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Solid-State Chemistry and Structures of a New Class of Mixed Dyes. Cyanine–Oxonol

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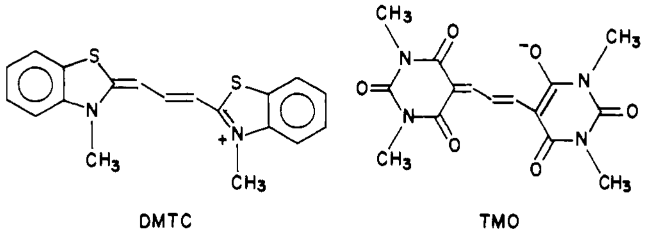
Abstract: Cyanine dye cations and oxonol dye anions are shown to form multiple polymorphic and pseudopolymorphic crystal forms, many of which undergo thermochromic solid-state phase transformations. The crystal structures of two polymorphs of a cyanine–oxonol dye salt, 3,3′-dimethylthiacarbocyanine and 3,3′,5,5′-tetramethyltrimethine–oxonol, both containing chloroform of solvation, have been determined by X-ray crystallography which shows that mixed dye stacks are present in both crystal forms. The cyanine and oxonol ions form mixed stacks, with the long molecular axes of the ions nearly orthogonal in one form, but parallel in the other. The thermochromic desolvation of these polymorphs is discussed in detail, and a summary is given of the phase transformations observed for several of the other crystal forms. Crystal data: $(C_{19}H_{17}N_2S_2)(C_{15}H_{15}N_4O_6)(CHCl_3)$, Ia, $a = 7.660$ (1) Å, $b = 23.950$ (5) Å, $c = 20.201$ (3) Å, $\beta = 82.35$ (2)°, $Z = 4$, $P2_1/c$, $R = 0.096$ (1032 observations); Ib, $a = 14.528$ (4) Å, $b = 13.676$ (3) Å, $c = 18.548$ (5) Å, $\beta = 90.54$ (2)°, $P2_1/a$, $Z = 4$, $R = 0.083$ (1610 observations).

Introduction

An understanding of the relationships between structures and properties of organic solids may be gained by systematically studying their polymorphic forms. This report is concerned with the characterization and solid-state chemistry of a new class of materials which exhibit extensive polymorphic behavior and multiple thermal solid-state transformations. The materials are mixtures of a cationic cyanine and an anionic oxonol dye which form complexes with a wide variety of structures and properties.

The chemistry and *self*-aggregating properties of cyanine dyes have been studied extensively because of their important traditional role as silver halide sensitizers[1] and their more recently discovered use as low-dimensional organic conductors.[2] Oxonol dyes are used as filter dyes in photographic processes and as indicators of membrane potential in biological processes. We have found that representatives of these two dyes, I, will coaggregate, yielding a remarkable number of polymorphs and pseudopolymorphs.



I

Among the relatively few cyanine dye structures which have been reported[3] are several salts of 3,3′-diethyl- or -dimethylthiacarbocyanines (DETC, DMTC),[4,5] DMTC–tetracyanoquinodimethane $(TCNQ)_2^-$,[6] two polymorphs of DETC$(TCNQ)_2$,[7] and DETC·$AuCl_2^-$,[8] salts of thiacyanines,[9] chain-substituted thiacarbocyanines,[10] simple cyanines,[11] merocyanines,[12] and benzimidazolocarbocyanine.[13] In all these structures the cyanine dyes self-aggregate into infinite stacks or dimers,[7] and the counterions serve as space-fillers or self-aggregate. There are no previous crystal structures reported for oxonol dyes.

We present here an overview of the polymorphism and solid-state chemistry of this new mixed dye system, including crystal structures of two polymorphs.

Experimental Section

Crystal Growth and Characterization. Cyanine–oxonol dye salts are prepared by the double decomposition of a cyanine salt and an oxonol salt in solution. The starting materials, obtained from the 3M-Harlow Laboratories, are the tosylate salt 3,3′-dimethylthiacarbocyanine (DMTC) and the tetramethylammonium salt of 3,3′,5,5′-tetramethyltrimethine–oxonol (TMO). The salt which precipitates from solution is compound I. Variations in solvents and conditions of crystallization lead to several different crystal forms of I. Described below are the methods which we found most reliable for producing a particular crystal form. A word of caution is required here, however, since a specific crystal form may not always result from the standard set of conditions. The dye salts themselves cannot be further purified or modified by solvent recrystallization because of their low solubilities in common solvents.

Polymorph Ia, referred to as the gold polymorph, is grown from a chloroform solution of equimolar amounts of DMTC and TMO which have been ground together and dissolved in chloroform. Long shiny gold needles form at the surface of the solution as slow evaporation occurs. The gold crystals are remarkably stable, retaining their high reflectivity after long exposures (years) to the atmosphere and days of exposure to X-ray radiation. Elemental analysis of freshly isolated crystals, after grinding and oven drying, is consistent with a composition of one DMTC and one TMO ion. Anal. Calcd for $C_{34}H_{32}N_6S_2O_6$: C, 59.6; H, 4.7; N, 12.3; S, 9.4. Found: C, 59.1; H, 4.6; N, 12.1 (S, O not determined). Subsequent crystal structure analysis of the gold crystals (described below) shows that this crystal form contains one chloroform molecule for each dye pair. The solvent was not detected by elemental analysis because the oven-drying procedure caused desolvation. Thus the correct empirical formula for Ia is $C_{35}H_{33}N_6S_2O_6Cl_3$. On occasion crystals longer than 5 mm can be grown, in which case transmission polarized microscopy reveals that these crystals are invariably twinned along their

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Table I. Crystal Forms Obtained from DMTC Tosylate and TMO Tetraethylammonium Salt Crystallization

crystal form	color	morphology	solvent
Ia	gold (reflection) red (transmission)	long, narrow plates	$CHCl_3$
Ib	red	plates	$CHCl_3$
Ic	purple	powder or fine needles	$CHCl_3$
Id	purple (reflection) red (transmission)	rhombohedra	$CHCl_3$
Ie	green	fibrous threads	H_2O
If	green–gold	fine needles	CH_3OH
Ig	gold	powder	$CHCl_3$, reflux
Ih	red	trapezoids	$CHCl_3$
Ii	pink	thick plates	$CHCl_3$
Ij	red	narrow plates	$CHCl_3$

