Chem. Mater. **1994,** *6,* 1317–1324 1317

Chromoisomers and Polymorphs of 9-Phenylacridinium Hydrogen Sulfate

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Received February 1, 1994. Revised Manuscript Received April 22, 1994[⊗]

The debate about the meaning of the defunct term *chromoisomerism* is reviewed. The central role of red and green crystals of 9-phenylacridinium hydrogen sulfate (1) in fueling this dialogue is highlighted. Single-crystal structures of a red (**1r**) and a green (**1g**) form were determined by X-ray diffraction. **1r**: monoclinic, space group $P2_1/c$, $a = 9.266(1)$ Å, $b = 8.582(1)$ Å, $c = 20.690(3)$ Å, $\beta = 98.03(1)°$, $Z = 4$. **1g**: triclinic, space group $P\bar{1}$, $a = 8.597(1)$ Å, $b = 10.449(1)$ Å, $c = 10.822(1)$ Å, $\alpha = 101.33(1)°$, $\beta = 108.73(1)°$, $\gamma = 114.65(1)°$, $Z = 2$. Differential scanning calorimetry revealed that the polymorphs **1r** and **1g** underwent comparable endothermic transitions. The thermal transformations were monitored and characterized by thermal gravimetric infrared spectroscopy and X-ray powder diffraction. Taken together these data failed to reveal a thermal transformation between **1r** and **1g**. Diffuse reflectance spectra of powders, coupled with INDO/S calculations, did not identify the origin of the color difference. Optical processes in related dye polymorphs are discussed. The short-lived and physically ill-defined term chromoisomerism is illustrative of the introduction, refinement, and abandonment of a concept in organic chemistry.

Introduction

Prior to the development of quantum chemistry, crystallographers were confused by solutions of pure compounds that deposited differently colored solids. Such compounds were said to be imbued with the attribute of *chromoisomerism.* The physical basis of chromoisomerism was the subject of a contentious debate between 1907 and 1918. Oddly, this debate focused on the chromoisomers of a particular substance, 9-phenylacridinium hydrogen sulfate (1), because it was observed that two crystalline forms, one red and the other green, precipitated *simultaneously* from solution. Moreover, it had been reported that crystals with a platelike habit sometimes showed tiling into four growth sectors that were alternately red and green.[2] These supposed twins undoubtedly underscored the phenomenon of chromoisomerism in 1. We desired to place this colorful example of polymorphism within the context of ongoing structural studies of acridine derivatives,[3,4] compounds recently considered as antivirals.[5]

Chromoisomerism and Homochromoisomerism

The term chromoisomerism was coined by Hantzsch[6] in 1907, in order to establish that color differences in some salts of *aci*-nitro compounds were worthy of special attention.[7] Having obtained differently colored solids with the same metal counterions, Hantzsch realized that the color differences could be attributed only in part to the conjugate metal. Consequently, he felt obliged to indicate the failure of "auxochromic" color theories.[8]

Auxochromism was a leading color theory in which so-called auxilliary groups of atoms were thought to induce the color latent in a chromophore. Kauffmann was its champion. Hantzsch and Kauffmann began a long debate on the viability of *auxochromism,* no part of which is particularly useful to a contemporary scientist.[9,10]

After a systematic study of color changes induced by solvent and temperature Hantzsch concluded that a "significant" color change must be accompanied by a change in constitution. Hantzsch's ideas gained credence if only because researchers invoked the term chromoisomerism in a descriptive sense.[11] Chemists identified differently colored polymorphs as chromoisomers but did not necessarily subscribe to Hantzsch's insistence on concomitant constitutional isomerism.

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

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[2] Winchell, A. N. *The Optical Properties of Organic Compounds;* McCrone Research Institute: Chicago, 1987; p 196. Groth, P. v. *Chem. Krystallogr.* **1919,** *5,* 818–820 (citing: Pauli, Krystall. Unters. d. Chromoisomeren des sauren Phenylacridoniumsulfats, Dissertation, University of Leipzig, 1912).

[3] Stowell, J. G.; Toma, P. H.; Byrn, S. R. *Acta Crystallogr., Sect. C* **1991,** *C47,* 1635.

[4] Stowell, J. G.; Toma, P. H.; Byrn, S. R. *Acta Crystallogr., Sect. C* **1991,** *C47,* 1637.

[5] Toma, P. A.; Ray, K. A.; Stowell, J. G.; Byrn, S. R. *Acta Crystallogr., Sect. C,* **1990,** *C46,* 1573.

[6] For biographical information see: Moore, T. S. *J. Chem. Soc.* **1936,** 1051. Weissberger, A. In Farber, E., Ed. *Great Chemists;* Interscience: New York, 1961; p 1067.

[7] Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1907,** *40,* 1533. In this paper, Hantzch merely distinguishes chromo forms of compounds from their colorless or leuco forms. "Chromo Isomers" first appears in a paper from the next year. See: Hantzsch, A. *Z. Ang. Chem.* **1908,** *20,* 1889.

[8] This rebuff may be better appreciated in the context their earlier discussion in which Kauffmannn (*Z. Phys. Chem.* **1904,** *37,* 618, 2468) debunked Hantzsch's proposition of the pseudo-acid (Hantzsch, A.; Barth, A. *Ber. Dtsch. Chem. Ges.* **1902,** *35,* 210). See also the discussion in: Wheland, G. W. *Advanced Organic Chemistry,* 3rd ed.; Wiley: New York, 1960; p 719.

[9] Their debate began prior to the proposition of the term chromoisomerism. See: Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1906,** *39,* 1084, 3072. Kauffmann, H. *Ibid.* 4237. Kauffmann, H.; Franck, W. *Ibid.* 2722.

[10] It continued subsequent to the publication of Hantzsch's paper.[7] See: Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1907,** *40,* 1556, 1572. Kauffmann, H. *Ibid.* 2341.

