attachment of the dye to the crystal surface.

It is impossible to follow Buckley's work without the Colour Index, the standard reference work for dyers and colourists. Buckley's dyes were identified with numbers in the first edition (1924)[10a] of the Colour Index. Modern dyes refer to the codes in the greatly expanded third edition (1984).[10b] A conversion table may be found in the second edition (1956).[10c] This is the only way to establish a constitutional link between substances manufactured today and the habit modifying dyes employed by Buckley.

COMPUTATIONAL ANALYSIS OF ISOMERIC DYES

In 1991, Davey and coworkers showed that tailor-made diphosphonates effectively inhibit of growth of $BaSO_4$ crystals, a principal component of the scale that precipitates in offshore pipelines.[1] In their model, inhibition proceeded when the length of the flexible spacer joining the charged phosphonate groups enabled a two-point attachment on the idealized crystallographic surface. Such a model certainly could be applicable to Buckley's disulfonated dyes.

Buckley speculated that the discovery of the habit modification mechanism would be facilitated by collecting his dyes in manageable subsets. In his 1951 book on *Crystal Growth*,[11] he summarized the habit modifying powers of nine constitutionally isomeric dyes for six surfaces of five crystalline salts. Following the presentation and contemplation of this data Buckley admitted, "Apart...from a general tendency of all the configurations to 'do something' it is evident that the effects are highly specific to the dye molecule and the crystal surface."[12]

Buckley's attempt to explain his habit modification data must be presented in the context of the limits of structural organic chemistry in the 1930s. At that time, some chemists thought that azo bonds were linear.[13] Such an assumption would have precluded any reasonable judgement as to the disposition of sulfonate groups. Moreover, many active dyes had more than one conformation. Conformational analysis was a nascent science in the 1930s.[14]

We carried out a conformational analysis of these nine molecules using the AM1[15] Hamiltonian employed in the MOPAC[16] family of programs. Shown in Figure 2 are ground state structures of the nine isomers. The relative enthalpies of formation are indicated in Table I, as is the intramolecular S-S distance, the dihedral angle between naphthyl rings, and the C-N-N-C torsion angle. Relevant structural parameters are summarized in Table I. They are in agreement with experiment.[17] The structures tend towards flat when sterically feasible, encouraged by the intramolecular hydrogen bonding.

We assumed that strong modifiers would find, in K_2SO_4 for example, SO_4-SO_4 distances on the surface being modified that closely matched the intramolecular S-S distance. This reasoning worked well for Davey.[1] We plotted habit modifying power, as defined by Buckley, versus the smallest differences in distance between molecular S-S vectors and surface anion-anion (measured from the central atom) vectors (Table II). The graph correlating S-S dye distances with S-S crystal distances for K_2SO_4 {010} is shown in Figure 3. Our eyes could not force a form on this scatter. Plots for other five surfaces for which Buckley reported data ($KClO_3$ {011}, K_2CrO_4 {010}, NH_4ClO_4 {011} and {102}, and Potash Alum {100}) were also unrevealing.

In these studies we employed ideal surfaces. A better approximation would account for secondary surface structures. Salt surface structures may be quickly predicted with the Periodic Bond Chain approach of Hartman and Perdok.[18] Here, a lattice is approximated by a graph in which edges represent strong bonds between nearest neighbor molecules or ions. Planes d_{hkl} through this graph give subgraphs where the lattice is broken in 0, 1, and 2 directions. They conform to flat, stepped, or kinked faces, respectively, and thus give quick approximations of secondary surface structures and their dimensions. Hartman-Perdok theory recently was applied to K_2SO_4 but it failed to predict the morphological importance of the {021} faces.[19] Its relevance to Buckley's habit modification data is a subject of continuing investigation.

TABLE I. AM1 structural parameters for constitutionally isomeric azo dyes.