Table II. Solid-State Transformations of Cyanine–Oxonol Salts

reactant	product	conditions	crystal changes
Ia	Ik	heat, 180 °C	deep purple front (transmitted light) moves from crystal edges inward
Ib	Ik	heat, 160 °C	crystal turns deep purple at 140 °C (transmitted light)
Id	Ic	X-rays, 4 h or room temp, 12 h	purple reflective faces turn pebbly and opaque, then develop an orange hue
Ic	Ig	heat, 275 °C	fibers become powdered and purple
Ij	In	heat, 80 °C, then to 200 °C	crystals crack and bend at 80 °C, then turn gold in reflective light by 200 °C

long axes. In transmitted light the crystals have a nearly transparent red appearance, and in reflected light, the largest face reflects a brilliant gold color.

Polymorph Ib, referred to as the red polymorph, is grown under the same conditions as Ia. Rarely do these conditions produce exclusively a single polymorph, but single crystals of the two forms can be readily separated manually. The red crystals are more fragile than the gold form, but good single crytsals of the red form can be isolated with care. These crystals are red in reflected as well as transmitted light. Elemental analysis on a powdered sample, air-dried, gave C, 52.7, H, 4.0, N, 11.0, all a few percent lower than calculated for a one-to-one complex of cyanine and oxonol. Crystallographic analysis showed that Ib also contains one chloroform molecule, and thus is a true polymorph of Ia.

The solvents and crystallization conditions for obtaining several other crystal forms of I are summarized in Table I. Because of experimental difficulties, some of the forms have not been completely characterized. We refer to these forms as pseudopolymorphs since they may be solvates or may contain tosylate or tetraethylammonium ions as well as cyanine and oxonol ions. For example, Id is obtained with no residual coprecipitated powder or polycrystalline material when chloroform solutions of equimolar amounts of DMTC and TMO are evaporated to dryness, suggesting that the large purple rhombohedral crystals contain both the dyes and their counterions. Where possible, X-ray powder patterns were used to differentiate polymorphs (these patterns have been deposited as supplementary material).

Thermal-Phase Transformations

Polymorph Ia undergoes an irreversible thermochromic transformation to a deep purple color at about 180 °C when heated on a hot stage. For a freshly recrystallized crystal the purple reaction front begins at one end of the long plate-like crystal and proceeds slowly down its length. If the crystal is removed from the hot plate during this process, the motion of the reaction front is arrested but the frontal motion is resumed upon heating. For older crystals, reaction fronts appear to develop at all the crystal edges and to move toward the center of the crystal. These changes have been recorded on a videotape from which we were able to monitor desolvation rates of several different crystals. For four different freshly grown crystals the temperature at which a color change was first visible ranged from 148 to 152 °C. Reaction was 50% complete, as determined by surface darkening, at about 160 °C and was complete at 170–174 °C. Differential scanning calorimetry showed that the thermochromic rearrangement was endothermic, requiring 8.1 kcal/mol. Thermal gravimetric analysis indicated that a marked weight loss occurred at 180 °C which corresponded to the loss of 1 mol of chloroform.

Polymorph Ib also undergoes an irreversible thermochromic phase transformation as observed by transmission hot-stage microscopy. At 89 °C, the entire crystal darkens but remains transparent. At 100 °C the crystals undergo mechanical stress causing the crystals to jump and bend. Deep purple domains develop at 89 °C, and by 140 °C the crystal has turned completely opaque. In reflected light the product crystals are shiny black. As the temperature is raised above 140 °C, a pink reflectance develops from some surface domains, and occasionally a frontal motion can be observed.

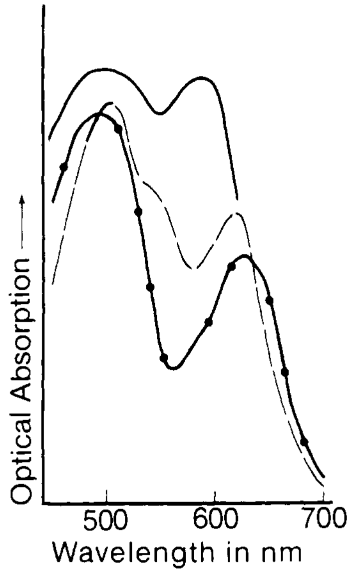

Figure 1. Solid state absorption spectra of cyanine–oxonol dye salts. The spectra were obtained as Nujol mulls: Ia (·–·–·), Ib (– – –), and Ik (—).

A unique polymorphic form, Ik, is obtained from the thermal solid-state transformations of either Ia or Ib. Ik was characterized by infrared and UV/vis spectroscopy and X-ray powder patterns. Ik is a desolvated form, obtainable only by solid-state rearrangement (see Figure 1).

Several of the other polymorphs were also observed to undergo either thermal or X-ray-induced phase changes. A summary of the solid-state changes is given in Table II. Powder pattern analysis of the products of these transformations was used to make product assignments. Ic undergoes a high-temperature transformation to a bright yellow-gold product, Ig. Ic can also be formed in the solid state from Id or Ie. Id crystals are among