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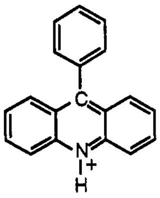
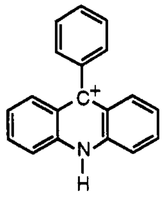
In 1910, Hantzsch launched the rhythmic term *homochromoisomerism*, to describe the relationship between two solids whose constituent molecules have the same molecular weight and are alike in color yet have different melting points.[12] Homochromoisomerism corresponds to the modern idea of polymorphism in the absence of color change. It is an odd *ad hoc* proposition. Hantzsch published a series of papers illustrating homochromoisomerism in nitroanilines, azophenols, and methylphenylpicramide.[13]

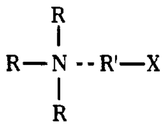
Biilmann attacked the necessity of homochromoisomerism. He sensibly declared that it is merely polymorphism.[14] The title of Hantzsch's response is the most instructive part: "Refutation of E. Biilmann's Identification of Homochromoisomerism as Polymorphism".[15] It is worth recalling the opinion of Moore, who, in a memorial lecture, characterized Hantzsch's combative style: "Few, if any, chemists have surpassed Hantzsch in the number and vigor of their controversies."[16]

...in Acridine Derivatives

Hantzsch first took an interest in acridines, also in 1910,[17] when he challenged Gomberg's suggestion that phenylacridine salts were carbonium ion salts rather than ammonium ions.[18] Hantzsch's paper on chromoisomerism in acridines described the preparation of 9-phenylacridinium salts with six different counterions.[19] Their colors ranged from yellow to red to green. Sometimes this variety of colors was seen in crystals containing the same counterion, and Hantzsch therefore concluded that the colorfulness was independent of the nature of the anion. N stereoisomerism was rejected as was the possible variability in the arrangements of the aromatic bonds. The "subdivision" of aromatic bonds was in the view of Kauffmann a less drastic form of constitutional isomerism.[20] Wolfgang Ostwald suggested that the chromoisomerism was colloidal in nature;[21] Hantzsch thought this was untenable. Ultimately, Hantzsch concluded that ammonium salts, containing a single weak linkage among its four valences, could exist in several forms depending upon which pendant group assumed the feeble position. Hantzsch extended this proposal of valence isomerism to explain the action of certain pH indicators.[22]


Hantzsch


Gomberg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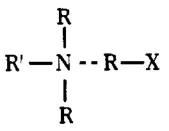
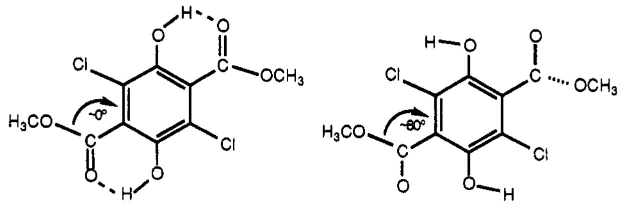

$$R'-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N}}\cdots R-X$$

Kehrmann believed that color often could be attributed to cross-conjugation as in quinoidal compounds.[23] Hantzsch felt that the coprecipitation of **1r** and **1g** was particularly strong evidence against the quinoid hypothesis.[24] Kehrmann then claimed "with absolute certainty" that the chromoisomerism is due to impurities that can be eliminated by vigorous treatment with charcoal. After scrubbing in this way, Kehrmann obtained only yellow crystals.[25] Hantzsch rebutted with the report of additional chromoisomers in *N*-methylphenylacridinium sulfites.[26] Kehrmann later insisted that one of these alleged chromoisomers was actually a monohydrate.[27]

Besieged, Hantzsch published a polemical in 1918 in which he claimed that chromoisomerism was merely a tentative term intended to inspire debate and to group those differently colored isomers for which no adequate structural difference had been found. Nevertheless, Hantzsch continued to debate Kehrmann[28] and Kauffmann.[29] The term chromoisomerism gradually disappeared from the chemical literature.[30]

Crystal and Molecular Structure of 9-Phenylacridinium Hydrogen Sulfate

We set out to find a structural basis for the chromoisomerism in the 9-phenylacridinium hydrogen sulfate polymorphs **1r** and **1g**. For example, the origin of the color difference in polymorphs of dimethyl-3,6-dichloro-2,5-dihydroxyterephthalate (**2**), described by Hantzsch in 1915,[31] was not discovered until the diffraction studies of Byrn, Curtin, and Paul in 1972.[32] Hantzsch proposed that the two crystalline forms were tautomers. Byrn et al. showed that the structural distinctions are more substan-



Yellow 2 Colorless

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(11) Torrey, H. A.; Hunter, W. H. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4332; Dimroth, O.; Dienstbach, O. *Ibid.* **1908**, *41*, 4055. Ismail'skii, V. A. *J. Russ. Phys. Chem. Soc.* **1915**, *47*, 1626; *J. Chem. Soc.* **1916**, *110*, 287. Piutti, A.; De'Conno, E. *Mem. Accad. Lincei* **1912**, *8*, 793. Dehn, W. M.; McBride, L. *J. Am. Chem. Soc.* **1917**, *39*, 1348. Oesper, R. E.; Cook, W. A. *J. Am. Chem. Soc.* **1925**, *47*, 422. Oesper, R. E.; Broker, W. *Ibid.* **1925**, *47*, 2606.

(12) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1651.

(13) Hantzsch. A. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1662, 2512.

(14) Biilmann, E. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 827.

(15) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2001.

(16) See Moore,[6] who also said that "no chemist with a reputation to lose committed so many errors as Hantzsch." Nevertheless, Hantzsch made a number of major contributions to organic chemistry. Not least was his discovery of cis/trans isomerization of C=N bonds.

(17) Hantzsch, A.; Meyer, H. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 336.

(18) Gomberg, M.; Cone, L. H. *Justus Liebigs Ann. Chem.* **1910**, *370*, 142.

(19) Hantzsch, A.; Hofmann, O. K. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 1776. Hantzsch, A. *Ibid.* 1783.

(20) Kauffmann, I. H. *Ber. Dtsch. Chem. Ges.* **1911**, *44*, 2341.

(21) Ostwald, W. *Grundriss der Kolloidchemie*; Theodor Steinkopff: Dreseden, 1910.

(22) Hantzsch, A. *Z. Electrochm.* **1915**, *9*, 418.