Dye CI No[10a, *]	Relative E (kcal/mol)	S-S Distance (Å)	Torsion Btwn. Rings (deg)	C-N-N-C (deg)
85	15.1	7.97	8.4	172.6
88	16.6	7.94	23.2	179.1
88'	17.5	7.93	32.4	178.9
89	30.2	5.44	7.6	176.1
91	14.0	7.97	7.3	171.7
179	6.2	11.64	22.5	178.9
179'	6.5	11.43	29.2	179.4
180	3.8	13.60	23.7	179.0
180'	6.8	13.75	0.0	180.0
182	3.4	12.84	23.6	178.6
182'	3.4	12.84	23.5	178.7
183	25.1	8.04	6.3	174.1
183'	29.6	8.72	49.1	170.0
194	0.0	13.37	11.8	179.8
194'	0.2	13.46	1.4	180.0

* (') indicates higher lying minimum obtained by rotation of C-N bonds.

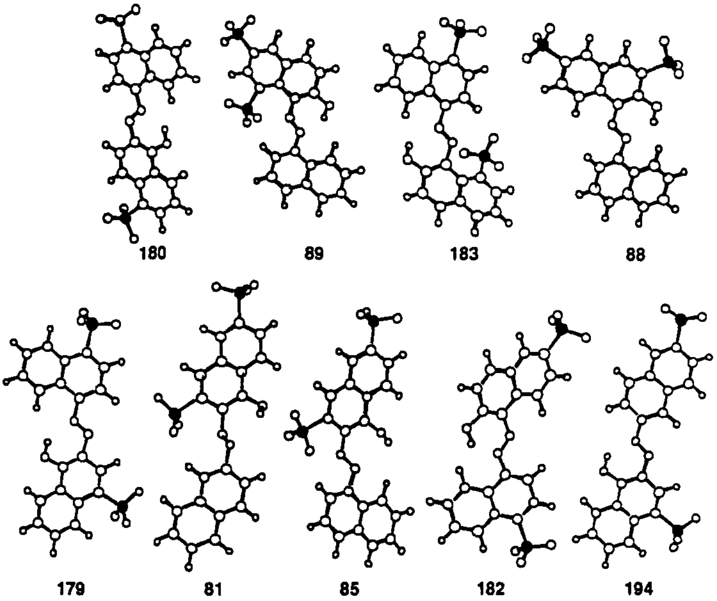

FIGURE 2 AM1 ground states of Buckley's nine constitutionally isomeric azo dyes. Numbers identify structures in the *Colour Index, 1st Ed.*[10a] Sulfur atoms are black.

TABLE II. S-S on the (010) face of K_2SO_4.*

SO_4^{2-}-SO_4^{2-} Distance (Å)	x	y (=0.0845)	z (=0.2642)
4.866	1/2	$2y$	$-2z+1$
5.183	1/2	$2y$	$-2z$
5.772	1	0	0
7.483	0	0	1
9.450	1	0	1
9.503	3/2	$-2y$	$-2z+1$
9.669	3/2	$-2y$	$2z$
11.510	1/2	$2y$	$-2z+2$
11.544	2	0	0
11.918	1/2	$2y$	$2z+1$
13.757	2	0	1
14.111	3/2	$-2y$	$2z-2$
14.445	3/2	$-2y$	$2z+1$
14.966	0	0	2

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*Based on coordinates from R. W. G. Wyckoff, *Crystal Structures*, Vol. 3, John Wiley, New York, 1965. This surface is constructed from tranlationally related ions in the *ac* plane and their centrosymmetric equivalents.

