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Crystal Structure of a Methanol Solvate of 3,3'-Diethyl-9-phenylthiacarbocyanine Iodide, a Photographic Sensitizing Dye

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Abstract

The crystal structure of the title compound, $(C_{27}H_{25}N_2S_2)^+I^- \cdot xCH_3OH$, $x \approx 0.5$, a spectral sensitizing dye in silver halide photography, has been determined by X-ray analysis. The compound crystallizes in the monoclinic space group $C2/c$, with eight formula units in a cell of dimensions: $a = 19.766$ (3), $b = 11.112$ (2), $c = 25.296$ (4) Å, and $\beta = 110.47$ (1)°. The structure was refined by block-diagonal least-squares calculations to a conventional R of 0.051 for 3301 observed [$|F_o| > 3\sigma(F)$] reflexions collected on an automatic diffractometer. The dye cation has approximate m symmetry: the methine chain assumes an extended all-*trans* form, the S atoms are *cis* about the chain, and the phenyl-ring plane is almost perpendicular to the conjugate system. In the crystals the cations are stacked in columns, the mean perpendicular separations between them being alternately 4.10 and 3.66 Å with the respective slip angle of about 90 and 25°. The columns aggregate to form a herring-bone-like pattern. The I^- ions occupy special positions having the site symmetries of $\bar{1}$ and 2. The disordered methanol molecules partially fill vacancies in the crystal structure.

Introduction

Thiacarbocyanines are useful spectral sensitizing dyes in silver halide photography. Various derivatives have been examined for practical use. A bulky *meso*-(or 9-)

substituent in a thiacarbocyanine dye causes a large steric influence on its conformation, and hence on its spectral sensitization (review articles: Sturmer & Heseltine, 1977; Herz, 1977). As a part of our studies on the spectral sensitizing dyes by means of X-ray crystallography, the present study has been undertaken to elucidate the influence of a *meso*-phenyl substituent on the molecular structure and the stacking of dyes in the crystals.

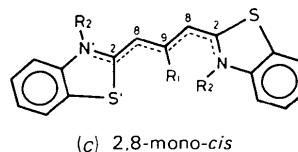
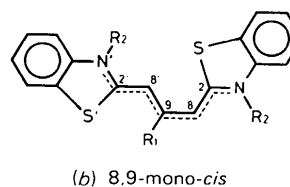
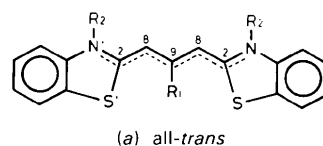


Fig. 1. Possible configurations of thiacarbocyanine dye. R_1 : alkyl or phenyl, R_2 : alkyl.

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Thiacarboyanine may exist in the extended all-*trans*, the 8,9- (or half-turned) mono-*cis*, or the 2,8-mono-*cis* forms (Fig. 1), and the equilibrium between these isomers in solution has been discussed (West, Pearce & Grum, 1967; O'Brien, Kelly & Costa, 1974; Simson, 1974; Steiger, Kitzing, Hagen & Stoeckli-Evans, 1974). Among the thiacarboyanines so far studied by X-ray structure analysis the dyes in 3,3'-diethylthiacarboyanine bromide and its ethanol solvate (Wheatley, 1959*a,b*) and 5,5'-dichloro-3,3',9-triethylthiacarboyanine bromide acetic acid solvate crystals (Potenza & Mastropaolo, 1974) assume the all-*trans* form while those in 5,5',7,7'-tetramethyl-3,3',9-triethylthiacarboyanine perchlorate (Stoeckli-Evans, 1974), 3,3',9-triethylthiacarboyanine bromide pentahydrate (K. Nakatsu *et al.*, unpublished work), and 3,3'-dimethyl-9-ethylthiacarboyanine iodide crystals (K. Nakatsu *et al.*, unpublished work) have the 8,9-mono-*cis* form. No dyes having 2,8-mono-*cis* or any other forms have been found, probably because of the extremely high overcrowding.

