Recognition of Dyes by K_2SO_4 Crystals: Choosing Organic Guests for Simple Salts

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Organisms use matrices of organic macromolecules to catalyze inorganic crystal growth thereby constructing teeth, shells, bones, and beaks.[1] Chemists also have been uniting inorganic and organic materials. Zeolites, clays, and sol–gel glasses serve as vessels for a variety of organic transformations.[2] Organic hourglass inclusions (HIs) are simple ionic salts containing oriented dyes. First described in 1854,[3] HIs were most intensively studied in the 1930s.[4] They were abandoned as curiosities before their structures were determined.[5] Here, we propose a model for the inclusion of triarylmethane dyes in K_2SO_4 that is consistent with polarized absorption spectroscopy. We used this structure as the basis for the rational design of an HI with prescribed optical properties.

The most appealing historical HI, K_2SO_4 stained by acid fuchsin (**1a**, Scheme 1), was discovered by Buckley.[4a] Water solutions (2.0×10^{-4} M **1a**, **1b**, or **1c** and 5.0×10^{-2} M K_2SO_4) were evaporated at room temperature; they deposited well-formed crystals[6] with dichroic fuchsia coloring in the {110}[7] growth sectors (Figure 1). We determined that there is 1 dye molecule for 10^3 unit cells in a substituted sector by quantifying the absorbance of dissolved crystals.

Structures like **1** have two distinct diastereomeric propeller conformations. In the symmetrical conformer (**S**) three sulfonates point to the same side of the mean molecular plane while the asymmetrical conformer (**A**) displays two up and one down (Figure 2). Their geometries, when associated with three K^+ ions, were calculated using the AM1 Hamiltonian.[8]

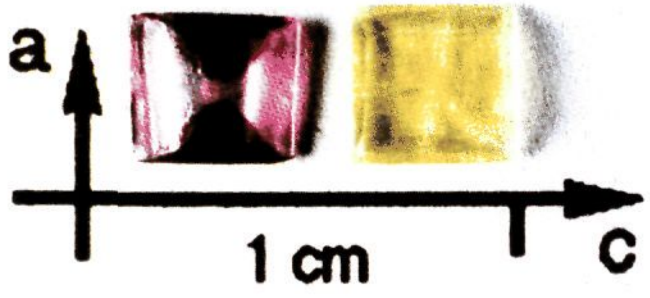


Figure 1. Photograph of K_2SO_4 crystals containing **1c** (left) and **2** (right).

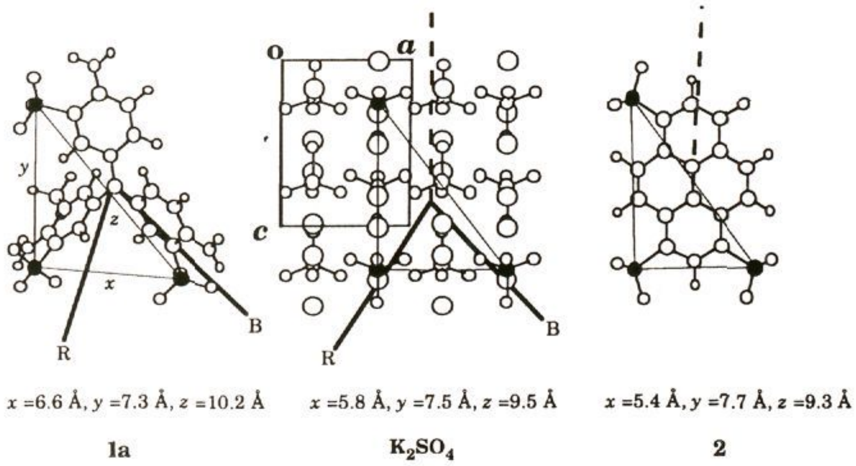
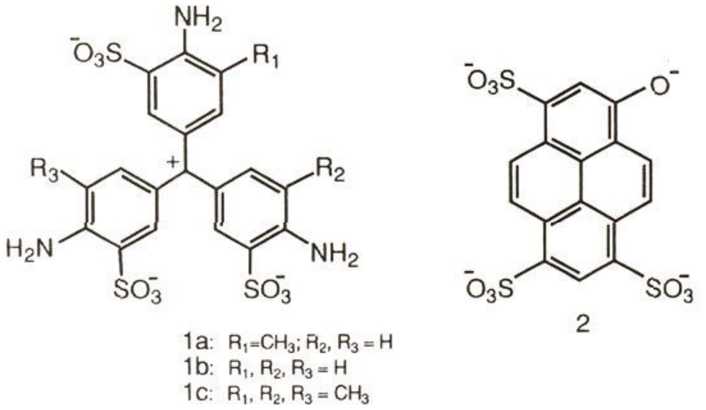