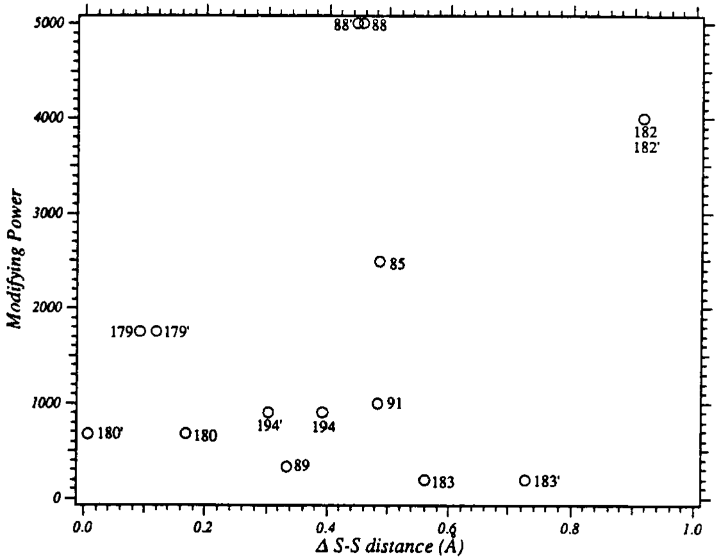

FIGURE 3 Results of correlation of habit modifying power and smallest difference in distance between surface S-S vectors and dye S-S vectors. Habit modifying power refers to the parts salt required for one part of dye to produce the standard effect.

WHY STRUCTURE-ACTIVITY RELATIONSHIPS FAIL FOR BUCKLEY'S HABIT MODIFICATION DATA

Having analyzed Buckley's oeuvre we can identify several reasons why a correlation between his habit modification data and molecular constitution and conformation yet has not been achieved.

a. Tables contain errors. Buckley writes,

> "Sometime in 1938, the Secretary of the Manchester Literary and Philosophical Society.....persuaded the author to give a summary, up to date, of his work and this was published in a preliminary paper [*ref 2*]. Shortly afterwards the author realized how dependent he (and probably others) had been, for samples, on the uninstructed counter assistant who was unaware of the existence of, say, fifty 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."[7]

In fact, the K_2SO_4 active dye Eosamine B cited from reference 8 on the third page of this manuscript is discovered, in the 1951 compilation,[7] to be inactive. Eosamine G has some modifying power. Buckley professes to have corrected any early errors by checking each result with "six hundred samples in the makers' original sealed bottles."

Buckley was a careful, inspired, and tireless experimenter. There is every reason to believe in the veracity of his observations. However, constitutional assignments of thousands of commercial compounds now 60 years old may be regarded with suspicion.

b. Dyes were impure. Most commercial dyes are impure and it is not uncommon for the unspecified portion of the sample to exceed 50%. The impurities in dyes are often isomers or starting materials in the dye syntheses, that have comparable or complementary habit modifying activities. Many of the azo dyes were prepared by electrophilic aromatic substitution of diazonium salts with naphthalene sulfonic acids. It is rare for these reactions to be regiospecific.

Buckley ignored the role of impurities. If a given dye, say 70% pure, produced the standard effect for a salt when present in one part per 50,000 of salt, he assumed that the impurity was inactive and increased the activity of the dye, by a factor of 100/70, to 71,000. This seems like a rash judgement given likely chemical constitution of impurities found in many commercial dyes.

Buckley's data contained many examples where two or more dyes carrying the same name and Colour Index number but supplied by different manufacturers showed remarkably varied actions on a particular crystalline surface. A fragment of one of his tables is reproduced below. For example, the activity of dye 246 for the (010) face of K_2SO_4 was 15 times greater when supplied by Leopold Casella than when supplied by British Dyestuffs Inc.

Whetstone, in a reevaluation of some of Buckley's work, similarly was convinced of the necessity of using pure dye samples.[20] He used only "specially laboratory-prepared dyes made from purified dye intermediates."

c. Buckley's database was so great that even he had trouble summarizing observations. Many of the dyes Buckley employed in his study were synthesized by coupling of a smaller number of fragments. There are a several of sulfanilic acid derivatives and naphthol or naphthylamine sulfonates that were the constituents of many dyes. He felt that while it may not be possible to rationalize the effect of a particular structure, trends should appear by averaging the effects of particular fragments each time that fragment appeared in a dye tested.

TABLE III. Selected data from reference 7*.