Experimental

The compound was obtained from the Japanese Research Institute for Photosensitizing Dyes (Okayama, Japan). Slow evaporation of a methanol solution of the compound yielded dark-red, single crystals elongated along **b**. Preliminary oscillation and Weissenberg photographs indicated the monoclinic space group *Cc* or *C2/c*; a successful structure determination was accomplished in *C2/c*. A specimen, approximately 0.21 × 0.42 × 0.21 mm, was used for X-ray data collection on a computer-controlled four-circle diffractometer. The cell parameters were determined with Mo *K* α radiation ($\lambda = 0.71069$ Å) by a least-squares fit of 25 reflexions in the range $26 < 2\theta < 35^\circ$. Table 1 gives the crystal data. Intensities for the independent reflexions for $2\theta < 50^\circ$ were measured with the ω - 2θ continuous scan mode at a 2θ rate of 4° min^{-1} by use of graphite-monochromatized Mo *K* α radiation. The scan width in 2θ was $(2.0 + 0.68 \tan \theta)^\circ$ with background counts of 10 s duration on either side of the peak. The intensities were corrected for Lorentz and polarization factors, but not for absorption. A total of 3301 reflexions with $|F_o| > 3\sigma(F)$ were used for the structure determination.

Table 1. Crystal data of 3,3'-diethyl-9-phenylthiacarboyanine iodide

$(\text{C}_{27}\text{H}_{25}\text{N}_2\text{S}_2)^+\text{I}^- \cdot x\text{CH}_3\text{OH}$, $x \approx 0.5$, FW 584.55	
Monoclinic	Space group: <i>C2/c</i>
$a = 19.766$ (3) Å	$Z = 8$
$b = 11.112$ (2)	$D_x = 1.492$ Mg m^{-3}
$c = 25.296$ (4)	$D_m = 1.45$
$\beta = 110.47$ (1) $^\circ$	$\mu(\text{Mo } K\alpha) = 1.42$ mm^{-1}
$V = 5205$ (1) Å 3	

Structure determination and refinement

The structure was solved by the usual heavy-atom method. Refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms gave R ($= \sum ||F_o| - |F_c|| / \sum |F_o|$) of 0.13, unit weight being assumed for all the reflexions. The aromatic H atoms and the solvent molecules were located from a difference Fourier map, but the ethyl H atoms were not found. Block-diagonal least-squares refinement with anisotropic thermal parameters for all atoms except for the solvent molecule and the H atoms converged to $R = 0.051$. The weighting scheme used in the final cycle of the refinement was $1/w = \sigma(F)^2 + 0.0005(F_o)^2$. The final $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ was 0.048. Atomic scattering factors for I $^-$, S, O, N, and C were taken from *International Tables for X-ray Crystallography* (1974); for H those of Stewart, Davidson & Simpson (1965) were used. All computations were carried out on a FACOM 270/20 computer of this university with the programs developed by the authors. The final positional parameters are listed in Table 2.*

Description of the structure and discussion

Molecular structure

A view of the dye cation is shown in Fig. 2. Table 3 lists the interatomic distances and bond angles. Table 4 gives equations of relevant planes, deviations of atoms from those planes, and the dihedral angles. The methine chain assumes an extended all-*trans* form and the S atoms are *cis* about the chain. The 9-phenyl-ring plane is almost perpendicular to the main cationic plane. The C(9)–C(14) length of 1.493 (7) Å is close to the accepted single-bond length between trigonal C atoms. These facts indicate that the phenyl group does not participate in the resonance of the thiacarboyanine skeleton. The CH $_3$ groups protrude from the benzothiazole planes in the same direction. The cation is slightly bowed rather than twisted, the interplanar angle between the benzothiazole planes, *A* and *B*, being 15.7° . Hence the dye cation has approximate *m* (C_s) symmetry.

