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Poppy Acid: Synthesis and Crystal Chemistry

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Abstract: It had long ago been reported that poppy acid crystals encapsulate and orient a great variety of molecules during solution growth and in so doing seem to egregiously violate the principle of isomorphism. To comprehend this surprising host–guest chemistry, and exploit it for measuring anisotropic molecular properties, we attempted to carry out the oft-used literature synthesis of poppy acid, (3-hydroxy-2,6-dicarboxy- γ -pyrone), but discovered that the standard procedures did not produce the title compound. We instead obtained a constitutional isomer as the potassium salt of 2-oxaloate-3-hydroxy-5-carboxyfuran. Therefore, we designed and carried out the first total synthesis of poppy acid. It crystallizes as either of two polymorphs, an orthorhombic form (*Pbca*) and a monoclinic form (*C2/c*), both characterized by weakly bonded layers consistent with perfect cleavages. The great majority of the dyes tested, 15 of 19, produced poppy acid crystals colored in particular growth sectors displaying strong linear dichroism. The observation of pronounced absorption anisotropy is consistent with a general mixed crystal growth mechanism in which the dyes substitute for poppy acid molecules within the layers and are further oriented in the direction of hydrogen bond rows of molecules within layers.

Introduction

Poppy acid (**1**, meconic acid, or 3-hydroxy-2,6-dicarboxy- γ -pyrone), 5 wt % of the latex of the opium poppy, *Papaver somniferum*, was isolated by Sertürner nearly 200 years ago,¹ but has been used in only two ways. It enabled identification of opium smokers in the early part of this century;² their urine, rich in **1**, turned bright red upon the addition of FeCl₃. And crystals of the trihydrate of **1** have served as hosts to an extraordinary number and variety of dyes. The resulting mixed crystals showed striking patterns of color and pronounced linear dichroism (LD). It is this second application, in the general context of our studies of dyeing crystals,³ that prompted the following inquiry into **1**.

Molecules must be oriented for the interpretation of their anisotropic physical properties. Furthermore, 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,⁴ 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, as **1** is purported to be, are highly desirable.

Before world-wide opium distribution was tightly restricted,⁵ **1** was a common laboratory chemical. No less than four scientists, Lehmann,⁶ Gaubert,⁷ Tammann,⁸ and Neuhaus,⁹ studied the process of dyeing poppy acid crystals during the late nineteenth and early twentieth centuries, however before structural organic chemistry, crystallography, and spectroscopy were sufficiently well-developed to account for the LD. The present paper describes our efforts to reproduce and comprehend the observations of the earlier researchers.

Syntheses

Great quantities of **1** are disposed of in the industrial processing of raw opium latex, but there are legal barriers to its acquisition. We surmised that the quickest route to a sample of **1** for crystalloptical studies would be its synthesis in our laboratories. The first reported synthesis of **1** was from Thoms and Pietrulla, who hydrolyzed diethylbromochelidonate (**2**) in KOH (Scheme 1).¹⁰ Garkusha and Khutornenko¹¹ later reported a slight modification by substituting the solvent acetone with dioxane. We employed both procedures and were surprised to find that neither method yielded the orthorhombic crystals of **1** previously described. Instead a furan (**3**, 2-oxaloate-3-hydroxy-5-carboxyfuran) was obtained as a potassium salt. Recrystalli-