(23) Kehrmann, F.; Wentzel, F. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 3815; **1908**, *41*, 2340. McBride, J. M. *Tetrahedron* **1974**, *30*, 2009.

(24) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1338.

(25) Kehrmann, F.; Danecki, A. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 1338.

(26) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1916**, *49*, 2169.

(27) Kehrmann, F.; Stahrfoss, K. *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 24.

(28) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1921**, *54B*, 2569, 2573.

(29) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1921**, *54B*, 2620.

(30) Nerdel, F.; Klamann, D.; Ebing, W. *Justus Liebigs Ann. Chem.* **1960**, *632*, 55.

(31) Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 797.

(32) Byrn, S. R.; Curtin, D.; Paul, I. *J. Am. Chem. Soc.* **1972**, *94*, 890.

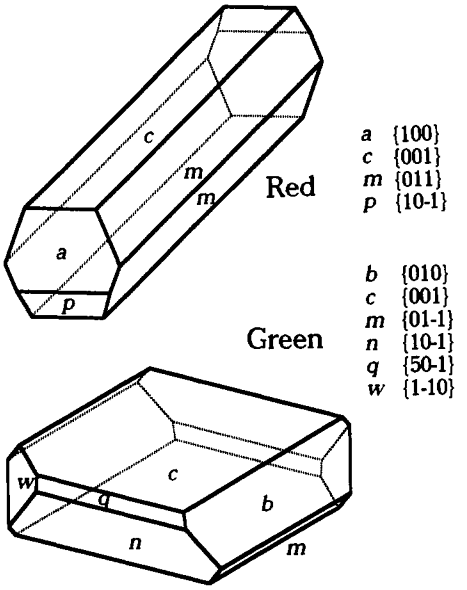

Figure 1. Crystal morphology for **1r** and **1g**.

tial; the yellow and colorless polymorphs have different intramolecular hydrogen bonds and conformations. This type of structural difference is commonly labeled conformational polymorphism.[33] Perhaps, a corresponding tautomerism or hydrogen-bond rearrangement might explain the color difference between **1r** and **1g**.

9-Phenylacridine was prepared from diphenylamine and benzoic acid with $ZnCl_2$ as a catalyst according to the procedure of Albert.[34] The HSO_4^- salt was precipitated from acidified ethanol solutions and the material was recrystallized from acetonitrile. Contrary to Kehrmann,[25] vigorous treatment with charcoal failed to wash away the color.

Red Form (1r). Crystals of the red form of 9-phenylacridinium hydrogen sulfate suitable for X-ray analysis were obtained by slow evaporation of a 10:1 solution of acetonitrile and DMSO. The saturated solution was prepared by dissolving 40 mg of 1 in 10 mL of boiling acetonitrile. DMSO (1 mL) was added, and the solution was filtered. Red and green crystals often precipitated simultaneously although exclusive crystallizations were easily obtained by seeding. The crystals **1r** exhibited {001}, {011}, {100}, and {-101} forms with the *a* direction being elongated and the {001} faces predominant (Figure 1). Occasionally, rapid growth along *a* was manifest in fine needles. The crystals were highly dichroic, absorbing light when the polarization was perpendicular to the needle axis.

Room-temperature intensity data were collected, and the structure was solved and refined in the space group $P2_1/c$ with $Z = 4$. The molecules sit on general positions and have approximate C_2 symmetry. An ORTEP representation of the molecule is shown in Figure 2. Atomic positional parameters and anisotropic thermal parameters are listed in Tables 1 and 2, respectively. The molecular geometry is unremarkable and compares favorably with analogous structures.[3,4]

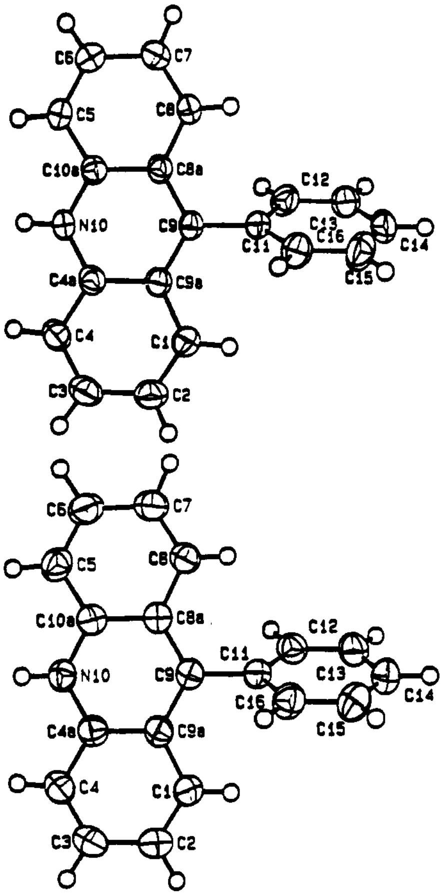

Figure 2. ORTEP structures **1r** (top) and **1g** (bottom).