The distances between C(14) and the S atoms, 3.000 (6) and 3.015 (5) Å, are considerably shorter than the sum of the van der Waals radii (1.7 Å for aromatic C and 1.85 Å for S). This shows that a propensity for retaining the dye planar to gain a larger overlap of π orbitals in the conjugate system is larger

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33979 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Final fractional coordinates ($\times 10^4$, for H $\times 10^3$) with standard deviations in parentheses

	x	y	z
I(1)	0	0	0
I(2)	0	7350.1 (7)	2500
S(1)	2029.3 (9)	1843 (2)	3474.6 (7)
C(2)	2870 (3)	2521 (5)	3785 (2)
N(3)	3369 (3)	1995 (5)	3596 (2)
C(4)	3502 (4)	329 (6)	2981 (3)
C(5)	3134 (5)	-611 (7)	2634 (3)
C(6)	2407 (5)	-809 (7)	2517 (3)
C(7)	2017 (4)	-109 (7)	2753 (3)
C(8)	3040 (3)	3450 (5)	4177 (2)
C(9)	2576 (3)	4072 (5)	4397 (2)
C(10)	3113 (3)	1025 (5)	3229 (3)
C(11)	2379 (4)	816 (6)	3110 (3)
C(12)	4149 (3)	2337 (7)	3796 (3)
C(13)	4574 (4)	1532 (8)	4292 (3)
S(1')	1648.3 (8)	5691 (2)	5011.7 (7)
C(2')	2579 (3)	5576 (5)	5141 (2)
N(3')	2955 (3)	6274 (4)	5582 (2)
C(4')	2786 (4)	7604 (6)	6317 (3)
C(5')	2263 (4)	8174 (6)	6488 (3)
C(6')	1542 (4)	8027 (6)	6204 (3)
C(7')	1294 (3)	7278 (6)	5743 (3)
C(8')	2902 (3)	4866 (5)	4839 (3)
C(10')	2537 (3)	6886 (5)	5842 (3)
C(11')	1800 (3)	6701 (5)	5571 (3)
C(12')	3766 (3)	6424 (6)	5776 (3)
C(13')	4114 (4)	5422 (7)	6180 (3)
C(14)	1780 (3)	3865 (5)	4171 (2)
C(15)	1349 (3)	4475 (6)	3700 (3)
C(16)	611 (3)	4298 (7)	3490 (3)
C(17)	305 (3)	3473 (7)	3752 (3)
C(18)	719 (3)	2865 (6)	4214 (3)
C(19)	1457 (3)	3064 (5)	4428 (3)
H(4)	409 (4)	57 (8)	311 (3)
H(5)	333 (4)	-112 (7)	241 (3)
H(6)	210 (4)	-145 (6)	233 (3)
H(7)	143 (4)	-16 (6)	266 (3)
H(8)	354 (3)	368 (5)	433 (2)
H(4')	332 (4)	768 (7)	654 (3)
H(5')	245 (4)	855 (6)	680 (3)
H(6')	115 (5)	855 (8)	622 (4)
H(7')	80 (3)	715 (5)	560 (2)
H(8')	344 (3)	489 (5)	504 (3)
H(15)	155 (3)	503 (5)	356 (2)
H(16)	25 (3)	471 (6)	310 (3)
H(17)	-16 (3)	311 (6)	359 (3)
H(18)	53 (4)	225 (5)	436 (2)
H(19)	169 (3)	272 (5)	470 (2)
C(20)*	0	1337 (21)	2500
O(21)*	370 (14)	495 (26)	2396 (11)

* The atoms of methanol. The occupancy for O(21) is 0.25.

than that for distorting the planarity to relieve overcrowding. The angles C(2)—C(8)—C(9) and C(2')—C(8')—C(9) are greater than 120° , whereas C(8)—C(9)—C(8') is less than 120° . These features in the methine chain were also observed in the 5,5'-dichloro-3,3',9-triethylthiacyanine cation (Potenza & Mastropaolo, 1974).