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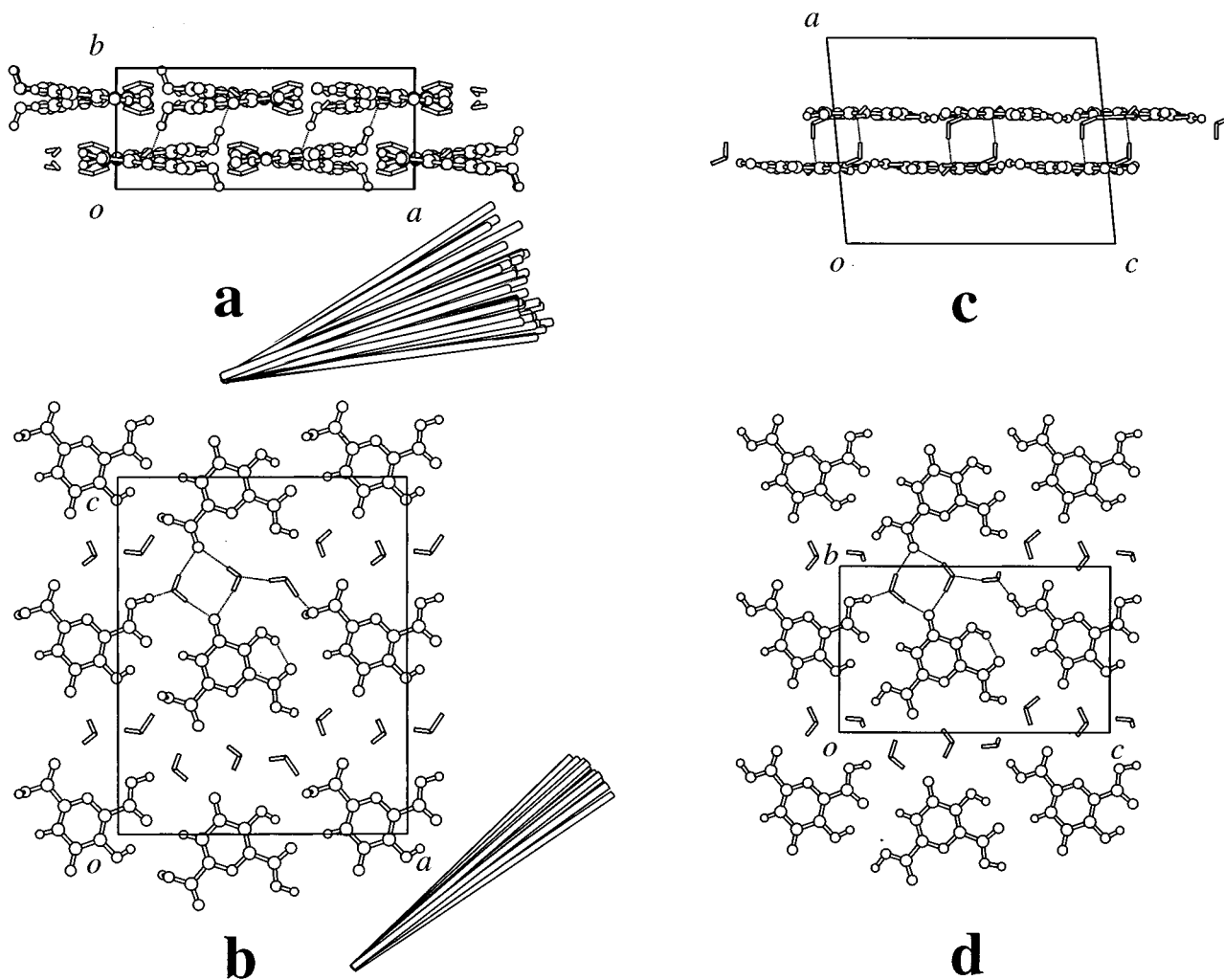
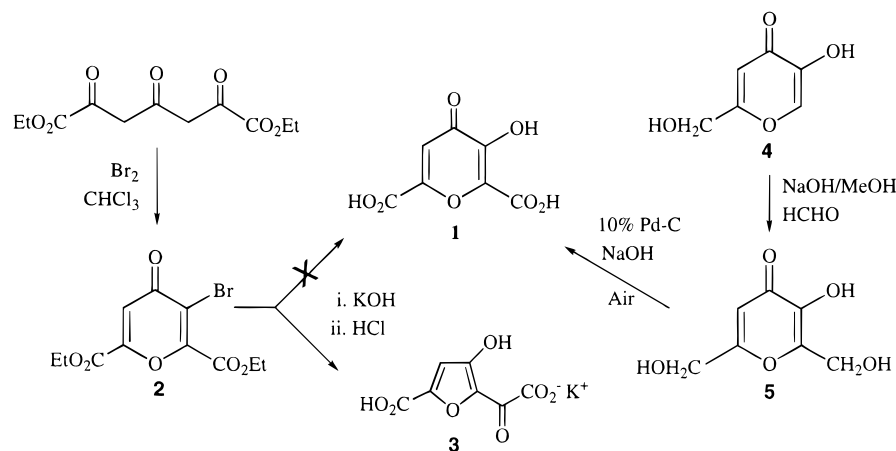


Figure 1. Packing diagrams of **1a** (a and b) and **1b** (c and d). Water molecules are represented as cylinders and representative H bonds are indicated by dashed lines.

Scheme 1



zation from H₂O gave a dihydrate (**3a**) while recrystallization from 50% aqueous ethanol gave a monohydrate (**3b**).¹² X-ray crystallography confirmed that **2** was indeed a γ -pyrone, therefore the furan was produced upon addition of KOH. It is well-known that γ -pyrones can open in base.¹³ The bromide

(12) The *Merck Index* refers to a monohydrate but provides no citation, and we have not found a reference to such a form in the literature (Merck and Co., Rahway, NJ, 1989; p 5670).