Table 1. Fractional Coordinates and Isotropic Thermal Parameters for 1r

atom	*x*	*y*	*z*	*B* (Å^2)
N(10)	−0.2076(2)	0.5168(2)	0.50770(7)	3.33(3)
C(1)	−0.1768(2)	0.4700(2)	0.68495(9)	3.86(4)
C(2)	−0.0847(2)	0.5887(3)	0.7042(1)	4.73(5)
C(3)	−0.0281(2)	0.6826(3)	0.6579(1)	4.89(5)
C(4)	−0.0657(2)	0.6586(2)	0.5935(1)	4.23(4)
C(5)	−0.3499(2)	0.3999(2)	0.41549(9)	3.92(4)
C(6)	−0.4545(3)	0.2974(2)	0.3913(1)	4.53(5)
C(7)	−0.5223(3)	0.2009(2)	0.4332(1)	4.44(4)
C(8)	−0.4808(2)	0.2059(2)	0.4989(1)	3.66(4)
C(9)	−0.3229(2)	0.3232(2)	0.59418(8)	2.98(3)
C(11)	−0.3734(2)	0.2110(2)	0.64090(8)	3.07(3)
C(12)	−0.5197(2)	0.1999(2)	0.64885(9)	3.56(4)
C(13)	−0.5634(2)	0.0966(3)	0.69301(9)	4.18(4)
C(14)	−0.4627(2)	0.0032(3)	0.72971(9)	4.63(4)
C(15)	−0.3184(3)	0.0111(3)	0.7216(1)	4.73(5)
C(16)	−0.2733(2)	0.1146(3)	0.67755(9)	4.01(4)
C(4a)	−0.1650(2)	0.5378(2)	0.57188(9)	3.31(3)
C(8a)	−0.3723(2)	0.3128(2)	0.52693(8)	3.00(3)
C(9a)	−0.2217(2)	0.4398(2)	0.61724(8)	3.15(3)
C(10a)	−0.3089(2)	0.4113(2)	0.48333(8)	3.13(3)
H(01)	−0.174(2)	0.584(2)	0.4797(9)	4.1(4)
S	0.07459(5)	0.14606(5)	0.57804(2)	3.402(8)
O(1)	−0.0653(2)	0.1498(2)	0.53586(7)	4.73(3)
O(2)	0.1848(1)	0.0753(2)	0.53615(7)	5.11(3)
O(3)	0.0728(2)	0.0538(2)	0.63417(8)	5.64(4)
O(4)	0.1291(2)	0.3012(2)	0.59128(7)	4.92(3)
H(02)	0.130(3)	−0.028(4)	0.509(1)	9.3(8)

Green Form (1g). Crystals of **1g** precipitated out of the same acetonitrile/DMSO solution that yielded **1r**. Nearly equal masses were obtained in this way. Crystals suitable for X-ray diffraction came from 1-propanol solutions. The saturated solution was prepared by dissolving 40 mg of 1 in 10 mL of boiling 1-propanol. The solution was filtered, and the filtrate was allowed to

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(33) A third polymorph was subsequently discovered. See: Yang, Q.-C.; Richardson, M. F.; Dunitz, J. D. *Acta Crystallogr., Sect. B* **1989**, *B45*, 312. Richardson, M. F.; Yang, Q.-C.; Novotny-Bregger, J. D.; Dunitz, *Acta Crystallogr., Sect. B* **1990**, *B46*, 653.

(34) Albert, A. *The Acridines: Their Preparation, Physical, Chemical, and Biological Properties and Uses*, 2nd ed.; St. Martin's Press: New York, 1966; pp 100–101.

Table 2. Fractional Coordinates and Isotropic Thermal Parameters for 1g

atom	x	y	z	B (Å^2)
N(10)	0.9279(1)	0.7149(1)	0.9592(1)	2.82(3)
C(1)	1.3569(2)	0.7122(2)	1.0437(2)	3.42(4)
C(2)	1.2939(2)	0.5808(2)	0.9375(2)	3.89(4)
C(3)	1.1087(2)	0.4938(2)	0.8353(2)	3.90(4)
C(4)	0.9870(2)	0.5375(2)	0.8404(2)	3.46(4)
C(5)	0.8368(2)	0.8734(2)	1.0638(2)	3.12(4)
C(6)	0.8857(2)	1.0024(2)	1.1663(2)	3.45(4)
C(7)	1.0693(2)	1.1033(2)	1.2688(2)	3.48(4)
C(8)	1.2034(2)	1.0736(2)	1.2695(2)	3.09(4)
C(9)	1.2923(2)	0.9011(2)	1.1605(1)	2.67(3)
C(4a)	1.0485(2)	0.6723(2)	0.9509(1)	2.83(3)
C(8a)	1.1608(2)	0.9400(1)	1.1653(1)	2.62(3)
C(11)	1.4892(2)	1.0049(2)	1.2651(1)	2.72(3)
C(12)	1.5844(2)	1.1520(2)	1.2699(2)	3.50(4)
C(13)	1.7686(2)	1.2489(2)	1.3655(2)	4.26(5)
C(14)	1.8578(2)	1.2013(2)	1.4559(2)	4.40(5)
C(15)	1.7654(2)	1.0580(2)	1.4524(2)	4.48(5)
C(16)	1.5811(2)	0.9593(2)	1.3588(2)	3.64(4)
C(9a)	1.2364(2)	0.7640(2)	1.0549(1)	2.79(3)
C(10a)	0.9743(2)	0.8411(2)	1.0620(1)	2.70(3)
H(01)	0.813(2)	0.660(2)	0.897(2)	4.1(4)
S	0.43480(4)	0.43524(4)	0.65425(4)	3.127(9)
O(1)	0.3112(1)	0.4697(1)	0.5458(1)	4.19(3)
O(2)	0.3129(2)	0.3240(1)	0.6876(1)	5.01(4)
O(3)	0.5710(2)	0.5778(1)	0.7729(1)	4.79(4)
O(4)	0.5228(1)	0.3777(1)	0.5843(1)	4.08(3)
H(02)	0.366(3)	0.522(2)	0.501(2)	7.3(7)

evaporate at room temperature. The crystals **1g** exhibited {01–1}, {10–1}, {50–1}, {1–10}, and {001} forms. The latter faces were predominant (Figure 1).

Room-temperature intensity data were collected and the structure was solved and refined in the space group $P\bar{1}$ with $Z = 2$. The molecular structure of the acridinium ion was virtually identical in **1r** and **1g**. The only highly variable molecular parameter is the dihedral angle between the phenyl and acridinium rings. These compare favorably in the two structures with respective angles of 61° and 62°. This agrees with our calculated value of 63° obtained with the AM1 Hamiltonian.[35] These values are typical for X-ray structures for 9-arylacridinium salts.[36] The ESR spectrum of the 9-phenylacridinium radical anion was interpreted in terms of a 65° angle.[37]

"Twinned" Crystals. This study was precipitated by a desire to reinvestigate those crystals, described by Pauli and by Winchell,[2] as plates showing a diagonal division into four sectors, that were alternately red and green. After more than 3 years during which time scores of 9-phenylacridinium hydrogen sulfate crystallizations were carried out in our laboratories, we never did observe any crystalline objects that would satisfy this description. However, only during the revision of this paper did we first spot these so-called "twins". The crystals were obtained by slow evaporation of a saturated 7:1 solution of acetonitrile and DMSO (80 mL) in which 1.0 g of **1** was dissolved.

