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The Crystal and Molecular Structure of the Acetic Acid Solvate of 5,5′-Dichloro-3,3′,9-Triethylthiacarbocyanine Bromide, a Photographic Sensitizing Dye

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The crystal structure of the title compound, a known spectral sensitizer of silver bromide photographic emulsions, has been determined by a single-crystal three-dimensional X-ray diffraction study. The compound crystallizes in space group $P\bar{1}$ with two $C_{23}H_{23}BrCl_2N_2S_2.CH_3COOH$ formula units in each unit cell of dimensions $a=9{\cdot}408$ (5), $b=16{\cdot}342$ (9), $c=8{\cdot}919$ (6) Å, $\alpha=101{\cdot}47$ (4), $\beta=91{\cdot}25$ (4) and $\gamma=79{\cdot}45$ (4)°. Calculated and observed densities are 1·514 and 1·51 (1) g cm^{-3}, respectively. Intensity data were obtained using an Enraf–Nonius CAD-3 automated diffractometer (Mo $K\alpha$ radiation, $\lambda=0{\cdot}71069$ Å). The structure was solved by the heavy-atom method and refined by full-matrix least-squares methods to a conventional R value of 0·073 for 1991 independent reflections. The structure consists of columns of $C_{23}H_{23}Cl_2N_2S_2^+$ dye cations separated by bromide ions and acetic acid molecules. Bromine–oxygen distances indicate the presence of a weak hydrogen bond between the latter two species. Within a given column, cations are stacked in two non-equivalent ways resulting in mean perpendicular distances between cation least-squares planes of 3·63 and 4·09 Å. The cations consist of two structurally equivalent halves, each planar to approximately ±0·05 Å; however, the dihedral angle between these planes is 8·6° and the cation is bowed, rather than twisted. Lastly, sulfur atoms are *cis*, and the nonbonding S···S distance [6·168 (5) Å] is considerably longer than those (5·3, 5·4 Å) calculated for similar planar or twisted dyes without the central 9-ethyl substituent. The cation geometry is used to examine possible geometric constraints on the epitaxic attachment of thiacarbocyanine dyes to the {111} and {100} surfaces of AgBr. For dye cations attached edge-on along [110] Ag^+ rows, it is shown that weak $Ag^+\cdots S$ ligand bonds between the dye and the crystal surface can form only if a certain fraction of surface silver sites are vacant. Using ideal models for the {111} and {100} surfaces, a regular attachment of dye molecules stacked edge-on to the {111} crystal surface with pairs of $Ag^+\cdots S$ ligand bonds contributing to the binding of each molecule appears to be possible. It is not now obvious how such an attachment with $Ag^+\cdots S$ bonds could occur on the {100} surface. A detailed consideration of surface packing requirements suggests that particular aggregates should form preferentially.

Introduction

Optical sensitization of photographic emulsions to different spectral regions is accomplished by the adsorption of an appropriate dye on a silver halide crystal surface (Mees & James, 1966). While the mechanism of sensitization is not completely understood, it must be related to the molecular structure of the sensitizer, the nature of its attachment to the crystal surface, and the geometric packing arrangement of dye molecules on the surface. Typical sensitizers contain extended aromatic fragments and are thought (Sheppard, Lambert & Walker, 1939; West, Carroll & Whitcomb, 1952) to form close-packed monolayers (aggregates) with the long axis of the dye molecules adsorbed edge-on to the crystal surface. The short axis may or may not be normal to the crystal surface while the angle between the line joining the midpoints of molecules in an aggregate column and the line parallel to the long axis of the molecule (slip angle) may vary over a wide range. In addition, a particular dye may contain functional groups which form relatively strong bonds to surface atoms (chemisorption), favoring epitaxic attachment.

Several models for aggregate structures, incorporating one or more of the above features, have been advanced. For example, it has been suggested that thiacarbocyanine dyes attach epitaxically to silver halide surfaces by forming weak $Ag^+\cdots S$ bonds (Bird, Norland, Rosenoff & Michaud, 1968) and that the slip angles of the resulting aggregates are related to electronic frequency shifts observed between the monomer and aggregate (Norland, Ames & Taylor, 1970). While accurate molecular dimensions are required to refine such models, only two detailed molecular structures of thiacarbocyanine dyes have, to our knowledge, been reported (Wheatley, 1959), and both were relatively imprecisely determined because of crystal decomposition. The present study was undertaken to add to the limited structural information available for thiacarbocyanine dyes and to provide a basis for examining geometric factors which could affect the attachment of such dyes to silver halide surfaces.