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intermediate **2** supplies a fine leaving group for the rearrangement to the five-member ring.

We next devised an original synthesis of **1** from kojic acid (**4**, 2-hydroxymethyl-5-hydroxy- γ -pyrone). Reaction of **4** with formaldehyde in base produced **5** (3-hydroxy-2,6-dihydroxymethyl- γ -pyrone), whose constitution was confirmed by X-ray crystallography. **5** was oxidized to **1**. Isomers **1** and **3**, not easily distinguished in a casual spectroscopic analysis, decomposed at discrete temperatures, 285 and 270 °C, respectively, but as

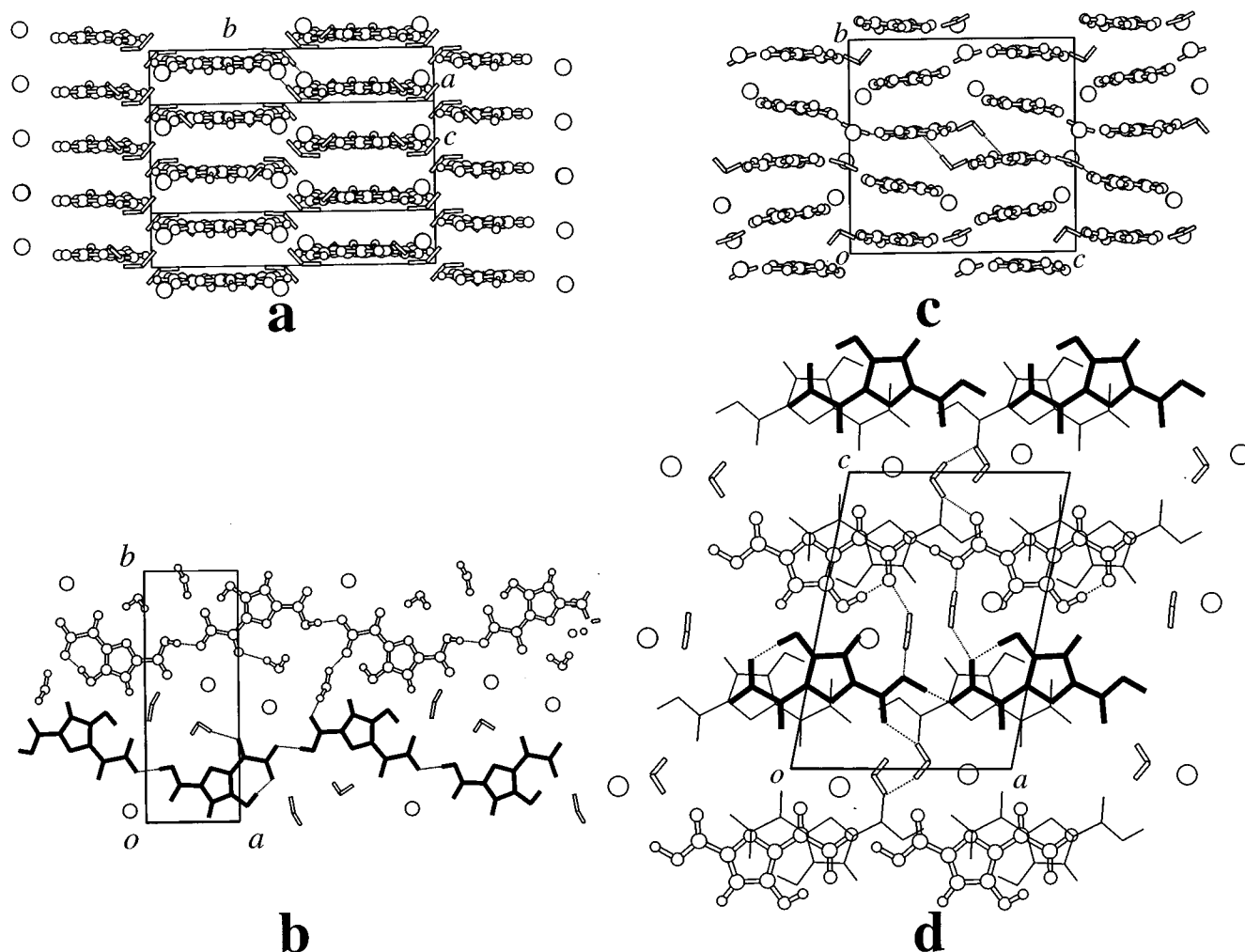


Figure 2. Packing diagrams of **3a** (a and b) and **3b** (c and d). Water molecules are represented as cylinders and representative H bonds are indicated by dashed lines. Alternate rows are indicated with cylinders and bold lines. A symmetry-independent layer below is distinguished by the fine line.