The crystals had a flattened morphology with very large {001} faces. The {10–1} growth sectors were red and the {010} sectors were green. In thicker crystals the red coloration through {10–1} is probably obscured by the green {001} contribution. Whole "twinned" crystals and fragments excised from red and green sectors indexed as **1g**. Thus, the mysterious red/green crystals have the lattice of **1g** but nevertheless show a reddish discoloration in some sectors. We do not know at this time whether or not the discoloration is at all related to the "chromoisomerism" that distinguishes **1r** and **1g** and will be subject to future study.

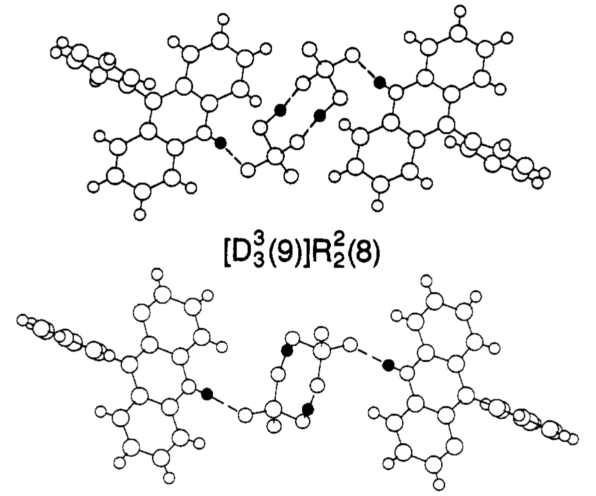

Figure 3. Dimer of **1r** (top) and **1g** (bottom) showing the predominant H-bond circuit typical of both polymorphs. Hydrogen atoms involved in H bonds are filled. Etter's subgraph notation is indicated.

Table 3. Selected Structural Parameters for 1r and 1g

parameter	1r	1g
angle between phenyl and acridinium planes (deg)	61.3	62.1
$d_{\mathrm{N\cdots N}}$ (Å)	9.17	9.08
$d_{\mathrm{S\cdots S}}$ (Å)	4.17	4.16
∠H---O–S (deg)	116.8	133.9
$d_{\mathrm{O\cdots S}}$ (Å)	2.59	2.64
$d_{\mathrm{O\cdots N}}$ (Å)	2.75	2.69

Hydrogen Bonding

The polymorphs **1r** and **1g** may be conveniently described in terms of the graph set analysis invented by Peggy Etter.[38] In both structures, the HSO_4^- ions form cyclic dimers with two H-bond donors and two H-bond acceptors to give eight-membered rings. These dimers are capped by additional H-bonds to the protons on the acridinium N atoms. The discrete units may be characterized as making paths with three H-bond donors and three H-bond acceptors and involving nine atoms. The Etter notation[39] and relevant subgraph for **1r** and **1g** is shown in Figure 3. These four-ion building blocks are remarkably similar in the two polymorphs. Salient structural parameters are summarized in Table 3. Packing pictures are shown in Figure 4. The lattice of **1g** is distinct from **1r** in the way in which it isolates the hydrogen sulfate dimers within channels.

Calorimetry. Differential scanning calorimetry (DSC) of powdered samples of **1r** and **1g** showed three endotherms: in each case a small feature was followed by two

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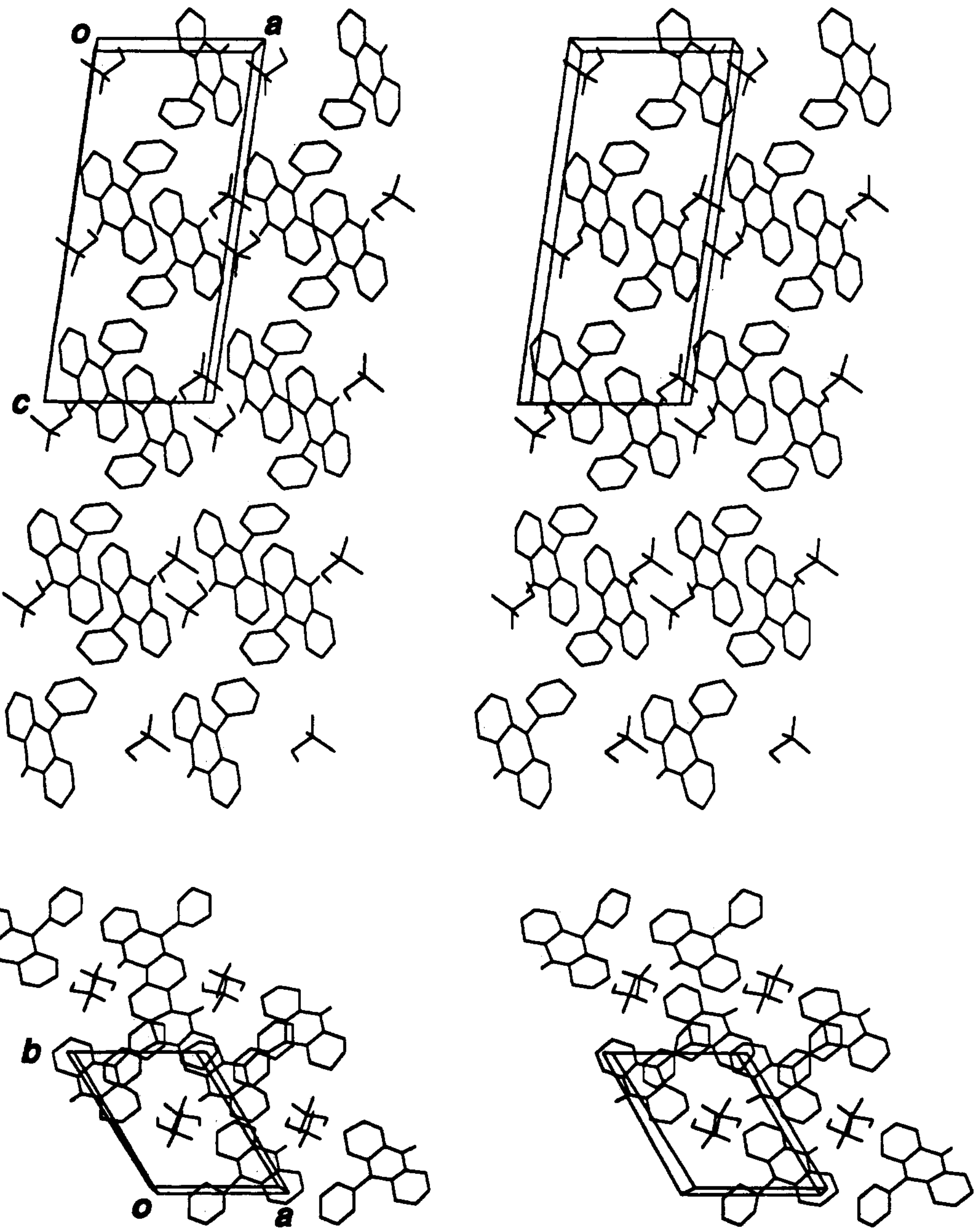