Table III. Positional Parameters and Their Estimated Standard Deviations—Polymorph Ia

atom	*X*	*Y*	*Z*	atom	*X*	*Y*	*Z*
S(1)	0.106 (1)	0.3032 (3)	0.3182 (3)	C(22)	0.660 (3)	0.264 (1)	0.388 (1)
N(1)	0.068 (3)	0.1986 (9)	0.302 (1)	C(23)	0.703 (4)	0.295 (1)	0.443 (2)
C(1)	0.116 (3)	0.236 (1)	0.346 (1)	N(4)	0.718 (3)	0.3537 (9)	0.437 (1)
C(2)	0.026 (3)	0.224 (1)	0.244 (1)	C(25)	0.783 (4)	0.389 (1)	0.489 (2)
C(3)	0.031 (3)	0.283 (1)	0.243 (1)	C(24)	0.586 (3)	0.376 (1)	0.268 (1)
C(4)	−0.006 (4)	0.316 (1)	0.193 (1)	C(26)	0.640 (3)	0.204 (1)	0.392 (1)
C(5)	−0.065 (4)	0.286 (1)	0.140 (1)	C(27)	0.690 (3)	0.166 (1)	0.442 (1)
C(6)	−0.081 (4)	0.229 (1)	0.136 (1)	O(1)	0.739 (3)	0.2766 (7)	0.4980 (9)
C(7)	−0.039 (4)	0.195 (1)	0.192 (1)	O(2)	0.703 (2)	0.4312 (7)	0.3707 (9)
C(8)	0.066 (3)	0.136 (1)	0.313 (1)	O(3)	0.560 (3)	0.2655 (7)	0.2838 (8)
C(9)	0.174 (3)	0.2173 (9)	0.407 (1)	C(28)	0.669 (3)	0.110 (1)	0.426 (1)
C(10)	0.215 (3)	0.2606 (9)	0.450 (1)	C(30)	0.688 (3)	0.011 (1)	0.428 (2)
S(2)	0.283 (1)	0.3641 (3)	0.5378 (3)	C(31)	0.709 (3)	0.063 (1)	0.466 (1)
N(2)	0.401 (3)	0.2867 (8)	0.609 (1)	N(5)	0.731 (3)	−0.038 (1)	0.465 (1)
C(11)	0.284 (3)	0.251 (1)	0.508 (1)	C(29)	0.775 (4)	−0.038 (1)	0.528 (2)
C(12)	0.319 (3)	0.295 (1)	0.550 (1)	N(6)	0.779 (3)	0.0129 (9)	0.560 (1)
C(13)	0.417 (3)	0.337 (1)	0.645 (1)	C(32)	0.759 (4)	0.066 (2)	0.530 (2)
C(14)	0.376 (3)	0.385 (1)	0.609 (1)	C(33)	0.722 (4)	−0.095 (1)	0.432 (2)
C(15)	0.378 (4)	0.439 (1)	0.636 (1)	C(34)	0.814 (4)	0.015 (1)	0.632 (1)
C(16)	0.454 (3)	0.441 (1)	0.694 (1)	O(4)	0.763 (3)	0.1097 (8)	0.563 (1)
C(17)	0.508 (4)	0.394 (1)	0.729 (1)	O(5)	0.645 (3)	0.0033 (8)	0.3747 (9)
C(18)	0.495 (4)	0.340 (1)	0.702 (1)	O(6)	0.801 (3)	−0.0786 (8)	0.561 (1)
C(19)	0.453 (3)	0.230 (1)	0.630 (1)	C(35)	0.071 (4)	0.481 (1)	0.350 (1)
C(20)	0.689 (3)	0.381 (1)	0.378 (1)	Cl(1)	0.150 (1)	0.4809 (4)	0.2643 (4)
N(3)	0.630 (3)	0.3475 (8)	0.328 (1)	Cl(2)	0.226 (1)	0.4426 (3)	0.3894 (4)
C(21)	0.615 (3)	0.289(1)	0.333 (1)	Cl(3)	0.9324 (1)	0.0477 (3)	0.1202 (4)

the easiest of the series of polymorphs to grow, readily forming large highly characteristic purple rhombohedra which have intense blue edges. Unfortunately, this is an unstable crystal form, rearranging to polycrystalline Ic in several hours under ambient conditions. Crystals of Ie, which have a spaghetti-like morphology, also rearrange to Ic with mild heat or abrasion. IR spectra of Ie are unique in lacking a 960-cm^{-1} band, suggesting that Ie contains cyanine dye molecules in an unstable cis conformation which rearranges to trans with heat or pressure.

Crystal Structure Analysis. Crystal Data for Polymorph Ia: $C_{35}H_{33}N_6O_6S_2Cl_3$, mol wt 804, monoclinic, $P2_1/c$, $a = 7.660$ (1) Å, $b = 23.950$ (5) Å, $c = 20.201$ (3) Å, $\beta = 82.33$ (2)°, $V = 3673$ Å^3, $D = 1.454$ g cm^{-1}, $Z = 4$, $\mu = 37.3$ cm^{-1}, 0.56 × 0.08 × 0.03 mm. Unit cell dimensions were obtained on a Nonius CAD-4 diffractometer (Cu Kα = 1.5418 Å, graphite monochromator) by a least-squares fit of 25 reflections ($6° < 2\theta < 68°$). A total of 7999 reflections was collected in the octants h, k, $\pm l$ to $2\theta = 150°$ for a total of 4861 unique reflections (after averaging equivalent reflections) of which 1032 were considered above zero at the $3\sigma(I)$ significance level. Lorentz and polarization corrections and empirical absorption corrections were applied. Transmission varied from 69.6 to 99.8%.

SHELX direct methods programs[15] were used for structure solution. An E-map showed all but four of the nonhydrogen atoms in the cyanine and oxonol ions, and also showed a solvent fragment. A difference map revealed the remaining nonhydrogen atoms. Several cycles of refinement of all the positional parameters with fixed isotropic temperature factors gave an R factor of 0.17. Using $1/\sigma(F^2)$ weights and conversion of the heavy atoms to anisotropic temperature factors, a final R factor of 0.096 was obtained, $R_w = 0.101$. Several hydrogen atoms were found in a difference map but were not included in the final refinements. No other electron density peaks greater than 0.4 e/Å^3 were observed. No significant improvement in R factors was obtained for cutoff values lower than $3\sigma(I)$. The final coordinates and molecular geometry are presented in Table III and Figure 2a.