decomposition temperatures are typically less well-defined than melting temperatures it is possible to imagine that the latter could have been mistaken for the former. The Merck index¹² reports 270 °C as the decomposition temperature for **1**, citing Garkusha and Khutornenko.¹¹ Undoubtedly, these researchers and others had prepared the furan, **3**.^{10,14}

Crystal and Molecular Structures

We prepared orthorhombic crystals of a trihydrate (**1a**) by evaporation of 50% aqueous ethanol solutions. A monoclinic polymorph **1b**, also a trihydrate, was obtained only from solutions containing the dye mordant orange 10 (**MO10**).¹⁵ The crystal structures of **3a** ($P2_1/n$) and **3b** ($P2_1/c$), a dihydrate and monohydrate of **3**, respectively, were determined as well. A common feature found among all four structures is the arrangement of molecules in hydrogen-bound rows.

In **1a**, rows of molecules propagate along the *a* axis. Interleaving water molecules buffer one row from another and together form sheets in the *ac* plane (Figure 1a,b). The molecules in **1a** are roughly planar, however a carboxyl hydrogen atom is

directed out of the molecular plane and forms the only H bond between molecules of **1** and between layers.

The monoclinic polymorph **1b** is similar to **1a**. Here, both carboxyl hydrogens are approximately in the mean molecular plane and cannot serve to join layers; a water molecule assumes this role (Figure 1c). Contacts within lamellae are similar to those in **1a** (Figure 1d). In **3a** and **3b**, molecules form corrugated chains via H bonds between adjacent carboxyl groups (Figure 2).

Linear Dichroism

We grew colored crystals of **1a** by slow evaporation from 50% aqueous ethanol solutions containing 10^{-4} mol of **1** and 10^{-6} mols of each of the 15 dyes representing many of the main classes. The dyes alizarin (**AZ**) and methyl red (**MR**) were studied by Neuhaus and served as a starting point.⁹ We then extended our selection to the larger azo dyes bismarck brown R (**BR**), bismarck brown Y (**BY**), and the mordant oranges 6 and 10 (**MO6**, **MO10**). We also tested acridines orange (**AO**) and yellow (**AY**), a phenylphenazinium, safranin O (**SO**), a phenoxazone, nile red (**NR**), a thiazine, methylene blue (**MB**), a tetrapyrrolineporphyrin (**TP**), and the triarylmethyl dyes, basic fuchsin (**BF**), crystal violet (**CV**), and ethyl violet (**EV**). Their Color Index¹⁶ numbers can be found in Table 1 and their

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Table 1. Spectroscopic Data

dye ¹⁷	CI no. ¹⁶	λ_{\max} (nm)		crystl 1a ^b	I_a/I_b (deg)	I_a/I_c (deg)
		50% EtOH	satd soln 1a ^a			
AZ	58000	443	442	454	11.0 (16.8)	1.5 (39.3)
MY	11020	448	522	537	31.7 (10.1)	2.2 (33.8)
TP		442	446	455	6.4 (21.5)	1.3 (41.3)
BR	21010	453	464	476	3.9 (26.9)	1.3 (41.3)
BY	21000	453	455	465	13.5 (15.2)	1.4 (40.2)
MO6	26520	424	425	452	9.0(18.4) ^c	1.3 (41.3)
MO10	26560	427	435	448	4.7(24.8) ^c	1.3 (41.3)
AO	46005:1	497	499	512	11.0 (16.8)	1.4 (40.2)
AY	46025	460	474	479	5.8 (22.5)	1.3 (41.3)
NR		577	597	609	28.8 (10.6)	1.6 (38.2)
BF	42500	550	550	589	4.9 (24.3)	1.6 (38.2)
CV	42555	595	601	606	2.1 (34.4)	1.3 (41.3)
EV	42600	602	602	608	2.3 (33.6)	1.5 (39.3)
MB	52015	671	670	680	14.6 (14.7)	1.4 (40.2)
SO	50240	535	536	551, 467	4.8 (24.3)	1.8 (36.7)

^a Also in 50% ethanol. ^b Light incident on {001}. ^c Dichroic ratios are c/b . ^d Angle to α in deg.

structures can be found in the Sigma-Aldrich handbook.¹⁷ Of the 19 dyes that we tested only four did not color growing crystals of **1a**, carminic acid, chicago sky blue, amaranth, and malachite green.