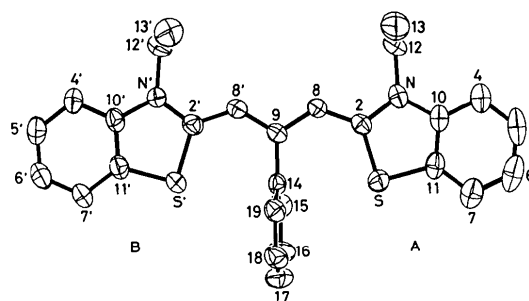


Fig. 2. Structure of the 3,3'-diethyl-9-phenylthiacyanine cation projected on the plane M defined by atoms C(2), C(8), C(9), C(8'), C(2'). Thermal ellipsoids are scaled to include the 50% probability level. H atoms are not shown.

The bond lengths and angles in both benzothiazole moieties, including the ethyl groups, are in near agreement with each other and also with those found in 3,3'-diethylthiacyanine (Nakatsu, Yoshioka & Aoki, 1972), 5,5'-dichloro-3,3',9-triethylthiacyanine (Potenza & Mastropaolo, 1974), and 5,5',7,7'-tetramethyl-3,3',9-triethylthiacyanine (Stoekli-Evans, 1974). A comparison of the chemically equivalent bond lengths between N(3) and N(3') shows slight tendency towards bond alternation.

Crystal structure

The crystal structure viewed along b and a is shown in Figs. 3 and 4 respectively. The structure consists of

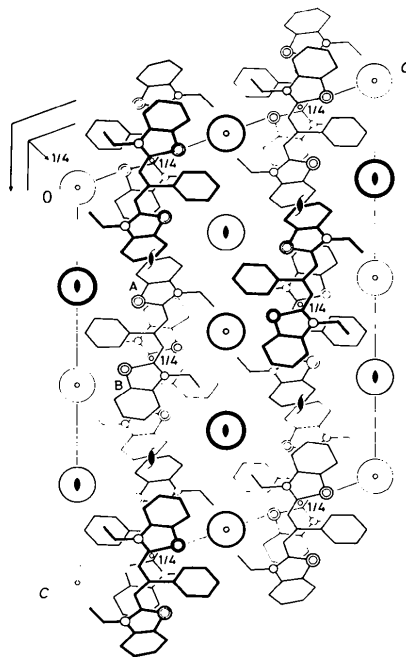


Fig. 3. Crystal structure viewed along b . Methanol molecules are not shown for clarity.

Table 3. *Interatomic distances (Å) and bond angles (°)*

E.s.d.'s are given in parentheses.