CI No[10a]	Dye and Manufacturer	$KClO_3$ (011)	K_2SO_4 (010)	K_2CrO_4 (010)
79	Ponceau 2R (A)	4,000	3,000	1,250
79	Ponceau RR (A)	4,000	2,000	1,000
79	Acid Scarlet R (BDC)	4,000	4,000	>0
79	Ponceau 2 RE (Gy)	6,500	0	0
79	Scarlet Ponceau R (Lev)	4,500	2,500	1,000
79	Ponceau R (MLB)	5,000	4,000	800
79	Naphtharine Scarlet (Southdown Chem. Co.)	4,000	4,000	1,000
79	Ponceau N2R (St. D)	1,250	1,000	500
246	Naphthol Blue Black (C)	2,500	5,000	1,000
246	Naphthalene Black 12B (BDC)	2,500	330	0
246	Amine Black 10B (A)	2,500	750	1,100
246	Azo Dark Blue S (S)	1,700	330	0
246	Pontacyl Blue Black SX (DuP)	5,000	1,500	1,000

*"Habit-modifying power of water soluble dyes on different crystal surfaces. Column values show the weight of crystal, dissolved to form a slightly supersaturated aqueous solution, used with one grain of dye to produce the habit-changes herein called STANDARD for the particular crystal surface."

A, Actinegesellsch., Berlin; BDC, British Dyestuffs Corp.; C, Leopold Casella; DuP, DuPont de Nemours; Gy, Geigy Colour Co.; Lev, Levinstein & Co. (Blackley); MLB, Meister, Lucius and Brüning (Höchst); S, Sandoz; St. D, Société Anonyme, etc., de St. Denis (Seine).

Buckley generated a list of general observations in this way. We paraphrase his conclusions below:[7]

(a) When a simple naphthalene sulfonate has OH or NH_2 in position 1 a change of SO_3Na from 5 to 4 occasions a fall in effectiveness.
(b) With OH or NH_2 in position 2, a change of SO_3Na from 6 to 7 or from 6 to 8 also causes a fall.
(c) Removal of a SO_3Na group from another position to 8 usually causes a fall.
(d) But when SO_3Na is added to position 8, there being other sulfonates present the opposite change takes place.
(e) NH_2 replaces OH most often with an increase.
(f) When a SO_3Na group is added to position 3 a rise in effectiveness occurs.
(g) When the single ring of a diazotised sulfanilic acid residue is changed to a double one there is an increase.

Buckley expressed the potencies of fragments occurring regularly in molecules of proven habit-changing power in terms of their average overall potency for the modification of $K_2Cr_2O_7$, $KAl(SO_4)_2 \cdot 12H_2O$, and borax. He also included results for K_2SO_4, $KCrO_4$, NH_4ClO_4, and $KClO_3$ as an average over the four salts. This can have little structural meaning. We ignored data averaged over different salt structures. We selected those fragments which occurred in more than ten dyes and used these most well-represented structural motifs to test Buckley's rules with respect to the habit modification data of $K_2Cr_2O_7$, $KAl(SO_4)_2 \cdot 12H_2O$, and borax. Eleven structures were represented more than ten times. A comparison of these structures enabled us to test rules (e), (f), and (g). *Rules (e) and (g) were contradicted by each salt.* Rule (f) was contradicted by borax alone. We caution future investigators to look at the raw data[7] and not rely on Buckley's summary judgements.

d. Data was reported as averages of different trials. Not only did Buckley report habit modifying power for dyes averaged over different salt surfaces, the widely available data for the nine constitutional isomers is often the average of trials with substances supplied by different manufacturers. Original data from reference 7 is included in Table IV for four of the nine isomers, along with the value Buckley supplied in *Crystal Growth.*[11] This averaging is implicit in the hybrid names that appear in Buckley's book such as "Bordeaux B etc." or "Mars Red Caromoisine Conc.", the latter of which is a marriage of a Sandoz product with one from Badische Aniline.

TABLE IV. Contradictory data for constitutionally isomeric azo dyes.