We often saw two different habits, even in the same crystallization dishes, from 50% aqueous ethanol solutions. Chromophores that recognized only the {101} growth sectors gave rise to crystals with an hourglass pattern of color and prominent {010} and {001} faces. These samples were typically elongated along b . Sometimes the dyes were incorporated through the {101} and {110} surfaces. The habit was quite sensitive to solvent. **1a** grown from 50% aqueous ethanol solutions containing **NR** showed the typical form, however when grown from pure ethanol its faces were markedly curved (Figure 3).

Crystals were dissolved and the amount of dye quantified by measuring the absorbance in the linear regime. A host:guest ratio in the dyed sectors ranged from 30:1 for **NR** to 4000:1 for **EV**. The smaller dye content is typical of what we have observed previously for dyed crystals of phthalic acid.^{3a} Spectroscopic data are shown in Table 1. In most cases, the absorption spectra resembled those of dilute solutions, however **CV** and **EV** showed spectra characteristic of monomers as well as dimers.¹⁸

Remarkably, each of the dyes were oriented by crystals of **1a** as evident by the strong, though significantly not complete, LD. For with polarized light incident upon (001), the maximum absorbance was achieved with the polarization parallel to a . (Here, we adopt the notation (001) _{a} to indicate the face to which light is incident and the direction of the electric field vector at the maximum absorbance.) The perfect ac cleavage plane enabled the determination of the polarization along c . The LD was small for (010) _{a} .

Among the {100} plates from solutions containing **MO10** were monoclinic prisms (**1b**) with the dye coloring {001}. The crystals were elongated along c and displayed {110} faces. Crystals of **1b** were obtained only in solutions containing **MO10**.¹⁵ The absorbance was strongest in the bc plane.

Surprisingly, the false poppy acid **3** also oriented dyes in the crystalline state. Solutions of **3** containing **MY** or **AZ** yielded

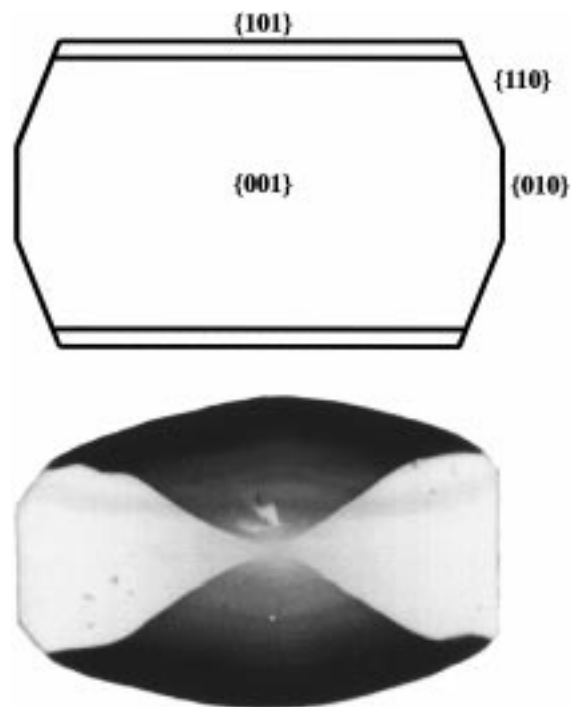


Figure 3. Idealized form for **1a** and photomicrograph of the curved habit from EtOH with **NR** coloring the {101} growth sectors. The horizontal dimension is 2 mm.

dyed **3a** and **3b**, respectively. Elliptical crystals **3a** grew as {010} plates elongated along c with {010} _{a} . The yellow color ($\lambda_{\max} = 465$ nm) was due to the neutral form of **MY** while the red ($\lambda_{\max} = 505$ nm) was due to protonation of an azo nitrogen.¹⁹ Crystals of **3a** were weakly dichroic for (001) _{a} . Crystals of **3b** containing **AZ** grew as {001} plates elongated along b . The maximum absorbance was again in the direction of the H-bound rows.

What we thought from the historical record was a unique property of **1a**, the ability to orient a wide variety of molecular guests, was now manifested by its polymorph **1b** as well as **3a** and **3b**. To test the generality of the tendency of benzoic acid crystals to orient dyes, we searched the Cambridge Structural Database for crystals with similar structure. Hemimellitic acid (1,2,3-benzenetricarboxylic acid)²⁰ crystallizes in the space group $P\bar{1}$ with H-bound columns stacking along b . Dichroic {010} _{c} plates were precipitated from ethanol containing **MY**.

The dyed crystals of **1a** are of X-ray quality despite containing up to 1% of the impurity by weight. A colored sector of such a crystal containing **NR** was analyzed with X-rays. We obtained a well-refined structure of **1a**, in which the dye was nowhere in evidence. The R value of the dyed crystal was 0.062 compared with 0.047 for the pure crystal. The largest peak in the final difference Fourier map was actually smaller for the dyed crystal.