S(1)—C(2)	1.741 (6)	S(1')—C(2')	1.756 (6)
S(1)—C(11)	1.754 (7)	S(1')—C(11')	1.748 (7)
S(1)—C(14)	3.000 (6)	S(1')—C(14)	3.015 (5)
C(2)—N(3)	1.369 (9)	C(2')—N(3')	1.349 (7)
C(2)—C(8)	1.388 (8)	C(2')—C(8')	1.400 (9)
N(3)—C(10)	1.397 (8)	N(3')—C(10')	1.399 (9)
N(3)—C(12)	1.495 (8)	N(3')—C(12')	1.512 (8)
C(4)—C(5)	1.394 (10)	C(4')—C(5')	1.405 (11)
C(4)—C(10)	1.387 (11)	C(4')—C(10')	1.382 (9)
C(5)—C(6)	1.381 (14)	C(5')—C(6')	1.361 (9)
C(6)—C(7)	1.370 (13)	C(6')—C(7')	1.376 (10)
C(7)—C(11)	1.390 (9)	C(7')—C(11')	1.379 (11)
C(8)—C(9)	1.409 (9)	C(8')—C(9)	1.392 (8)
C(10)—C(11)	1.394 (10)	C(10')—C(11')	1.392 (8)
C(12)—C(13)	1.530 (10)	C(12')—C(13')	1.505 (10)
C(14)—C(15)	1.377 (7)	C(14')—C(15')	1.383 (9)
C(15)—C(16)	1.380 (9)	C(18)—C(19)	1.385 (8)
C(16)—C(17)	1.386 (11)	C(17)—C(18)	1.351 (9)
C(9)—C(14)	1.493 (7)		
C(4)—H(4)	1.12 (8)	C(4')—H(4')	1.01 (7)
C(5)—H(5)	0.98 (9)	C(5')—H(5')	0.85 (7)
C(6)—H(6)	0.95 (7)	C(6')—H(6')	0.98 (10)
C(7)—H(7)	1.11 (7)	C(7')—H(7')	0.92 (6)
C(8)—H(8)	0.97 (5)	C(8')—H(8')	1.01 (6)
C(15)—H(15)	0.88 (7)	C(19)—H(19)	0.77 (5)
C(16)—H(16)	1.09 (6)	C(18)—H(18)	0.91 (6)
C(17)—H(17)	0.96 (6)	C(20)—O(21)	1.27 (3)
C(2)—S(1)—C(11)	91.7 (3)	C(2')—S(1')—C(11')	91.4 (3)
S(1)—C(2)—N(3)	110.3 (4)	S(1')—C(2')—N(3')	110.6 (5)
S(1)—C(2)—C(8)	126.8 (5)	S(1')—C(2')—C(8')	126.0 (4)
N(3)—C(2)—C(8)	122.8 (5)	N(3')—C(2')—C(8')	123.4 (5)
C(2)—N(3)—C(10)	115.1 (5)	C(2')—N(3')—C(10')	115.0 (5)
C(2)—N(3)—C(12)	123.9 (5)	C(2')—N(3')—C(12')	123.2 (6)
C(10)—N(3)—C(12)	120.8 (6)	C(10')—N(3')—C(12')	121.8 (5)
C(5)—C(4)—C(10)	116.9 (7)	C(5')—C(4')—C(10')	116.8 (6)
C(4)—C(5)—C(6)	122.0 (8)	C(4')—C(5')—C(6')	122.1 (6)
C(5)—C(6)—C(7)	121.2 (7)	C(5')—C(6')—C(7')	121.1 (7)
C(6)—C(7)—C(11)	117.6 (8)	C(6')—C(7')—C(11')	117.8 (6)
C(2)—C(8)—C(9)	128.2 (5)	C(2')—C(8')—C(9)	128.6 (5)
N(3)—C(10)—C(4)	127.0 (6)	N(3')—C(10')—C(4')	126.9 (5)
N(3)—C(10)—C(11)	112.3 (6)	N(3')—C(10')—C(11')	112.7 (5)
C(4)—C(10)—C(11)	120.7 (6)	C(4')—C(10')—C(11')	120.4 (7)
S(1)—C(11)—C(7)	127.9 (6)	S(1')—C(11')—C(7')	128.0 (5)
S(1)—C(11)—C(10)	110.5 (4)	S(1')—C(11')—C(10')	110.2 (5)
C(7)—C(11)—C(10)	121.6 (7)	C(7')—C(11')—C(10')	121.7 (6)
N(3)—C(12)—C(13)	109.6 (6)	N(3')—C(12')—C(13')	108.6 (6)
C(8)—C(9)—C(14)	121.3 (5)	C(8')—C(9)—C(14)	122.4 (6)
C(9)—C(14)—C(15)	120.4 (6)	C(9')—C(14)—C(15)	121.2 (5)
C(14)—C(15)—C(16)	120.9 (6)	C(14')—C(15)—C(16)	121.0 (5)
C(15)—C(16)—C(17)	119.3 (6)	C(15')—C(16)—C(17)	119.6 (7)
C(15)—C(16)—C(14)	118.4 (5)	C(15')—C(16)—C(14)	120.7 (6)
C(8)—C(9)—C(8')	116.5 (5)		
C(5)—C(4)—H(4)	129 (5)	C(5')—C(4')—H(4')	122 (5)
C(10)—C(4)—H(4)	114 (5)	C(10')—C(4')—H(4')	121 (5)
C(4)—C(5)—H(5)	125 (5)	C(4')—C(5')—H(5')	112 (5)
C(6)—C(5)—H(5)	112 (4)	C(6')—C(5')—H(5')	125 (5)
C(5)—C(6)—H(6)	132 (5)	C(5')—C(6')—H(6')	127 (5)
C(7)—C(6)—H(6)	106 (5)	C(7')—C(6')—H(6')	110 (5)
C(6)—C(7)—H(7)	126 (4)	C(6')—C(7')—H(7')	116 (4)
C(11)—C(7)—H(7)	116 (4)	C(11')—C(7')—H(7')	126 (4)
C(2)—C(8)—H(8)	116 (3)	C(2')—C(8')—H(8')	108 (4)
C(9)—C(8)—H(8)	116 (3)	C(9')—C(8')—H(8')	123 (4)
C(14)—C(15)—H(15)	118 (3)	C(14')—C(15)—H(15)	120 (5)
C(16)—C(15)—H(15)	121 (3)	C(18)—C(19)—H(19)	119 (5)
C(15)—C(16)—H(16)	123 (4)	C(17)—C(18)—H(18)	122 (3)
C(17)—C(16)—H(16)	117 (4)	C(19)—C(18)—H(18)	118 (3)
C(16)—C(17)—H(17)	126 (4)	C(18)—C(17)—H(17)	112 (4)