Colour Index No.	Dye name and maker	$KClO_3$ (011)	K_2SO_4 (010)	K_2CrO_4 (010)
85	Palatine Red A (B)	670	2,000	1,750
85	Benzyl Bordeaux B (CAC)	670	3,000	>0
85	"Palatine Red A"*	670	2,500	1,200
88	Bordeaux B (S)	6,000	4,000	670
88	Bordeaux B Extra (A)	8,000	4,000	425
88	Archelline (?) BB (Lev)	10,000	7,000	1,000
88	"Bordeaux B etc."*	8,000	5,000	550
179	Carmoisine Conc. (S)	1,700	2,500	4,000
179	Mars Red G (B)	1,000	1,000	6,000
179	"Mars Red G Caromoisine Conc."*	1,330	1,750	5,000
194	Coomasie Scarlet 9012K (BDC)	3,000	1,000	670
194	Scarlet 2R (B)	6,000	2,000	1,000
194	"Coomasie Scarlet 9012K"*	4,500	900	1,500

A, Actinegesellsch., Berlin; B, Badische Aniline; BDC, British Dyestuffs Corp.; CAC, Clayton Aniline Co.; Lev, Levinstein & Co. (Blackley); S, Sandoz; (*) As appears in *Crystal Growth.*[11]

e. Buckley did not account for the simultaneous modification of the reference face. If the reference face and the face of interest were comparably modified by a dye, that dye would have appeared ineffectual. The reference face may not have been passive as it grew in the same crystal and in the same environment as the face of interest. Since Buckley only determined modification in relation to a reference face, his data may be misleading in some cases.

f. "Habit-modifying power" expressed as a number may be an oversimplification of complex phenomena. Three of Buckley's nine constitutional isomers currently are available from Aldrich. The modern products, Bordeaux R ($CI_{3rd\ ed}$ = 16180), Crystal Scarlet ($CI_{3rd\ ed}$ = 21016-1), and Chromotrope FB ($CI_{3rd\ ed}$ = 14720) correspond to Buckley's compounds "Bordeaux B, etc." ($CI_{1st\ ed}$ = 88), "Crystal Ponceau 6B, etc." ($CI_{1st\ ed}$ = 89), and "Mars Red G Carmoisine" ($CI_{1st\ ed}$= 179).

We repeated the habit modification of $KClO_3$ and K_2SO_4 with these three dyes. In each case we observed the rough rank ordering reported by Buckley. However, we observed considerable differences in the quantities required to produce the standard effect at room temperature. Bordeaux R at the standard concentration produced crystals of $KClO_3$ as fine as hair. Since we know that Buckley's data are reported as averages we cannot know if our materials are closer to one old manufacturer than another. Moreover, small changes in temperature and evaporation rates can exert a sizeable effect.

There were a number of other effects that Buckley never indicated. For example, Bordeaux R, at the standard concentration for K_2SO_4, readily induced trilling. Some of the symmetry related {110} growth sectors of these twins produced pleochroic inclusions while others did not. This complex phenomenology is not faithfully described by a single number.

IS THEIR ANY EVIDENCE FOR THE SULFONATE-ANION SUBSTITUTION MODEL?

Both Buckley and France[13] argued that habit modification of simple salts by dyestuffs with anionic functionalities proceeds through the substitution of groups like sulfonates for anion positions in the lattice. This proposition is still reasonable. We therefore sought to substantiate it in at least one case.

Acid fuchsin (CI_{3rd} Ed=42685) is a triarylmethane dye which inhibits the growth of K_2SO_4 in the *b* direction. It is a trisulfonated derivative of pararosaniline with one methyl group in a *meta* position. While sold in 70% purity, it is well-known that the common impurities have 0, 2, or 3 methyl groups and are therefore structurally quite similar to the compound on the label.[21]

The desymmetrization of the triarylmethyl skeleton as in acid fuchsin produces four diastereomers. One diastereomer has the three sulfonate groups pointing to the same side of the mean molecular plane. The three others have virtually the same geometries; they differ only in which ring carries the methyl group. The former are labeled S for symmetric and the latter are labeled A for asymmetric.