We quantified the LD in each mixed crystal of **1a** (Table 1) and calculated the electronic transition dipole moments (ETDM) from the $\cos^2 \theta$ dependence of the absorbance on angular deviations from the crystallographic axes. The projection of the ETDM in the (001) and (010) faces of **1a** was angled with respect to a between 34.4° (**CV**) and 10.1° (**MY**) (Figure 1a), and between 33.8° (**MY**) and 41.3° (**BR**) (Figure 1b), respectively.

Conformations for all dyes were optimized by using the AM1 Hamiltonian and the molecular ETDMs were calculated by using

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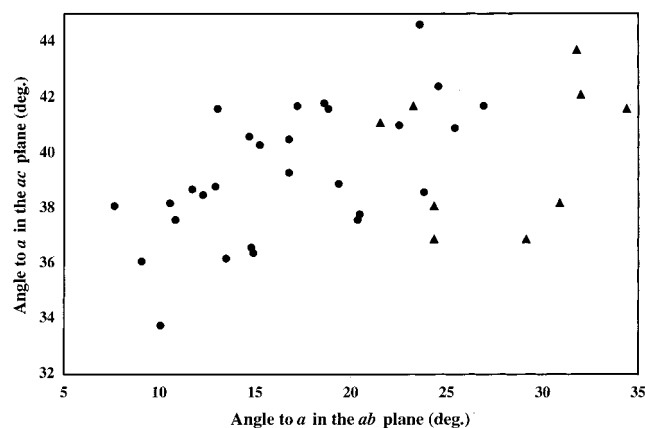


Figure 4. Plot of I_a/I_b versus I_a/I_c for dyed crystals of **1a** expressed as angular deviations of the transition moments. Circles represent planar dyes (AZ, MY, BY, BR, MO6, MO10, AY, AO, MB, NR) whereas triangles represent propeller-shaped dyes (BF, CV, EV, TP).

the INDO/S-CI method.²¹ The vast majority of the visible transitions were $\pi-\pi^*$ in nature and polarized in the mean molecular planes of the flat or disk shaped dye molecules and along the long molecular axes. The collected experimental transition moments were plotted in the crystallographic space of **1a** (Figure 1, a and b) and are suggestive of a general orientation for the dye molecules, which must span two or in some cases three layers in the crystals of **1a** depending on their sizes.

This most obvious interpretation of the experimental results was unsettling for two reasons: (1) The characteristic feature of the crystals, their lamellar structure, seemed to play no role in the orientation of the dye molecules. The guests would be protruding from the layers. Nevertheless, the maximum absorption in every case was observed when the incident light was polarized in the layers of **1a**. (2) If the layers are not responsible for orienting dye molecules, why then would the crystals of **1a** be so effective at orienting in similar directions so many molecules with very different sizes and shapes? In other words, what could be the general recognition mechanism?

An alternative way to look at the LD data I_a/I_b and I_a/I_c is to consider the projections of the transition moments as deviations from 0° in the first case and deviations from 45° in the second case. A transition moment calculated to lie between orthorhombic crystallographic axes is not distinguished from a transition that is disordered in the *ac* plane. If we assume that the lamellae served to orient the dyes in the *ac* plane and that growth anisotropy preferentially orientated the dyes in the lamellae along *a* rather than *c*, then the data could be consistent with such a family of structures so long as in every case a component of the absorption came from molecules in other minor orientations, or from molecules in random orientations, as might occur with dyes trapped in solution inclusions. Disorder would drive the polarization directions away from the *a* axis.

A simple test of this supposition is to plot deviations from the *a* axis of the transition moment projected in (001) versus the deviation from the *a* axis of the transition moment projected in (010). The more disorder, the greater would be the deviation from 0° for light incident on *ab*, and the smaller would be the deviation from 45° for light incident on *ac*. Such a correlation is shown in Figure 4, with a standard deviation of the residuals of 2.1 with respect to the ordinate. In this figure we have separated the planar dyes from the propeller-shaped dyes using circles and triangles, respectively. The clustering of points for

propellers on the high side is consistent with an interpretation of the LD in terms of deviations of the dyes from the layers. Furthermore, LD always decreased markedly with increasing temperature indicating the prevalence of thermally excited internal reorientations or librations of weakly bound dyes.