Experimental section

A sample of 5,5′-dichloro-3,3′,9-triethylthiacarbocyanine tosylate was kindly provided by Ms R. L. Hill of the Research Division of Polaroid Corporation. Crystals of the bromide were prepared by slow evapora-

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tion of an acetic anhydride solution containing potassium bromide and the tosylate salt of the dye. Since many dye molecules crystallize as solvates (Wheatley, 1959; Smith & Luss, 1972), acetic anhydride was chosen to minimize the possibility of solvate formation. Bromide crystals grew quite slowly from solution and we determined later that trace hydrolysis gave crystals containing one acetic acid molecule per dye cation. No suitable crystals could be obtained using dry acetic anhydride.

Crystal and X-ray data

A crystal of dimensions $0{\cdot}33 \times 0{\cdot}17 \times 0{\cdot}10$ mm was mounted in a sealed glass capillary parallel to the long dimension. Preliminary Weissenberg photographs showed no systematic absences and the crystal was assumed to be triclinic; successful solution and refinement of the structure showed the space group to be $P\bar{1}$. Unit-cell parameters $a = 9{\cdot}408(5)$, $b = 16{\cdot}342(9)$, $c = 8{\cdot}919(6)$ Å, $\alpha = 101{\cdot}47(4)$, $\beta = 91{\cdot}25(4)$, and $\gamma = 79{\cdot}45(4)°$ were determined from a least-squares analysis of the θ, χ and φ values of 20 reflections obtained using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) and an Enraf–Nonius CAD-3 automated diffractometer. The unit-cell volume based on these dimensions is $1321{\cdot}1$ Å^3. A density of $1{\cdot}51(1)$ g cm^{-3} was determined by flotation of several crystals in aqueous zinc iodide solution and this agreed rather poorly with the value of $1{\cdot}381$ g cm^{-3} calculated assuming two unsolvated dye molecules per unit cell. With the addition of one acetic acid molecule per asymmetric unit, the calculated density ($1{\cdot}514$ g cm^{-3}) agreed well with that observed.

In total, 6500 reflections were collected at room temperature (22 ± 1 °C) with the Enraf–Nonius diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was detected with a scintillation counter and a pulse-height analyzer set to admit approximately 95% of the $K\alpha$ peak. A θ-2θ scan was used to collect a unique data set in the range $2 \le \theta \le 30°$. Background measurements were made at the beginning and end of each scan with the counter stationary; the total time for background counting was equal to the scan time. The scan rate was $\frac{1}{6}°$ per second and each reflection was scanned repeatedly to a maximum of six scans or until 6000 total counts were obtained. Intensities were placed on a common scale by dividing by the number of scans. The intensities of two standard reflections, measured at 50 reflection intervals, were consistent to ± 2% and showed no significant trend. Lorentz and polarization factors were applied to the 6500 measured