Figure 2. Left: AM1 geometry of **1a** in the **A** conformation. Center: K_2SO_4 lattice for a {110} growth sector viewed along [010]. Right: AM1 geometry of **2**. Sulfonate S atoms are filled. The sulfate triangle in the K_2SO_4 lattice which serves as the site of attachment for **1** and **2** is indicated in this way. Relevant triangles, drawn in fine line, are viewed in a perpendicular direction. INDO/S calculated transition dipoles are marked on the molecules (— for **1** and – – – for **2**). Their experimental counterparts, measured through polarized absorption spectroscopy, are indicated on the K_2SO_4 lattice. Blue-shifted (B) and red-shifted (R) transitions for **1a** are labeled. We cannot distinguish between symmetry-related sulfate triangles. Lengths (Å) of the legs (x, y, z) of the sulfur triangles are listed below each drawing.

Scheme 1



We measured the polarized visible absorption spectra of oriented $1/K_2SO_4$ crystals (Figure 3).[9] The broad bands in the visible region were fitted as the sum of two Gaussian functions with a separation varying between 35 and 40 nm for different crystal orientations. From the ratios of integrated intensities of the transitions for spectra with light incident in and polarized along the principal directions, we determined the transition moments for the guest in the crystal.[10] Using the INDO/S method[11] we

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[1] Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. *Science* **1993**, *261*, 1286. Addadi, L; Weiner, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 153.

[2] Izumi, Y.; Urabe, K.; Makoto, O. *Zeolite, Clay, and Heteropoly Acid in Organic Reactions*; VCH: New York, 1992. Klein, L. C. *Sol-Gel Optics: Processing and Applications;* Kluwer: Dordrecht, 1993. Ramamurthy, V., Ed. *Photochemistry in Organized and Constrained Media*; VCH: New York, 1991. See also: Kirkor, E. S.; David, D. E.; Michl, J. *J. Am. Chem. Soc.* **1990,** *112,* 139. Böttcher, H.; Hertz, O.; Fox, M. A. *Chem. Phys. Lett.* **1989**, *160*, 121.

[3] de Sénarmont, H. *Ann. Phys. (Leipzig)* **1854**, *167*, 491.

[4] (a) Buckley, H. E. *Z. Kristallogr.* **1934**, *88*, 248. Buckley, H. E. *Crystal Growth*; John Wiley: New York, 1951; pp 377–378. (b) Part XII: France, W. G.; Wolfe, K. M. *J. Am. Chem. Soc.* **1941**, *63*, 1505.

[5] For some structural inferences, see: Neuhaus, A. *Angew. Chem.* **1941**, *54*, 527. Slavnova, E. N. *Growth of Crystals*; Consultants Bureau: New York, 1958; pp 117–125. Hartmann, H. *Zur Physik und Chemie der Kristallphosphore*; Akademie-Verlag: Berlin, 1960; p 136.

[6] X-ray topographic studies indicate that HIs are excellent "single crystals" of K_2SO_4 and argue against dye aggregation. Dudley, M.; Vetter, W.; Kahr, B. In *National Synchrotron Light Source Report;* Hurlburt, S. L., Lazarz, M. L., Eds.; Brookhaven National Laboratory: Upton, New York, 1993; in press. The growth of these crystals was described as an experiment for students. Kahr, B.; Chow, J. K.; Peterson, M. *J. Chem. Educ.*, in press.

[7] In order to be consistent with Buckley, Miller indices refer to ratios determined by classical goniometry: $a = 5.772$ Å, $b = 10.072$ Å, $c = 7.483$ Å for *Pmcn*, No. 62. See: von Groth, P. *Chemische Krystallographie, v. 2*; Wilhelm Engelmann: Leipzig, 1908; p 337. Wyckoff, R. G. *Crystal Structures, v. 3*; Wiley Interscience: New York, 1965; p 95.

[8] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Stewart, J. J. P. Quantum Chemistry Program Exchange, Bloomington, Indiana, No. 455.

[9] We used well-developed faces and the extinction directions of the biaxial crystals to orient samples relative to a sheet polarizer. Spectra were collected by using a tungsten light source, a double grating monochromator with a pinhole aperture, and a photomultiplier interfaced to a Macintosh II computer.

[10] Hartshorne, N. H.; Stuart, A. *Crystals and the Polarizing Microscope, 4th ed.*; Edward Arnold: London, 1970. Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*, VCH: New York, 1986.