Figure 4. Stereoviews of lattices for **1r** (top) and **1g** (bottom).

sharp ones. The DSC traces are shown in Figure 5. For **1r** and **1g**, the small endotherm was observed at 196 and 209 °C, respectively. In either case, the first substantial endotherm appeared between 255 and 260 °C. The crystals appeared to melt when viewed on a microscope hot stage. However, there was a simultaneous recrystallization of fine needles. No exotherm was observed. A homogenous melt was finally indicated by the endotherms at 277–280 °C. The two polymorphs, **1r** and **1g**, were not dramatically distinguished by calorimetry.

Thermal Gravimetric Infrared Spectroscopy (TGIR). Both polymorphs **1r** and **1g** showed a marked reduction in mass upon heating. **1r** lost 14% of its mass upon heating from 25 to 300 °C at 10 °C min^{-1}. **1g** lost 35% of its mass under the same conditions. The onset of mass loss was about 200 and 210 °C for **1r** and **1g**, respectively. These temperatures correspond with those at which the early endotherms were observed by calorimetry. The IR spectra of the vapors were characteristic of SO_2 and H_2O and attest to sample decomposition.

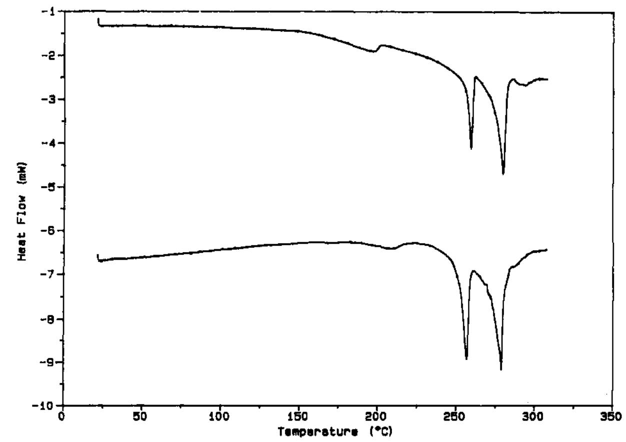

Figure 5. DSC traces of **1r** and **1g**. Top (**1r**): endotherms peaks at 195.6, 259.5, and 279.6 °C. Bottom (**1g**): endotherms peak at 208.5, 256.9, and 278.7 °C.

X-ray powder diffraction (XRPD) patterns were obtained as a function of temperature for both **1r** and **1g**.

Table 4. Results of Selected INDO/S Calculations

model	transition moment[a] x	y	z	transition energy (cm^{-1})	dipole strength (Å^2)
1r	4.87	0.32	−0.54	27 082	0.3036
	−0.05	3.64	−0.01	30 081	0.1887
(**1r**)$_2$[b]	6.93	0.33	−0.72	27 653	0.6277
	0.15	5.13	−0.03	30 461	0.3779
1g	4.45	−0.07	0.54	27 011	0.2518
	0.11	−3.32	0.62	29 531	0.1541
(**1g**)$_2$[b]	6.82	0.94	0.73	27 102	0.6041
	−0.83	4.41	−0.74	29 893	0.2838

[a] The transition moments were referred to a Cartesian coordinate system with the x axis defined by the N and C(9) atoms, and the y axis is fixed along the acridine ring system. [b] Dimer as indicated in Figure 6.

These spectra were compared with standard **1r** and **1g** diffractograms obtained at room temperature. These experiments indicate that neither **1r** nor **1g** transformed to one another upon heating. Between the high-temperature endotherms, that stage during which we observed concomitant recrystallization and melting, the diffraction patterns indicated a crystalline material that was neither **1r** nor **1g**. However, in each case crystallinity of any sort was lost at ~277 °C as indicated by the absence of a powder diffraction pattern.

Diffuse reflectance spectra of powdered samples of **1r** and **1g**, recorded between 200 and 2400 nm, were barely differentiated. One can conclude that these orientationally averaged spectra obscure the differences in optical processes that are plain to the eye. In the visible region of the spectra it is clear that there is a greater absorbance of red light at ~600–650 nm in **1g**. Given the highly anisotropic nature of some optical processes in molecular crystals, it is unlikely that such spectra are interpretable.

Discussion

Upon heating, **1r** and **1g** samples decomposed losing substantial percentages of their masses. The evolution of SO_2 and H_2O with concomitant sample decomposition was indicated by TGIR at ~180 °C in each case. The thermal gravimetric analyses and the DSCs both indicated features at around this temperature that correspond to the onset of decomposition. Nevertheless, the bulk of the sample maintained its initial crystalline structure, that of **1r** or **1g**, as evidenced by hot-stage powder diffraction. In either case, mass loss increases precipitously at about 250 °C. Visual inspection showed that the sharp endotherms at ~255 °C were accompanied by melting and concomitant recrystallization of fine needles. A new crystalline substance was indicated by powder diffraction, stable between 225 and 275 °C. Upon further heating a homogeneous melt was obtained.