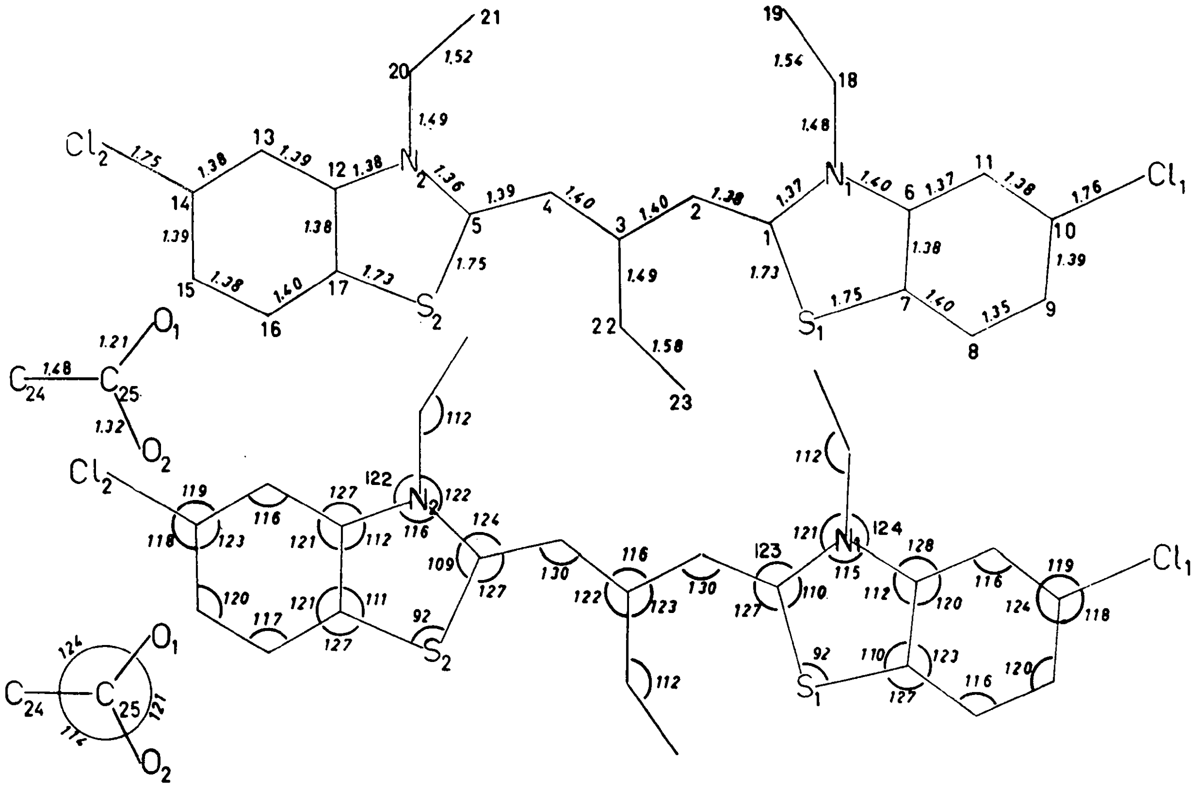

Fig. 1. Bond distances and angles. Average e.s.d.'s are: Cl–C ($\pm 0{\cdot}013$ Å); S–C ($\pm 0{\cdot}011$ Å); O–C ($\pm 0{\cdot}015$ Å); N–C ($\pm 0{\cdot}013$ Å); C–C ($\pm 0{\cdot}016$ Å); Cl–C–C ($\pm 0{\cdot}9°$); S–C–N ($\pm 0{\cdot}7°$); S–C–C ($\pm 0{\cdot}8°$); C–S–C ($\pm 0{\cdot}5°$); O–O–C ($\pm 1{\cdot}2°$); O–C–O ($\pm 1{\cdot}1°$); C–N–C ($\pm 0{\cdot}9°$); N–C–C ($\pm 0{\cdot}9°$); C–C–C ($\pm 1{\cdot}0°$). The following distances are not given in the figure: Br···O(2) $3{\cdot}178$ (9); Cl(1)···Cl(2) $17{\cdot}458$ (9); S(1)···S(2) $6{\cdot}168$ (5); S(1)···C(22) $3{\cdot}11$; S(2)···C(22) $3{\cdot}14$ Å.

intensities. Of these, 1991 with $F^2 \geq 3\sigma(F^2)$ were used in the structure solution and refinement; here $\sigma(F^2)$ is the standard deviation as estimated from counting statistics. The linear absorption coefficient ($\mu = 22{\cdot}0$ cm^{-1} for Mo $K\alpha$ radiation) was sufficiently small that absorption corrections were not considered necessary for a crystal of the size used to collect data.

Solution and refinement of the structure

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. Approximate bromine, chlorine and sulfur coordinates were obtained from a normal sharpened Patterson map, while carbon, oxygen and nitrogen positions were deduced from a difference synthesis based on the heavy-atom phases. A modified version of *ORFLS* (Busing, Martin & Levy, 1962) was used for the structure-factor calculations and refinement. Atomic scattering factors were those of Cromer & Waber (1965) except for hydrogen scattering factors which were obtained from *International Tables for X-ray Crystallography* (1968). All atoms were treated as neutral species.

Initial refinement was based on F^2. Six cycles of refinement using isotropic temperature factors gave values of 0·15 and 0·27 for the functions $R_F = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_{wF^2} = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$ respectively; weights were set according to $w = 1/\sigma^2(F^2)$. The bromine, chlorine and sulfur atoms were then allowed to vibrate anisotropically, and both real and imaginary parts of the anomalous dispersion corrections were applied to bromine (*International Tables for X-ray Crystallography*, 1968). Two cycles of refinement reduced R_F and R_{wF^2} to 0·092 and 0·19 respectively.