Crystal Data for Polymorph Ib: monoclinic, $P2_1/a$, $a = 14.528$ (4) Å, $b = 13.676$ (3) Å, $c = 18.548$ (5) Å, $\beta = 90.54$ (2)°, $V = 3685$ Å^3, $D = 1.449$ g cm^{-1}, $Z = 4$, $\mu = 37.8$ cm^{-1}, 0.34 × 0.44 × 0.02 mm. Unit cell dimensions were obtained on a Nonius CAD-4 diffractometer (Cu Kα 1.5418 Å) by a least-squares fit of 25 reflections ($12° < 2\theta < 50°$). A total of 5190 reflections was collected in the octants h, k, $\pm l$ to $2\theta = 110°$ for a total of 4625 unique reflections (after averaging equivalent reflections) of which 1610 were considered above zero at the $3\sigma(I)$ significance level. Lorentz and polarization corrections were applied, but absorption corrections were not made.

The crystal structure was solved using the MULTAN direct methods programs available in the Nonius Structure Determination Package.[16] An E-map revealed nearly all the heavy atom positions and indicated the unexpected presence of chloroform solvent. Subsequent least-squares refinements and difference maps revealed 26 of the 33 hydrogens. These positions were included and refined, but the hydrogen temperature factors were fixed at 6.0 Å^2. A final R factor of 0.083 and $R_w = 0.099$ ($1/(\sigma F^2)$ weights) were obtained. A final difference map showed no electron density peaks greater than 0.47 e/Å^3. No extinction corrections were made, but several low-order reflections for which $F_c \gg F_o$ were rejected from the final refinement. The final coordinates and molecular geometry are presented in Table IV and Figure 2b. (Structure factor tables and thermal parameters for both polymorphs are available as supplementary material.)

Molecular and Crystal Structures

In polymorphs Ia and Ib, DMTC cations are in an all trans conformation. The sulfur atoms are in a cis arrangement and the hydrogens along the chain are trans to one another. The ions are planar to within ±0.05Å with a 9° angle between the benzthiazole rings in Ia and 7° in Ib. As seen from the bond lengths in Figures 2a and 2b, both cyanines have nearly equivalent bond lengths along the chain from N_1 to N_2, indicating extensive electron delocalization along the cyanine chains. This intramolecular geometry is very similar to that found for other unsubstituted carbocyanine dye structures.[3-13]

The intramolecular geometries of the TMO anions are also similar for the two polymorphic forms, both of them showing equivalent bond lengths along the hydrocarbon chains and adopting conformations which are planar to within ±0.05 Å (7° between oxonol rings in both Ia and Ib). In addition, both polymorphs are stabilized by a hydrogen bond between the chloroform C(35)–H and the oxonol O(6) atom. The C(35)···O(6) distances are 3.02 (2) and 3.04 (1) Å for Ia and Ib, respectively. To our knowledge, these are the first crystal structures of oxonol dyes

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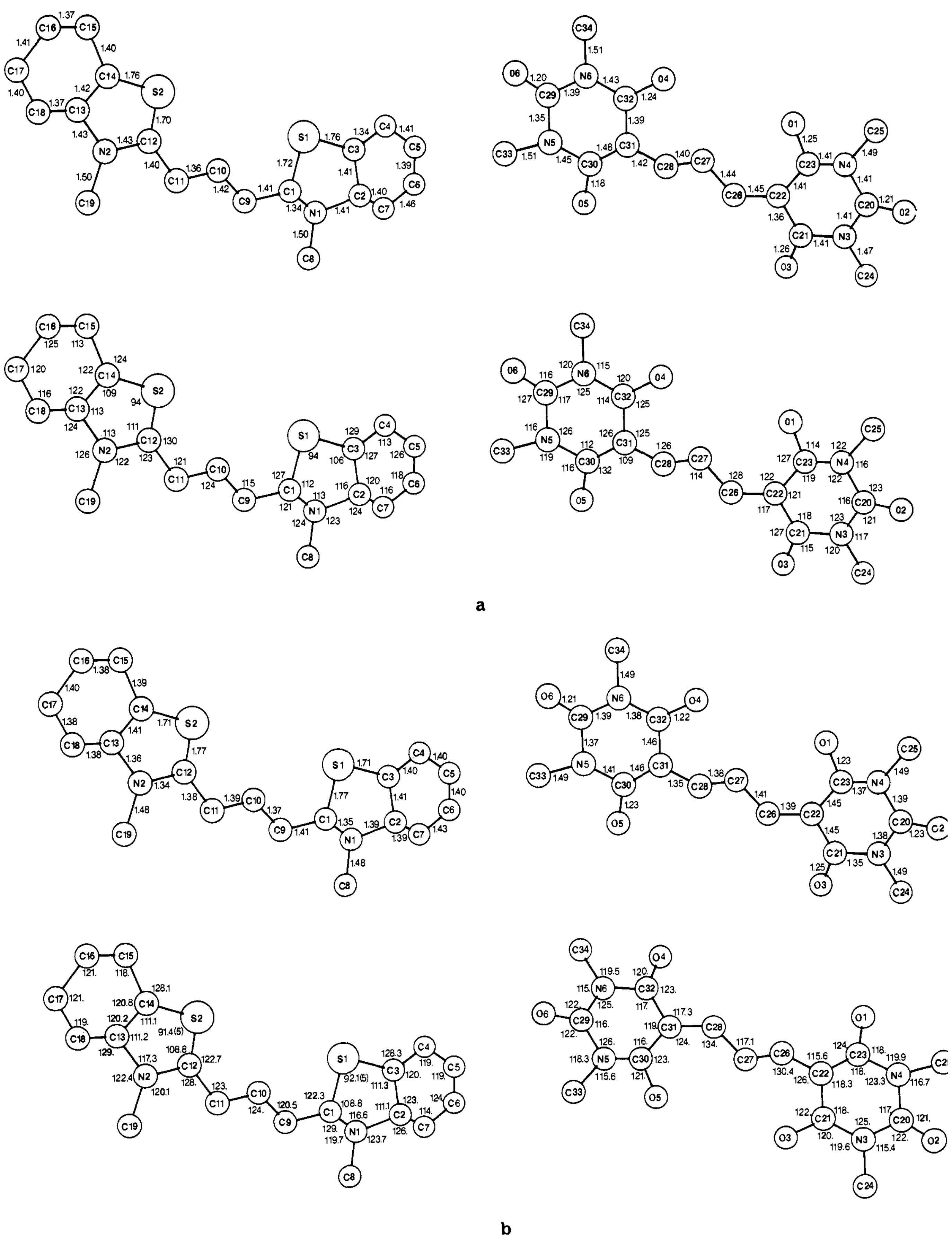

Figure 2. Bond lengths and angles obtained from crystal structure analysis of Ia and Ib. (a) Geometry of the cyanine and oxonol ions present in Ia (esd's are from 0.02 to 0.04 Å, and 1.0 to 2.6°). (b) Geometry of the dye ions in polymorph Ib (esd's, 0.008 to 0.012 Å and 0.5 to 1.0°).