The difference in color between **1r** and **1g** cannot be attributed to different molecular conformations in the solid state. The dihedral angle between the phenyl and acridine rings in both structures is virtually identical and in agreement with the calculated ground-state structure. We used Zerner's INDO/S method[40] to predict the absorption spectra of the two acridinium ions in their solid-state conformations. The spectra were indistinguishable. Thus, we may infer that the color difference is not monomolecular in origin. Selected INDO results are listed in Table 4.

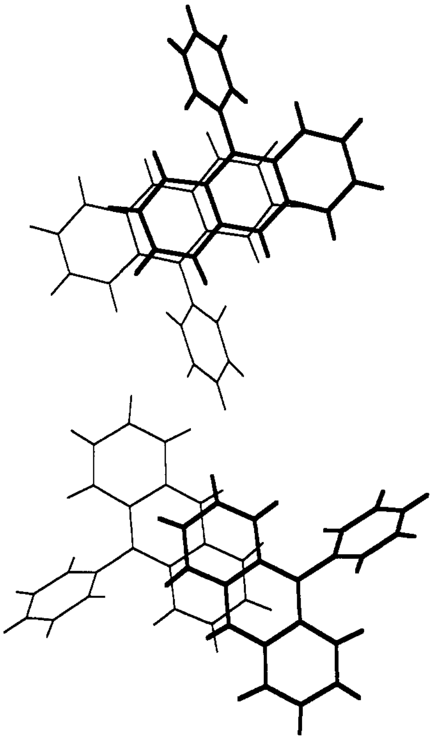

Figure 6. Pairwise overlap of molecules in **1r** (top) and **1g** (bottom).

There is greater π overlap between pairs of molecules in **1r** than in **1g** (Figure 6). This suggested that the formation of an absorption complex or a charge-transfer absorption may give rise to spectroscopic features absent in **1g**. Absorption spectra were then calculated for pieces of the **1r** and **1g** lattices. No dimers, with or without attendant hydrogen sulfate counterions, gave calculated spectra that were distinct from those calculated for the single 9-phenylacridinium ions. Bimolecular interactions seem also to be an unlikely source of color difference.

The problem of the color difference between **1r** and **1g** is not uncommon, but a resolution is by no means straightforward. Crystals composed of molecules with large oscillator strengths such as dyes will often show optical structures not present in solution. However, it is often necessary to measure the specular reflection spectra at low temperature in order to get accurate data from highly absorbing crystals.[41] Philpott has treated some of the optical consequences of dye aggregation in terms of exciton–photon (polariton) coupling.[42]

Eckhardt and co-workers have used polymorphic dye systems to correlate optical properties with differences in crystal packing. They found a new example of chromoisomerism in polymorphs of the squarilium dye, 2,4-bis-(2-hydroxy-4-(dibutylamino)phenyl)-1,3-cyclobutadienediylium-1,3-diolate (HEAPS, **3**); cocrystallization of green and purple forms were observed.[43] Spectral differences were explained in terms of an extended molecular exciton–polariton theory.[44] Isomorphous crystals of pseudocyanine (**4**) chloride, bromide, and iodide were subjected to a similar

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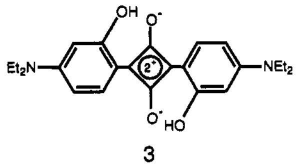

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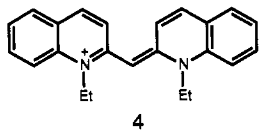

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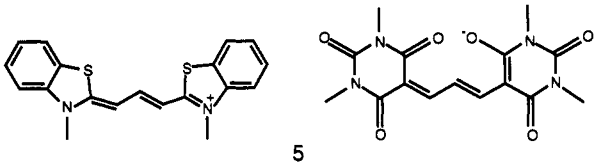

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analysis.[45] Most relevant to this special issue of *Chemistry of Materials* are the mixed cyanine–oxonol (**5**) crystals described by Etter and co-workers.[46] The polymorphism and chromoisomerism of this system allowed Eckhardt and co-workers to systematically study structural effects on exciton–polariton coupling.[47]

Conclusion

Lucas and Kemp developed a theory of chromoisomerism that was based on crystal structure and concluded that "whenever a compound exists in two or more colored forms, the crystal structure of the darker colored one possesses the greater symmetry.... For example, the cubic modification of mercuric sulfide is black, the trigonal is red; the cubic modification of thallous iodide is deep red, the rhombic is yellowish-green; the tetragonal modification of mercuric iodide is red, the rhombic is yellow; the trigonal modification of antimony triiodide is red, the rhombic is yellowish-green, and the monoclinic is greenish-yellow."[48] Monoclinic **1r** does appear "darker" than **1g** and hence consistent with the aforementioned proposition. However, the phenomenological basis of their conclusion is slender even by 1921 standards. And our visual system is ill-equipped to judge the intensity of different colors.

Despite the subsequent advances in the determination of single-crystal X-ray structures that have led to our ability to rapidly fix idealized positions for all the atoms in a crystal, the interpretation of optical properties does not follow directly from the static structure.[49] In studying the packing of **1r** and **1g**, it does not become obvious why one is red and the other green. Chromoisomerism in this case is just as puzzling to this group of crystallographers as it was to Arthur Hantzsch and his contemporaries more than 80 years ago.