Further refinement was based on F and a weighting scheme was chosen by an analysis of variance (Ricci, Eggers & Bernal, 1972) to make $\Delta F/\sigma(F_o)$ independent of F_o. This led to the following assignments for $\sigma(F_o)$:

$$\begin{array}{lll} \sigma(F_o) = -0{\cdot}029|F_o| + 1{\cdot}340 & \text{for} & 0 < |F_o| \leq 9{\cdot}0, \\ \sigma(F_o) = \ \ 1{\cdot}10 & \text{for} & 9{\cdot}0 < |F_o| \leq 17{\cdot}0, \\ \sigma(F_o) = \ \ 0{\cdot}134|F_o| - 1{\cdot}136 & \text{for} & |F_o| > 17{\cdot}0. \end{array}$$

An additional cycle of refinement reduced R_F to 0·085 and $R_{wF} = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, the function minimized, to 0·10. A difference Fourier map was calculated at this point in an attempt to locate hydrogen atoms. Only broad, diffuse maxima could be found; thus, hydrogen atom positions were calculated assuming typical C–H bond distances and angles. Methyl group hydrogen atoms were rotated about the ethyl group C–C bond vectors every 20° until their positions best fit positive areas of electron density in the difference map. Hydrogen atoms were included for further refinement as fixed contributors to F_c with isotropic temperature factors equal to those of the carbon atom to which they are bonded. Three cycles of refinement gave final values of 0·073 and 0·091 for R_F and R_{wF} respectively. For the last cycle all parameter changes were less than 0·1 σ, where σ is the estimated standard deviation obtained from the inverse matrix. A final difference map showed a general background of ap-

Table 1. *Fractional atomic coordinates* (× 10^4) *and anisotropic thermal parameters* (× 10^5) *and isotropic thermal parameters* (× 10^2) *for* 5,5′*dichloro*-3,3,9-*triethylthiacarbocyanine bromide* (1:1 *acetic acid solvate*)

Estimated standard deviations are given in parentheses.

	x	*y*	*z*	*B*
Br	−1516·8 (1·6)	8420·0 (8)	9952·5 (1·2)	–
Cl(1)	829·7 (4)	13708·1 (2·0)	4484·9 (3·6)	–
Cl(2)	−7002·5 (4·1)	4646·4 (2·1)	2217·8 (4·1)	–
S(1)	−1935·9 (3·4)	10967·8 (1·8)	6571·7 (2·7)	–
S(2)	−4605·1 (3·5)	7735·1 (1·8)	5843·9 (2·8)	–
N(1)	−1214 (9)	10911 (5)	3809 (8)	192 (17)
N(2)	−4221 (9)	7156 (5)	2979 (9)	209 (17)
C(1)	−1773 (11)	10445 (6)	4682 (10)	180 (20)
C(2)	−2209 (12)	9680 (6)	4050 (11)	226 (22)
C(3)	−2772 (11)	9123 (6)	4769 (11)	220 (22)
C(4)	−3208 (11)	8430 (6)	3778 (11)	216 (22)
C(5)	−3924 (11)	7808 (6)	4080 (10)	199 (21)
C(6)	−885 (11)	11682 (6)	4624 (10)	185 (20)
C(7)	−1202 (11)	11811 (6)	6176 (10)	186 (20)
C(8)	−920 (12)	12517 (7)	7242 (11)	263 (22)
C(9)	−317 (12)	13090 (7)	6674 (12)	309 (26)
C(10)	14 (12)	12954 (7)	5130 (12)	271 (24)
C(11)	−287 (11)	12262 (6)	4066 (11)	220 (21)
C(12)	−5031 (12)	6633 (6)	3463 (11)	233 (22)
C(13)	−5531 (12)	5938 (6)	2569 (11)	246 (22)
C(14)	−6319 (13)	5499 (7)	3306 (12)	292 (25)
C(15)	−6621 (13)	5718 (7)	4866 (12)	314 (27)
C(16)	−6108 (13)	6392 (7)	5760 (12)	297 (25)
C(17)	−5300 (11)	6844 (6)	5024 (11)	220 (21)
C(18)	−969 (11)	10662 (6)	2132 (10)	185 (21)
C(19)	−2278 (13)	11029 (7)	1243 (13)	341 (28)
C(20)	−3787 (12)	7043 (6)	1343 (11)	248 (23)
C(21)	−4937 (13)	7517 (7)	453 (13)	331 (27)
C(22)	−2835 (12)	9221 (6)	6464 (11)	254 (24)
C(23)	−4302 (15)	9788 (8)	7191 (15)	421 (31)
C(24)	1397 (16)	5203 (9)	−1548 (16)	494 (35)
C(25)	1033 (13)	6139 (7)	−1049 (12)	312 (26)
O(1)	1858 (10)	6621 (6)	−1124 (11)	519 (24)
O(2)	−328 (9)	6432 (5)	−600 (9)	390 (20)
H(C2)	−2743	8357	2659	226
H(C4)	−1883	9441	3006	216
H(C8)	−991	12538	8383	263
H(C9)	−253	13673	7458	309
H(C11)	170	12122	3029	220
H(C13)	−5601	5810	1272	246
H(C15)	6913	5296	5319	314
H(C16)	6400	6600	6800	297
H(C18–1)	−1424	10095	1715	185
H(C18–2)	184	10530	1904	185
H(C19–1)	−3175	10717	1343	341
H(C19–2)	−2600	11717	1738	341
H(C19–3)	−1970	10954	38	341
H(C20–1)	−4080	6453	703	248
H(C20–2)	−2608	6992	1281	248
H(C21–1)	−4604	7373	769	331
H(C21–2)	−5950	7343	591	331
H(C21–3)	−4992	8205	894	331
H(C22–1)	−3963	9296	6890	254
H(C22–2)	−2412	9793	7065	254
H(C23–1)	−5115	9383	7203	421
H(C23–2)	−4137	10077	8445	421
H(C23–3)	−4672	10279	6593	421
H(C25–1)	1262	5010	−2796	312
H(C25–2)	2537	4975	−1284	312
H(C25–3)	713	4900	−947	312
H(O2–1)	−539	7066	−538	390