Table IV.[a] Positional Parameters and Their Estimated Standard Deviations—Polymorph Ib

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Cl1	0.7520 (3)	−0.1863 (4)	0.2035 (2)	7.5 (1)	C24	0.6625 (9)	0.002 (1)	0.4509 (7)	5.0 (4)
Cl2	0.6891 (4)	−0.1413 (3)	0.0622 (2)	8.3 (1)	C25	0.688 (1)	−0.332 (1)	0.3624 (7)	4.9 (3)
Cl3	0.7211 (4)	−0.3402 (3)	0.1044 (3)	11.0 (2)	C26	0.5811 (8)	−0.2797 (9)	0.6080 (6)	2.8 (3)
S1	0.6890 (3)	0.1787 (3)	0.3197 (2)	4.29 (9)	C27	0.5523 (8)	−0.2367 (9)	0.6731 (6)	3.3 (3)
S2	0.5740 (2)	0.1805 (3)	0.5725 (2)	3.87 (9)	C28	0.5224 (8)	−0.2992 (9)	0.7268 (6)	3.3 (3)
O1	0.6271 (6)	−0.3934 (6)	0.4918 (4)	4.6 (2)	C29	0.4385 (9)	−0.270 (1)	0.9426 (7)	4.5 (3)
O2	0.7141 (6)	−0.1358 (6)	0.3565 (4)	4.7 (2)	C30	0.4914 (9)	−0.1900 (9)	0.8306 (7)	3.9 (3)
O3	0.6020 (5)	−0.0701 (6)	0.5777 (4)	4.0 (2)	C31	0.4927 (8)	−0.2854 (9)	0.7948 (6)	2.9 (3)
O4	0.4601 (6)	−0.4538 (6)	0.8080 (4)	5.2 (3)	C32	0.4627 (9)	−0.3720 (9)	0.8348 (7)	3.8 (3)
O5	0.5123 (6)	−0.1130 (6)	0.8004 (4)	4.7 (2)	C33	0.467 (1)	−0.093 (1)	0.9406 (8)	6.0 (4)
O6	0.4172 (7)	−0.2640 (7)	1.0054 (4)	6.2 (3)	C34	0.402 (1)	−0.444 (1)	0.9478 (8)	5.9 (4)
N1	0.7374 (7)	0.3411 (7)	0.2641 (5)	3.5 (2)	C35	0.763 (1)	−0.221 (1)	0.1145 (7)	4.9 (4)
N2	0.5601 (7)	0.3458 (7)	0.6337 (5)	3.2 (2)	H1	0.794 (7)	0.463 (8)	0.309 (6)	6*
N3	0.6536 (6)	−0.1041 (7)	0.4670 (5)	3.1 (2)	H2	0.706 (7)	0.466 (8)	0.232 (6)	6*
N4	0.6668 (7)	−0.2661 (7)	0.4238 (5)	3.1 (2)	H3	0.811 (7)	0.445 (8)	0.217 (6)	6*
N5	0.4647 (7)	−0.1903 (8)	0.9037 (5)	4.2 (3)	H4	0.497 (7)	0.477 (8)	0.619 (6)	6*
N6	0.4354 (7)	−0.3583 (7)	0.9053 (5)	3.9 (3)	H5	0.611 (7)	0.477 (8)	0.606 (6)	6*
C1	0.7000 (8)	0.3074 (9)	0.3258 (6)	3.3 (3)	H6	0.541 (7)	0.462 (8)	0.697 (6)	6*
C2	0.7541 (9)	0.2723 (9)	0.2106 (7)	3.6 (3)	H8	0.830 (8)	0.223 (8)	0.041 (6)	6*
C3	0.7344 (9)	0.1771 (9)	0.2349 (7)	3.9 (3)	H10	0.738 (7)	0.052 (8)	0.207 (6)	6*
C4	0.749 (1)	0.096 (1)	0.1898 (7)	5.7 (4)	H11	0.532 (7)	0.042 (8)	0.683 (6)	6*
C5	0.7848 (9)	0.111 (1)	0.1209 (7)	5.2 (4)	H13	0.500 (8)	0.231 (8)	0.846 (6)	6*
C6	0.804 (1)	0.207 (1)	0.0988 (7)	4.8 (3)	H14	0.521 (7)	0.363 (8)	0.785 (6)	6*
C7	0.7895 (9)	0.292 (1)	0.1425 (7)	4.1 (3)	H16	0.640 (8)	0.246 (8)	0.440 (6)	6*
C8	0.7614 (9)	0.446 (1)	0.2577 (7)	4.5 (3)	H18	0.463 (7)	−0.478 (8)	0.955 (6)	6*
C9	0.6718 (8)	0.3602 (9)	0.3869 (6)	3.3 (3)	H19	0.365 (7)	−0.477 (8)	0.908 (6)	6*
C10	0.6370 (9)	0.3123 (9)	0.4457 (7)	3.7 (3)	H20	0.351 (7)	−0.416 (8)	0.980 (6)	6*
C11	0.6128 (8)	0.3590 (9)	0.5093 (6)	3.4 (3)	H21	0.539 (7)	−0.081 (8)	0.935 (5)	6*
C12	0.5835 (9)	0.3094 (9)	0.5694 (7)	3.6 (3)	H22	0.406 (7)	−0.079 (8)	0.919 (6)	6*
C13	0.5388 (8)	0.2807 (9)	0.6866 (6)	3.1 (3)	H23	0.483 (7)	−0.119 (8)	1.008 (6)	6*
C14	0.5444 (8)	0.1838 (9)	0.6614 (6)	3.6 (3)	H24	0.521 (7)	−0.366 (8)	0.708 (6)	6*
C15	0.5269 (9)	0.105 (1)	0.7070 (7)	4.4 (3)	H25	0.561 (8)	−0.170 (8)	0.677 (6)	6*
C16	0.504 (1)	0.125 (1)	0.7777 (7)	5.1 (4)	H27	0.719 (7)	0.016 (8)	0.474 (6)	6*
C17	0.501 (1)	0.221 (1)	0.8030 (8)	5.5 (4)	H28	0.599 (7)	0.009 (8)	0.443 (6)	6*
C18	0.5158 (9)	0.299 (1)	0.7573 (7)	4.1 (3)	H30	0.722 (8)	−0.331 (8)	0.392 (6)	6*
C19	0.5640 (9)	0.453 (1)	0.6467 (7)	4.7 (3)	H31	0.736 (7)	−0.407 (9)	0.388 (6)	6*
C20	0.6810 (8)	−0.1663 (9)	0.4129 (6)	3.1 (3)	H32	0.675 (8)	−0.316 (9)	0.309 (6)	6*
C21	0.6223 (8)	−0.1328 (9)	0.5317 (6)	3.2 (3)	H15	0.617 (7)	0.428 (8)	0.514 (5)	6*
C22	0.6137 (8)	−0.2370 (8)	0.5453 (6)	2.9 (3)	H12	0.510 (7)	0.047 (8)	0.800 (6)	6*
C23	0.6351 (8)	−0.3044 (9)	0.4871 (6)	3.2 (3)					