Our consternation is tempered by a developing theme in solid-state organic chemistry. As Eckhardt and co-workers have recently pointed out, we must consider collective interactions manifested as phonons or excitons, as well as crystal structure, in order to properly account for the reactivity and physical properties of molecular crystals.[50] While the inferences drawn from static X-ray structures have enabled the development of solid-state organic chemistry, it is becoming increasingly clear that a greater emphasis on the vibrational structure of crystals and energy transfer within crystals will be requisite for further progress. The contemporary nature of the "chromoisomerism" in the famous 9-phenylacridinium hydrogen sulfate polymorphs may require the reconciliation of low-temperature specular reflection spectra with molecular polariton calculations.[51]

Experimental Section

X-ray Crystallography. *Single-Crystal Studies.* X-ray intensities were measured at room temperature on an Enraf-Nonius CAD4 diffractometer by applying Mo Kα radiation (λ = 0.710 73 Å, graphite monochromated) and an ω–2θ scan technique. Data were not corrected for absorption, although Lorentz and polarization corrections were applied. The structure was solved using the direct methods algorithms employed in SHELX-86.[52] Remaining atoms were located in successive difference Fourier syntheses. Hydrogen atoms were located and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least-squares procedure where the function minimized was $\Sigma(w|F_0| - |F_c|)^2$. All calculations were performed on a VAX computer using the MolEN package of programs.[53]

Crystal of **1r** were obtained from 10:1 acetonitrile:DMSO solution. Crystals of **1g** precipitated simultaneously at room temperature. A crystal of **1r**, measuring 0.39 × 0.28 × 0.20 mm, was mounted on a glass fiber in preparation for X-ray intensity measurements. Crystal data: $C_{19}H_{14}N^+\cdot HSO_4^-$, M_4 = 353.40; monoclinic, space group $P2_1/c$, a = 9.266(1) Å, b = 8.582(1) Å, c = 20.690(3) Å, β = 98.03(1)°, V = 1629.2(6) Å^3, d_{calc} = 1.441 g cm^{-3}, Z = 4. A total of 3436 reflections were recorded with 3° $\le 2\theta \le$ 52°. Of these, 2688 with $I > 3.0\sigma(I)$ were considered unique and observed. The linear absorption coefficient was 2.1 cm^{-1} for Mo Kα radiation. The final cycle of refinement included 286 variable parameters and converged (largest parameter shift/error = 0.06) with R = 0.039 and R_w = 0.057. The final difference Fourier map was featureless and the largest peak was 0.35 e Å^{-3}.

A crystal (**1g**) was obtained from propanol (0.60 × 0.51 × 0.36 mm) and was mounted on a glass fiber. Crystal data: $C_{19}H_{14}N^+\cdot HSO_4^-$, M_r = 353.40; triclinic, space group $P\bar{1}$, a = 8.957(1) Å, b = 10.449(1) Å, c = 10.822(1) Å, α = 101.33(1)°, β = 108.73(1)°, γ = 114.65(1)°, V = 805.0(5) Å^3, d_{calc} = 1.458 g cm^{-3}, Z = 2. A total of 3161 reflections were recorded with 3° $\le 2\Theta \le$ 52°. Of these, 2833 with $I > 3.0\sigma(I)$ were considered unique and observed. The linear absorption coefficient was 2.15 cm^{-1} for Mo Kα radiation. The final cycle of refinement included 286 variable parameters and converged (largest parameter shift/error = 0.24) with R = 0.041 and R_w = 0.064. The final difference Fourier map was featureless and the largest peak was 0.21 e Å^{-3}.

X-ray Powder Diffraction. X-ray powder diffraction patterns were obtained with a Philips APD 3200 automated powder diffraction system equipped with a Philips control temperature stage. The diffractograms were collected at 45 kV/40 mA using Cu Kα radiation and a graphite monochromator. Approximately 100 mg of sample were spread evenly on the hot-stage X-ray holder and heated in a stepwise fashion. The samples were equilibrated for 10 min after evey 20 °C of heating and an X-ray scan was recorded. The scans were taken at 0.075°/min with 2 < 2θ < 40°. The samples were heated, under a nitrogen atmosphere, until they displayed no peaks in the X-ray powder diffraction pattern.

Molecular Orbital Calculations. Spectroscopic calculations were performed using the INDO/CI algorithm developed by Zerner and co-workers and employed with the Tektronix CAChe

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system operating on a Macintosh fx computer.[40] The integrals used were parameterized for spectroscopic applications. The spectra were generated from single excitation configuration interaction (CI) calculations. The CI space for all molecules included the 18 highest occupied molecular orbitals and the 18 lowest unoccupied molecular orbitals, for a total of 325 configurations. Transition energies and moments are listed in Table 4. The geometries for **1g** and **1r** and their respective dimers, were obtained from the X-ray diffraction data above.

Calorimetry. Differential scanning calorimetric curves were obtained with a DuPont 910 thermal analyzer. Samples (5–10 mg) in aluminum pans were heated at 1 °C/min from 25 to 310 °C under a nitrogen atmosphere.

Thermogravimetric analyses were obtained with a Perkin-Elmer TGA-7 system. Samples (2–10 mg) in platinum pans under a nitrogen atmosphere were heated at 1 °C min^{-1} from 25 to 310 °C.

Thermogravimetric analysis/IR data were collected on a TA Instruments TGA51 interfaced with a Nicolet Magna-IR 550 spectrometer. Samples (15–20 mg) in platinum pans were heated at 10 °C min^{-1} from 25 to 310 °C under a nitrogen atmosphere. A spectrum was collected every 30 s (60 spectra total).

Diffuse reflectance absorption spectra were obtained with a Hitachi U-3501 spectrophotometer. Powdered samples were prepared by grinding either **1r** or **1g** crystals with a mortar and pestle and placing the powder in a screw container with a quartz window. Tungsten iodide and deuterium light sources were used for the visible/near-IR and UV regions of the spectra, respectively. The reflected light from 2400 to 850 nm was detected by a cooled PbS cell. A PMT detector was used from 850 to 200 nm. Data were collected and analyzed on a NEC Powermate SX/16 computer running under MS Windows.

Acknowledgment. Thanks is offered to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research (ACS-PRF 24331-G6) and the Joint Project for the Investigation of the Effect of Water on Molecular Mobility in Pharmaceutical Solids. M.P.K. appreciates fellowship support from the Purdue Research Foundation. P.H.T. thanks Merck Research Laboratories for the use of analytical instruments. We are deeply indebted to Professor Craig Eckhardt for instructive discussions and for suggesting the interpretation of the color difference we express in this manuscript.

Supplementary Material Available: Bond lengths, valence angles, torsion angles, anisotropic thermal parameters, additional hydrogen atom positions and isotropic thermal parameters, XRPD patterns, TGA traces, and diffuse reflectance spectra (31 pages); tables of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.