Conclusion

Are there crystals that, like polymers, can serve as general hosts for guest molecules, yet provide the narrow orientational distributions expected of crystals? The intriguing descriptions of poppy acid prompted us to evaluate this possibility. We carried out the first total synthesis of **1** while properly characterizing the product (**3**) of earlier purported syntheses. We determined the crystal structures for two polymorphs, **1a** and **1b**. The great majority of the dyes tested, 15 of 19, produced crystals of **1a** colored in particular growth sectors. **1b** also oriented dyes as did the hydrates of **3**. The observations of pronounced LD were consistent with mixed crystal growth mechanisms in which the flat dyes substituted for molecules of **1** within the layers and were directed by hydrogen-bound rows of molecules. Many of the details of the recognition process still remain to be worked out in ongoing studies. Nevertheless, the ability of **1** or molecules such as **1** to orient such a wide variety of chromophores in their crystals indicates that the application of single crystal matrix isolation may not be nearly as restricted by constraints of isomorphism as is commonly assumed.

Experimental Section

Synthesis. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker AC-200 MHz and AC-300 MHz spectrometers, respectively. NMR spectra of all compounds were obtained in DMSO- d_6 except **2** (CDCl_3). The EI and high-resolution mass spectra were recorded with a JEOL HX-110 double focusing magnetic sector mass spectrometer. IR and UV-vis spectra were recorded with Perkin-Elmer 1640 FT-IR and Hitachi U-2000 dual beam spectrophotometers, respectively.

3-Bromo-2,6-diethylcarboxylate- γ -pyrone (2**).** To a flask equipped with a reflux condenser, stirrer, and dropping funnel was added diethylacetonedioxalate (51.6 g) in dry CHCl_3 (170 mL). Sodium sulfate (20 g) and a solution of bromine (35.2 g) in CHCl_3 (18 mL) were added dropwise at $\sim 25^\circ\text{C}$ over a period of 12 h. The reaction mixture was then allowed to stand overnight. The filtrate was washed in a separating funnel with H_2O , 2% NH_3 , and again with H_2O . The CHCl_3 solution was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure until a pale yellow solid was obtained. The product was recrystallized from absolute EtOH to give **2** (32.0 g, 50% yield), mp 68°C ; IR (Nujol) 1738, 1667, 1263, 1228, 1152, 1103, 1017, 990, 880, 857, 775 cm^{-1} ; ^1H NMR (200 MHz, CDCl_3) δ 7.14 (s, 1H), 4.40 (q, $J = 7.3$ Hz, 2H), 4.36 (q, $J = 7.3$ Hz, 2H), 1.41 (t, $J = 7.3$ Hz, 3H), 1.34 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ 173.5, 159.0, 158.8, 152.2, 151.8, 118.4, 116.6, 63.7, 63.5, 14.0, 13.9; EI (direct probe, 70 eV) 318, 290, 273, 262, 246, 234, 218, 200, 190, 177, 149, 147; high-resolution mass spectrum m/z 317.97500 (calcd for $\text{C}_{11}\text{H}_{11}\text{O}_6^{79}\text{Br}$ 317.97500).

2-Oxalo-3-hydroxy-5-carboxyfuran, potassium salt (3**).** Diethylbromochelidonate (17.1 g, 53.6 mmol) dissolved in dioxane (135 mL) was heated to 70°C in a 1 L flask to which was added a solution of KOH (1 M, 267 mL). After the mixture was heated for 1 h, the dark red solution obtained was cooled to room temperature, acidified with 5% HCl, and filtered over activated carbon. The dioxane was evaporated under reduced pressure. The resulting precipitate was filtered, washed with ether, and dissolved in hot water. The product was recrystallized from dioxane to give **3** (4.8 g, 45% yield), mp 270°C dec; IR (Nujol) 3490, 1623, 1584, 1299, 1214, 1100, 1003, 952, 918, 809, 770 cm^{-1} ; ^1H NMR (200 MHz, DMSO- d_6) δ 6.97 (s, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6) δ 174.8, 163.1, 159.3, 157.5, 148.1, 139.7, 110.9; EI (70 eV) 200, 155, 128, 111, 69, 44; high-resolution mass spectrum m/z 199.99649 (calcd for $\text{C}_7\text{H}_3\text{O}_7$ 199.99684).