Table 1 (*cont.*)

Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	1768 (19)	411 (5)	737 (11)	−148 (8)	407 (12)	126 (6)
Cl(1)	1764 (54)	346 (13)	1172 (40)	−400 (21)	0 (40)	177 (19)
Cl(2)	1819 (54)	454 (14)	1511 (48)	−609 (21)	−71 (44)	105 (22)
S(1)	1113 (44)	295 (12)	326 (26)	−218 (19)	259 (28)	64 (15)
S(2)	1355 (43)	370 (12)	581 (28)	−243 (18)	280 (28)	43 (15)

proximately 0·5 e Å^{-3} and revealed no significant features.* Table 1 gives the positional and thermal parameters.

Description of the structure

The structure consists of columns of $C_{23}H_{23}Cl_2N_2S_2^+$ cations separated by bromide ions and acetic acid molecules. A line drawing of the cation, showing the crystallographic atom numbering scheme, and bond distances and angles, is given in Fig. 1. Bond distances and angles were calculated using program *ORFFE* (Busing, Martin & Levy, 1964). Sulfur atoms from each half of the dye cation are *cis* and all three methyl groups (*N*,*N′* and *meso*-C) are to one side of the cation plane. Previous structures of thiacarbocyanine dyes (Wheatley, 1959), without substituents at the 9 position, have also shown sulfur atoms to be *cis*; however, in 3,3′-diethylthiacarbocyanine bromide, the terminal *N*,*N′* methyl groups were to one side of the cation, while in the ethanol solvate of 3,3′-diethylthiacarbocyanine, the methyl groups were on opposite sides of the cation plane. Presumably, the location of the *N*,*N′* methyl groups results from the detailed nature of the packing forces in the various crystals.

Corresponding distances and angles within each half of the dye cation are equivalent to within experimental error, although this is not required crystallographically. These parameters, in general, agree well with accepted values, but there are significant differences from the values expected for pure sp^2 hybridization. For example, the angles C(9)–C(10)–C(11) and C(13)–C(14)–C(15) are equivalent and significantly larger than the 120° value found in benzene, while C(10)–C(11)–C(6) and related angles are less than 120° by approximately the same amount. Bond distances in the central carbon chain [C(1)–C(2), C(2)–C(3), C(3)–C(4) and C(4)–C(5)] are equivalent; their magnitudes indicate partial double bond character and suggest electron delocalization between the two halves of the cation. The non-bonding S(1)···S(2) distance [6·168(5) Å] is significantly longer than the corresponding distances of 5.3 and 5·4 Å

Table 2. *Equations of least-squares planes*

Equations are expressed in the form $AX_0+BY_0+CZ_0=D$ where X_0, Y_0 and Z_0 are Cartesian axes lying along $\mathbf{b}\wedge\mathbf{c}^*$, $\mathbf{b}$ and $\mathbf{c}^*$ respectively.