The geometries of the two representative diastereomers, S and A, with three associated K^+ ions, were calculated using the AM1 Hamiltonian. They were nearly equienergetic. The twists of the aryl rings out of the plane-of-coordination of the central carbon atom is 44° for the three rings in S and 25°, 25°, and 50° for the rings in A.

In either case the sulfonate groups define triangles. In S, the triangle is nearly equilateral and parallel to the mean molecular plane, while for A the triangle is right. A least square fit of the molecular sulfonate triangles and crystal sulfate triangles was performed. The S diastereomer fits well by substituting for three sulfates related to one-another as x, y, z; $x, y, z+1$ and $x+1, -y+1/2$, and $z+1/2$ ($\Delta d_{S\text{-}S}$: 0.14 Å, 0.15 Å, and 0.22 Å). The A diastereomer makes a match with the sulfonate triangle defined by positions x, y, z; $x+1, y, z$; and $x, y, z+1$ ($\Delta d_{S\text{-}S}$: 0.23 Å, 0.37 Å, and 0.59 Å). In each case, as shown in Figure 4, the conformers would interrupt growth on the (010) surface.

CONCLUSION

We are disappointed at our inability to rescue Buckley's habit modification data. Our frustration is not of the same character as that which Buckley expressed, since we believe that his data is too soft to accommodate a structural interpretation. (Moreover, we have only 2 years into the job, not 18.) This is not to say that a shrewder set of investigators would not fashion a suitable hypothesis. We acknowledge that a more sophisticated analysis that incorporates the role of hydroxyl groups and nitrogen lone-pairs of electrons may produce a satisfactory explanation. More realistic view of surface topography may help.[22] We are confident nevertheless that it will not be possible to develop a comprehensive understanding without the exact compositions of the compounds that Buckley used. Perhaps we were foolish not to conform to Buckley's premonition: "For, 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."[23]

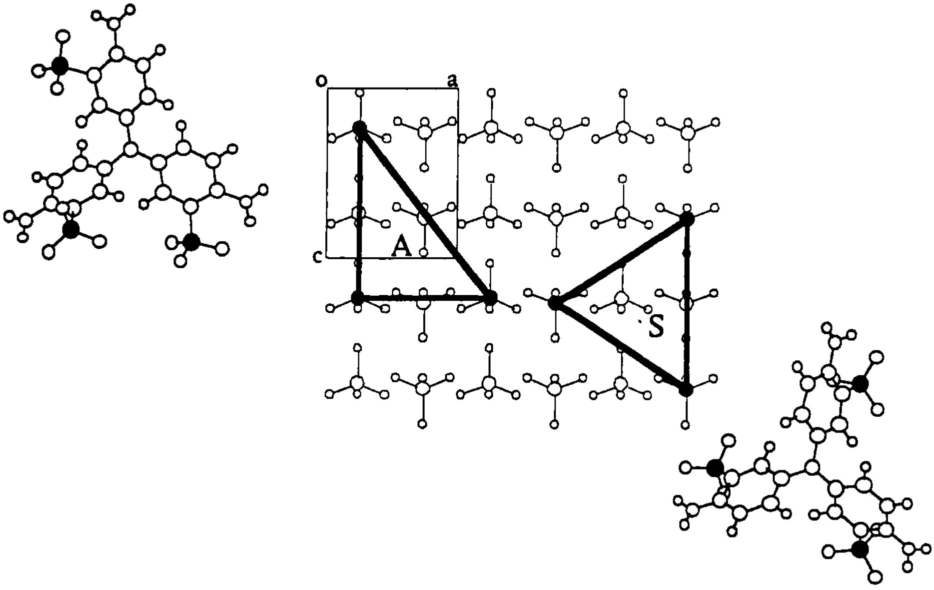

FIGURE 4 The S and A diastereomers of the acid fuchsin skeleton, and likely positions for substitution on the K_2SO_4 lattice. View is along the *b* direction. Neither K^+ ions in the lattice nor coordinating K^+ ions of the conformers are shown. Sulfonate sulfur atoms are black.

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