[11] Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111; **1976**, *42*, 223.

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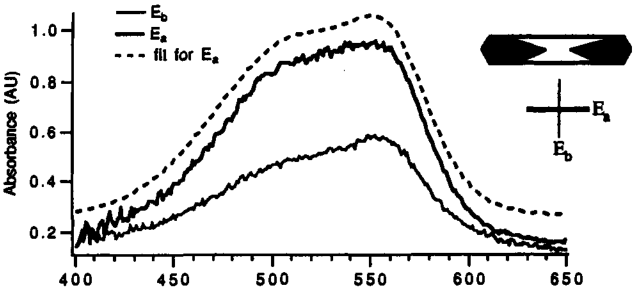

Figure 3. Polarized absorption spectra for light propagating along [001] in **1a** and polarized parallel to *a* and *b*. Best sum of two Gaussians is fitted to the *a* polarization. The base line is offset for clarity.

calculated the difference in the wavelength of the two visible transitions for A (37 nm) and for S (**1a**, 7 nm; **1b** and **1c**, 0 nm). The agreement of experiment with the calculation for A suggested to us that the two peaks resulted from the lifting of the degeneracy of the triarylmethyl first excited state in the non axially symmetric A-type chromophore. However, it is conceivable that S in the lattice could give rise to the spectra shown in Figure 2, depending upon precisely how the host/guest interactions perturb the E-state degeneracy.[12]

Previous researchers presumed that dyes recognized ionic salts by substituting negatively charged functionalities for anions.[4,13] Triangles defined by sulfonate sulfur atoms in the dye conformers were least squares fitted to triangles defined by sulfate sulfur atoms in the lattice. For A, a reasonable superposition of sulfur atoms occurs at lattice positions which correspond to *a* and *c* translations as indicated in Figure 2; the average distance between corresponding S atoms was 0.39 Å.[14] By importing the calculated dye structures[15] with their attendant INDO/S transition moments into the fractional coordinate space of K_2SO_4 we could compare our model for A with the experimental transition vectors. The match was within 8° for the blue-shifted (B) transition and 15° for the red-shifted (R) transition (Figure 2).

Pyranine (**2**), a laser dye and fluorescent probe,[16] was chosen as a rigid analog of A. Luminescent yellow crystals (Figure 1) were grown by evaporating basic solutions (2×10^{-5} M **2**, 5×10^{-2} M K_2SO_4, 0.1 M KOH). The characteristic hourglass is difficult to observe because the dye is included in {010} and {110} sectors. The absorbance at 470 nm is characteristic of the deprotonated form of **2**.[16] The calculated transition moment is essentially along the long pyrene axis as indicated in Figure 2. The crystals only absorb light when the polarization is parallel to [001]. These observations are consistent only if the SO_3^- groups occupy three sites defined by *a* and *c* translations proposed for **1**/K_2SO_4. We have thus designed an organic hourglass inclusion.

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Supplementary Material Available: Details of MO calculations including coordinates for relevant models, spectra, and their fits (45 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] Lueck, H. B.; McHale, J. L.; Edwards, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 2342.

[13] Davey, R. J.; Black, S. N.; Bromley, L. A.; Cottier, D.; Dobbs, B.; Rout, J. E. *Nature* **1991**, *353*, 549. Kelley, M. P.; Chow, J. K.; Kahr, B. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 201.

[14] For the S diastereomer, sulfonates substitute for sulfates that are related to one another as (x, y, z), $(x, y, z + 1)$, and $(x + 1, -y + {}^1/_2, z + {}^1/_2)$ with an average distance between corresponding S atoms of 0.17 Å.

[15] J. Whetstone (*Trans. Faraday Soc.* **1955**, *51*, 1142; *J. Chem. Soc.* **1956**, 4841; **1957**, 4284) attempted to rationalize the qualitative dichroism of **1a**–**c**, in NH_4NO_3. He carried dye conformers, drawn on celluloid, over projections of the lattice until he got good fits of the SO_3^- groups for NO_3^- anions. We could not reconcile Whetstone's dye structures with the results of our semiempirical MO calculations. His geometries were taken from unpublished reports of the German dye industry, collected by British teams after World War II, in which triarylmethane dyes were mistakenly described as flat, not propeller-shaped. See: BIOS (British Intelligence Objectives Subcommittee) microfilm, R20, P. B. 73,564, FDX 226. For a listing, refer to: *Bibliography of Scientific and Industrial Reports*, Vols. 1–11 (1946–1949).

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