Table 4. *Description of the best planes*

(a) Equations of planes. Orthogonal coordinates X , Y , and Z (Å), are taken along \mathbf{a} , \mathbf{b} , and \mathbf{c}^* respectively.

Plane A : Benzothiazole ring A
 $-0.047X - 0.628Y + 0.777Z = 5.075$

Plane B : Benzothiazole ring B
 $-0.193X - 0.766Y + 0.600Z = 2.407$

Plane M : Methine chain
 $-0.104X - 0.715Y + 0.691Z = 3.900$

Plane P : Phenyl group
 $-0.353X + 0.732Y + 0.584Z = 8.974$

(b) Deviations of atoms (in 10^{-3} Å) from the mean plane. Atoms with an asterisk are used to define the plane.

	Plane A	Plane B	Plane M	Plane P			
S(1)	-8*	S(1')	44*	C(2)	56*	C(9)	-6
C(2)	26*	C(2')	-5*	C(8)	-40*	C(14)	-3*
N(3)	-10*	N(3')	-49*	C(9)	-58*	C(15)	-5*
C(4)	-19*	C(4')	40*	C(8')	8*	C(16)	9*
C(5)	20*	C(5')	21*	C(2')	33*	C(17)	-5*
C(6)	5*	C(6')	-30*	C(14)	-121	C(18)	-3*
C(7)	-3*	C(7')	-25*			C(19)	7*
C(8)	99	C(8')	2				
C(10)	0*	C(10')	-3*				
C(11)	-10*	C(11')	7*				
C(12)	56	C(12')	-178				
d^\dagger	14	30	43	6			

(c) Dihedral angles (°) between the planes

$A-B$	15.7	$A-M$	7.7	$B-M$	8.1
$M-P$	85.2	$A-P$	89.4	$B-P$	81.4

† R.m.s. deviation from the plane.

columns separated by the layers of I^- ions, of which $I(1)$ is situated on the set of $\bar{1}$ of (0,0,0) and (0,0, $\frac{1}{2}$), while $I(2)$ is on the twofold axis. The methanol molecules with disordered OH groups are situated in the vacancies around $I(2)$. No unusual intermolecular contact is found in the crystal structure ($I \cdots C \geq 3.957$, $S \cdots C \geq 3.684$, $C \cdots C \geq 3.538$ Å).