[a] Cl, S, and O atoms were refined anisotropically; the hydrogen temperature factors were not refined. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

to be reported in the literature.

Although intramolecular geometries are similar, there are striking differences in the packing patterns of the two polymorphs. In both structures the dyes are aggregated into mixed stacks with the DMTC and TMO ions alternating along the stack. In Ia the nearest neighbor cyanine and oxonol ions are approximately coplanar and pack with their long molecular axes crossed, as seen in Figure 3a. The closest nonhydrogen contact between these molecules is 3.2 Å between N(2) of the cyanine and O(1) of the oxonol portion. In Ib, the cyanine and oxonol ions are not only coplanar but also have their long molecular axes aligned nearly parallel to one another (Figure 3b) with the closest interion contact being 3.3 Å between N(2) and O(2).

In Ia, the dyes form stacks by translation along the *a* direction; in Ib, the stacks are formed along the *a*-glide direction. Stereoviews along the *a* axes (Figure 4) show the contents of the unit cells of the two structures. The cyanines form extended chain structures with close contacts between C(8) and C(16) of 3.8 Å. The cyanine molecules in Ib are isolated from one another by chloroform molecules and pack in a pattern much like that of the oxonol ions. In both structures, chloroform molecules fill the planes between adjacent dye stacks. Morphologically, the (011) plane corresponds to the long narrow edge of the elongated plates of Ia, and the (101) plane corresponds to the smallest plate edge of Ib, as shown in Figure 5.

The (010) planes of Ia and Ib show nearly isostructural packing of the mixed dye stacks, with only 5° difference between their respective slip angles (Figure 6). Since the (010) plane in Ia is a highly reflective face, similar reflectivity is expected from the (010) face of Ib, but this face is not well enough developed to

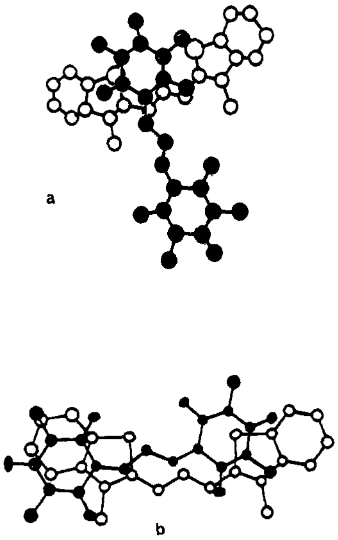

Figure 3. Intermolecular interactions between neighboring cyanine and oxonol dyes in Ia and Ib. (a) The geometrical arrangement of neighboring cyanine (open circles) and oxonol (shaded circles) dyes as seen along [100] in the structure of Ia. This pair is repeated along the *a* axis to form an infinite stack. (b) The analogous arrangement of neighboring dyes in the structure of Ib, viewed along [100]. This unit is also repeated along its *a* axis to form a mixed dye stack.