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3-Hydroxy-2,6-dihydroxymethyl- γ -pyrone (5). To a solution of kojic acid **4** (4 g, 28 mmol) in H₂O (28 mL) and MeOH (40 mL) was added aqueous NaOH (25%, 5 mL). Formaldehyde (2.3 mL, 30.8 mmol) in ice water (4 mL) was then added to the above mixture, stirred for 48 h, acidified with dilute H₂SO₄, and extracted with EtOAc (5 \times 40 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give a crude solid. Recrystallization from EtOH gave colorless crystals of **5** (2.4 g, 71% yield), mp 177 °C; IR (Nujol) 3268, 1649, 1611, 1555, 1277, 1244, 1162, 1095, 1002, 976, 852, 775, 721 cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆) δ 8.98 (s, 1H), 6.31 (s, 1H), 5.68 (t, 1H), 5.38 (t, 1H), 4.39 (d, *J* = 4.4 Hz, 2H), 4.30 (d, *J* = 5.1 Hz, 2H); ¹³C{¹H} NMR (DMSO-*d*₆) δ 175.1, 168.7, 150.5, 142.8, 110.0, 60.7, 56.2; EI (70 eV) 172, 154, 143, 125, 113, 101, 71; high-resolution mass spectrum *m/z* 172.03710 (calcd for C₇H₈O₅ 172.03717).

3-Hydroxy-2,6-dicarboxy- γ -pyrone (1). To a mixture of **5** (2 g, 11.6 mmol) in water (20 mL) was added aqueous NaOH (50%, 1.2 mL) and Pd-C (10%, 0.668 g). Air was passed through the solution at room temperature for 6 days. After filtration of the catalyst, the pH of the solution was adjusted to 0.5 by adding concentrated HCl (2.4 mL). The filtrate was reduced by three-quarters under vacuum and stirred at room temperature overnight. A brownish solid was collected by filtration and recrystallized from 50% aqueous ethanol yielding **1** (0.7 g, 30% yield), mp 290 °C; IR (Nujol) 3382, 1760, 1679, 1626, 1306, 1268, 1235, 908, 787 cm⁻¹; ¹H NMR (200 MHz, DMSO-*d*₆) δ 6.76 (s, 1H); ¹³C{¹H} NMR (DMSO-*d*₆) δ 174.9, 163.4, 160.7, 151.8, 150.7, 135.8, 115.2; EI (direct probe, 70 eV) 200, 156, 115, 69, 44; high-resolution mass spectrum *m/z* 199.99482 (calcd for C₇H₄O₇ 199.99570).

X-ray Crystallography. Data were collected with a Nonius KappaCCD diffractometer for **1a**, **1b**, **2**, **3a**, and **5** and an Enraf-Nonius CAD4 for **3b**, using graphite monochromated Mo K α radiation (λ = 0.7107 Å). Samples were mounted with epoxy on glass capillaries. Integration of intensities and cell refinement for KappaCCD data was carried out with DENZO and HKL SCALEPACK,²² respectively. Structures were solved with SIR92²³ and refined with SHELXL-97.²⁴ All non-hydrogen atoms were refined anisotropically by full-matrix least squares. Hydrogen atoms were refined with a riding model and *U*_{iso} values were fixed such that they were 1.1 *U*_{eq} of their parent atom

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(1.5 *U*_{eq} for –OH). All hydrogen atoms were located by difference Fourier syntheses except H11A, H11B, and H11C in **2** which were placed in tetrahedral positions (*d*_{C–H} = 1.01 Å). An empirical absorption correction was applied for **2** with SORTAV²⁵ (*t*_{min} = 0.397, *t*_{max} = 0.435).

Crystal Growth. All dyes were obtained from Aldrich and used without further purification. In a typical crystallization 0.20 g of **1** was dissolved in 25 mL of 50% ethanol in a 80 \times 40 mm crystallization dish and stirred at 40 °C. Two milliliters of a 10⁻³–10⁻⁴ M dye solution was added with continued stirring. The solvent was evaporated slowly overnight at room temperature and the resulting crystals were washed with hexanes.

Polarization Spectroscopy. Absorption spectra were measured with a SpectraCode Multipoint-Absorbance-Imaging (MAI-20) Microscope that consists of an Olympus BX-50 polarizing microscope connected to a Spectra Pro-300i triple grating monochromator (Acton Research Corporation). A fiber optic cable containing a linear stack of 20 fibers connects the microscope to the monochromator and Princeton Instruments CCD detector. The instrument is controlled with a Macintosh IIfx with use of the program KestrelSpec. Corrections of the absorbance for birefringence^{4,26} were not applied as they were well within the errors from positioning the crystal.

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Supporting Information Available: Crystallographic parameters, tables of atomic coordinates, bond lengths, valence angles, anisotropic displacement parameters, and observed and calculated structure factors for **1a**, **1b**, **2**, **3a**, **3b**, and **5**, as well as crystal habits, representative spectra for **AZ**, **NR**, **CV**, and **SO**, and plot of *I*_a/*I*_b vs temperature for **AZ**, **NR**, and **MO10** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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