In each dye column, the neighboring dye molecules stack face-to-face in two ways alternately, as shown in Fig. 5. In the first stacking (Fig. 5a) the neighboring molecules are almost eclipsed, that is, the slip angle* is about 90°, the perpendicular distance between the dye plane is 4.10 Å. On the other hand, the second stacking (Fig. 5b) shows a longitudinally and slightly laterally displaced arrangement with a perpendicular separation of 3.66 Å. The resulting slip angle is about 25°. The columnar slip angle, or the angle between the column direction (\mathbf{b} in the present crystal) and the long molecular axis, is 42°.

* The 'slip angle' or 'tilt angle' is defined as that between the long molecular axis and the line joining the centers of gravity of the adjacent molecules, and used to describe the mutual orientation of dyes in the aggregate. Here the long molecular axis is taken as the line joining N(3) and N(3').

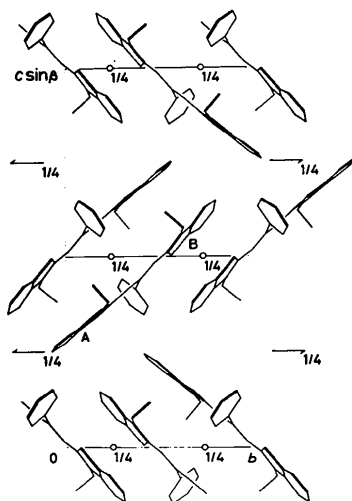


Fig. 4. Projection of the unit-cell content between 0 and $a/2$, illustrating the dye columns.

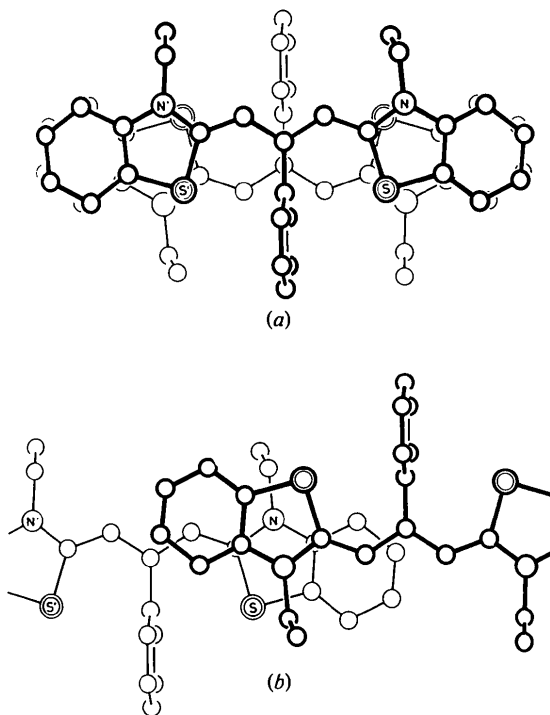


Fig. 5. Nearest-neighbor overlap of the dye cations. (a) Dyes related by \bar{i} at $(\frac{1}{4}, \frac{1}{4})$. (b) Dyes related by \bar{i} at $(\frac{1}{4}, \frac{3}{4})$.

A similar type of column, having alternate high and low slip angles, is found in crystals of 5,5'-dichloro-3,3,9-triethylthiacarbocyanine bromide acetic acid solvate (Mastropaolo, Potenza & Bird, 1974; Potenza & Mastropaolo, 1974) and 3,3'-diethylthiacarbocyanine bromide (Wheatley, 1959b). Smith (1974) described this type of column as 'a combination of Scheibe's ladder and staircase models'.

These columns are assembled to give two-dimensional arrays of a herringbone-like pattern (Fig. 4), which appears to resemble that proposed by Reich (1974) for the adsorbate of a particular dye on silver halide crystals. Similar arrays are found in the crystal structures of 1,1'-diethyl-4,4'-carbocyanine iodide (K. Nakatsu *et al.*, unpublished work) and 3,3',9-triethylthiacarbocyanine bromide pentahydrate (K. Nakatsu *et al.*, unpublished work). Thus the herringbone-like arrangement of cyanine dyes should be taken as an adequate model for the two-dimensional packing in the aggregate formed on the surface of silver halide grains in photographic emulsions.

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