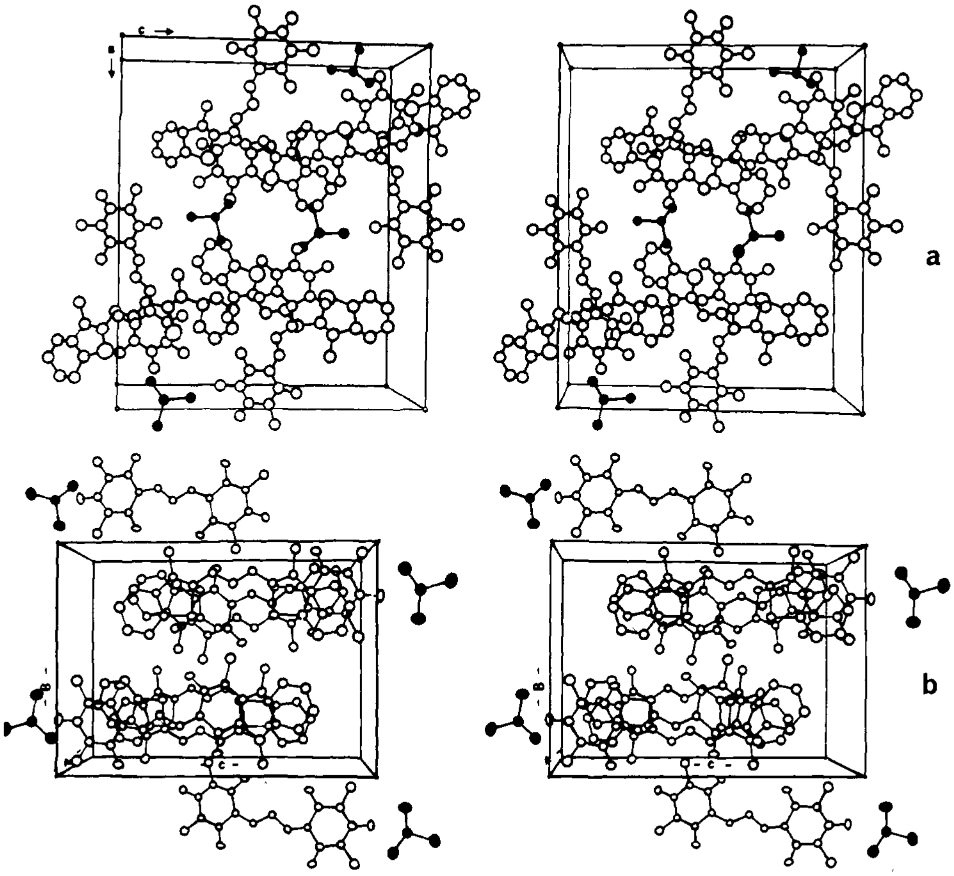

Figure 4. Stereo pair views of the unit cells of Ia and Ib. (a) [100] stereoview of the entire unit cell of Ia. Chloroform molecules of solvation (shaded black in the figure) fill (010) planes of the structure, providing stabilization via a hydrogen bond interaction with the oxonol dye. The solvent also provides a barrier to interstack dye interactions along *b*. (b) [100] stereoview of the entire unit cell of Ib. Chloroform molecules (shown in black) are hydrogen bonded to oxonol dyes, analogous to Ia. They pack in the (001) planes and prevent interstack interactions along the *c* axis. In this polymorph there is no apparent interweaving of neighboring stacks, as found in Ia. Both figures are viewed looking down the mixed dye stack axes.

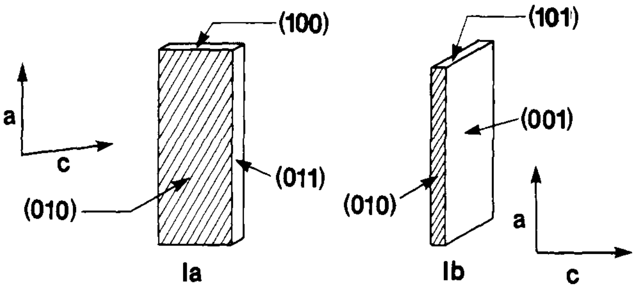

Figure 5. Crystal morphologies and Miller indices of the major faces are shown schematically for (a) Ia, and (b) Ib. The (010) face of Ia gives pseudo-metallic gold reflectance. These crystals can be grown such that they are greatly elongated along the *a* direction. A (100) twin plane can frequently be seen in large crystals of Ia. Crystals of Ib are more fragile than those of Ia, striations and cracks frequently occurring on the (001) face due to cleavage along (010). The (010) and (101) planes of Ib are usually very small.

observe its specular reflectance.

Polymorphism and Solid-State Transformations

The plethora of polymorphic forms and solid-state transformations described here for I may initially seem uncharacteristic of organic solids. However, the available literature on cyanine dye chemistry indicates that many dyes exhibit polymorphism and that the number of known polymorphic forms often increases in proportion to the extent of the research effort. Linear *trans*-quinacridone, for example, has been found to exist in seven polymorphic forms.[17] In addition, it is well known that cyanine dyes can simultaneously form multiple aggregate structures in solution,[18] each of which could be a nucleus for crystallization of a different polymorph.

There is evidence in the cyanine dye literature that solid-state reactivity occurs frequently among cyanine dyes, but it clearly is an unexplored area of research. Examples include cyanine halide crystals which are unstable in light, causing crystals which look perfect to the eye, having well-defined edges and faces, to give very poor diffraction patterns and little or no extinction under polarized light;[5] DETC bromide–methanol crystals spontaneously disintegrate when removed from the mother liquor. Interestingly, the same phenomenon occurs for the unsolvated bromide crystals, so disintegration is not simply a desolvation.[5] Such unpredictable crystal behavior is usually considered a nuisance, particularly if crystal structure analysis is necessary; consequently, much of the crystal chemistry of dyes remains unstudied.

In the crystal system reported here, 14 polymorphic or pseudopolymorphic forms of I have been identified and several of their solid-state changes characterized. The crystal structures of only two of these forms have been obtainable because of practical problems with crystal quality and stability. The structures of Ia and Ib presented here show that cyanine and oxonol dyes aggregate into mixed stacks, despite the fact that each dye independently is a self-aggregating dye.[19] The geometrical relationship between neighboring dye molecules in the stacks differs in the two polymorphs. In Ia the long molecular axes of the cyanine and oxonol dyes are almost nearly orthogonal, and their molecular slip angle is 20° (Figure 3a). In Ib the mixed dyes are stacked like a deck of cards, analogous to the stacking patterns of many cyanine dye

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(17) Whitaker, A. "Analytical Chemistry of Synthetic Dyes"; Wiley: New York, 1977; p 269.

(18) Smith, D. L.; Luss, H. R. *Acta Crystallogr., Sec. B* **1972**, *28*, 2793.

(19) Cash, D. J. *J. Chromatogr.* **1981**, *209*, 405.

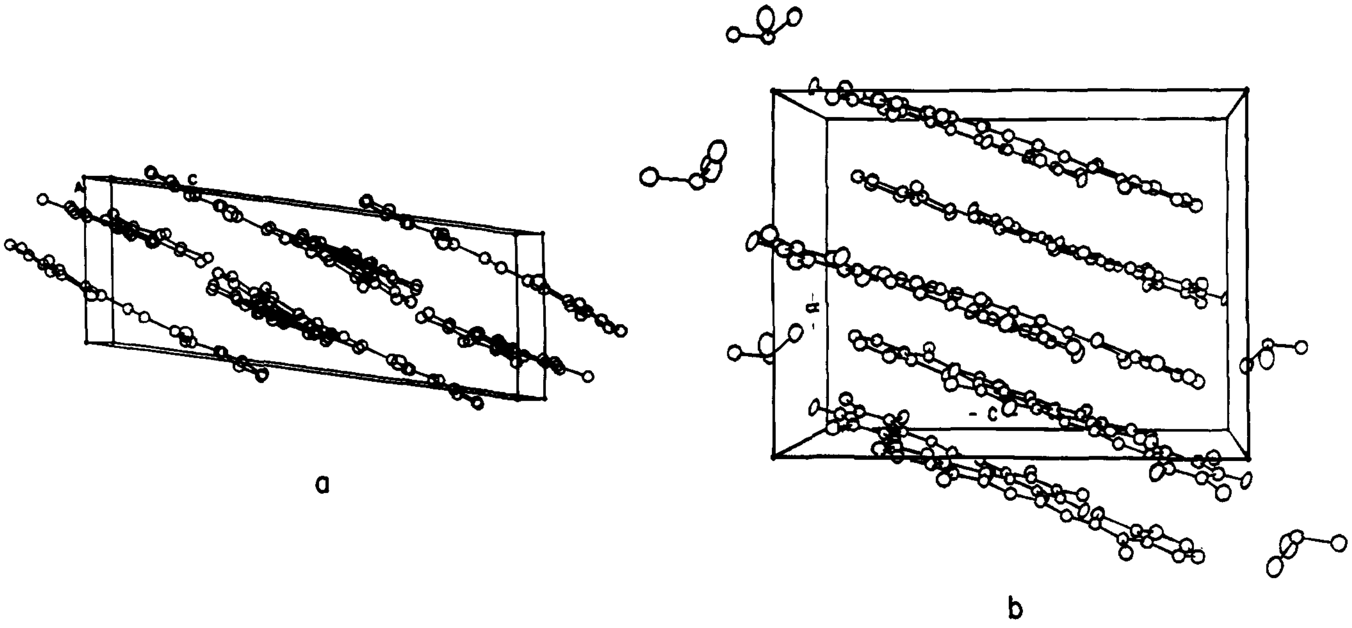

Figure 6. Direction of isomorphous packing in Ia and Ib. The packing of cyanine and oxonol dyes in the (010) planes of (a) Ia and (b) Ib show a remarkable similarity. Viewed in this direction, the dye aggregation pattern is similar to that suggested for aggregation of cyanine dyes in solution.[14] The molecular slip angles measure 20° for *Ia* and 25° for Ib. (Chloroform molecules have been deleted from part a for clarity.)

crystals,[3] with a molecular slip angle of 25° (Figure 3b).

These differences in spatial relationships are manifested in their solid-state spectra. The peak on the long-wavelength side of the band at 600 nm in Ib is shifted to 620 nm in Ia. The short-wavelength side of the band is also significantly different in the two polymorphs. A detailed analysis of the correlation between observed spectra and specific crystal structural features can be made from polarized spectroscopic studies of single crystals. Reports describing this technique have appeared recently.[20]

Many cyanine dyes crystallize with solvent of crystallization, but the role of solvent in stabilizing the crystal structures is often unclear. Chloroform is present in the structures of both Ia and Ib and is hydrogen bonded to the terminal oxonol carbonyl group in each case. Cocrystallization of cyanine and oxonol dyes in chloroform solution may be a general way to produce stable cyanine dye crystals for crystallographic studies. The aggregates formed in Ia and Ib are extremely stable to light, atmospheric conditions, and mild heating, unlike some cyanine structures where the aggregates are more light sensitive than the independent molecules.[13]

Thermochromic phase transformations caused by loss of chloroform occur for both Ia and Ib. The two polymorphs transform to the same deep purple polycrystalline form, as confirmed by X-ray powder pattern analysis and UV/vis spectroscopy. Crystal morphologies remain unchanged during the process, but mechanical strength and crystal transparency are lost. Crystal structure analyses of polymorphic forms Ic–e, and Ij are needed to fully characterize their solid-state chemistry. The spontaneous topotactic decomposition of Id may be a desolvation process, but the new diffraction pattern which develops does not correspond to diffraction patterns of other crystal forms. The color changes associated with the transformations of Ie and Ic may involve conformational changes in the cyanine molecules and possibly rearrangements of dye stack geometry. From these observations it is clear that the isolation and characterization of particular solid-state forms of cyanine dyes are not straightforward, and that one easily can be misled about composition and structure of individual crystals.

This work has demonstrated that cyanine dyes can form mixed aggregate stacks with oxonol dyes. A multiplicity of polymorphic forms exists in this system suggesting that cyanine and oxonol dyes can interact in many favorable configurations. In two of the crystal forms, characterized here by crystal structure analysis, mixed aggregate stacks are observed. Many of the crystal forms undergo thermal phase changes involving desolvation and polymorphic transformations; each of these phenomena perturbs the electronic structures of the complexes. A systematic study of these uniquely solid-state events requires the application of both structural and spectroscopic methods to provide the basis for understanding and predicting structure–property relations in dye systems.

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Registry No. I, 92346-44-6.

Supplementary Material Available: Structure factor tables, temperature factors, and X-ray powder pattern *d*-spacings (23 pages). Ordering information is given on any current masthead page.

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[20] (a) Tanaka, J.; Tanaka, M.; Hayakawa, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3109. (b) Makio, S.; Kananmuru, N.; Tanaka, J. *Ibid.* **1980**, *53*, 3120. (c) Tristani-Kendra, M.; Eckhardt, C. J.; Bernstein, J.; Goldstein, E. *Chem. Phys. Lett.* **1983**, *98*, 57.