Plane	*A*	*B*	*C*	*D*	Atoms defining the plane
1	0·9028	−0·4218	0·0837	−7·928	Cl(1), Cl(2), S(1), S(2) N(1), N(2), C(1) through C(20), C(22).
2	0·9165	−0·3679	0·1572	−6·656	Cl(1), S(1), N(1), C(1) C(2), C(3), C(6) through C(11), C(18), C(22).
3	0·8502	−0·5032	0·1545	−8·174	Cl(2), S(2), N(2), C(3), C(4), C(5), C(12) through C(17), C(20), C(22).

Deviations of atoms from the planes (Å)

Plane	Cl(1),	Cl(2)	S(1),	S(2)	N(1),	N(2)	C(1),	C(5)
1	−0·161,	−0·255	−0·042,	0·031	0·100,	0·261	0·133,	0·214
2	0·036	–	−0·032	–	−0·030	–	−0·004	–
3	–	−0·019	–	0·019	–	0·046	–	−0·024

Plane	C(2),	C(4)	C(3)	C(6),	C(12)	C(7),	C(17)	C(8),	C(16)
1	0·227,	0·284	0·299	−0·051,	0·080	−0·132	−0·016	−0·229,	−0·195
2	0·020	–	0·030	−0·062	–	−0·053	–	−0·024	–
3	–	0·105	−0·134	–	0·022	–	0·034	–	0·020

Plane	C(9),	C(15)	C(10),	C(14)	C(11),	C(13)	C(18),	C(20)	C(22)
1	−0·253,	−0·273	−0·154,	−0·146	−0·081,	0·035	0·184,	0·404	0·457
2	−0·016	–	−0·006	–	−0·058	–	−0·055	–	0·287
3	–	−0·003	–	0·014	–	0·032	–	0·053	0·144

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30512 (10pp.). Copies may be obtained from the authors or through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

found for 3,3′-diethylthiacarbocyanine bromide and its ethanol solvate respectively. The lengthening most likely results from steric crowding caused by the central 9-ethyl substituent in the present structure. This view is supported by the rather short S(1)···C(22) and S(2)···C(22) distances [3·11, 3·14 Å, respectively], and by the rather large values of the angles C(1)–C(2)–C(3) and C(3)–C(4)–C(5) [130(1)°]. In addition, C(22) and C(23) are on opposite sides of the cation plane (plane 1, Table 2) which is the correct configuration for overcrowding.

The dye cations show significant deviations from planarity. This is evident from the data in Table 2 which gives least-squares planes and atomic deviations for each half of the cation, and for the entire cation (excluding terminal methyl groups). For the entire cation, deviations from planarity are large and systematic. For example, both chlorine atoms show large negative deviations from the least-squares plane, while atoms on the central carbon chain show large positive deviations. This suggests that the cation is bowed, rather than twisted, so that it is clearly not in the class of twisted antisensitizing dyes (Sheppard, Lambert & Walker, 1941). Atoms from each half of the cation show an average deviation from planarity of approximately ±0·05 Å; the dihedral angle between these planes, 8·6°, gives an estimate of the extent of bowing.

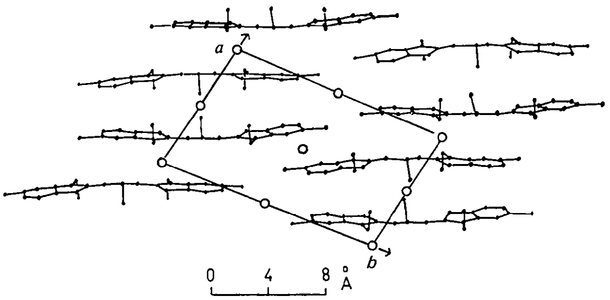

Fig. 2. The cation packing arrangement viewed along **c***.

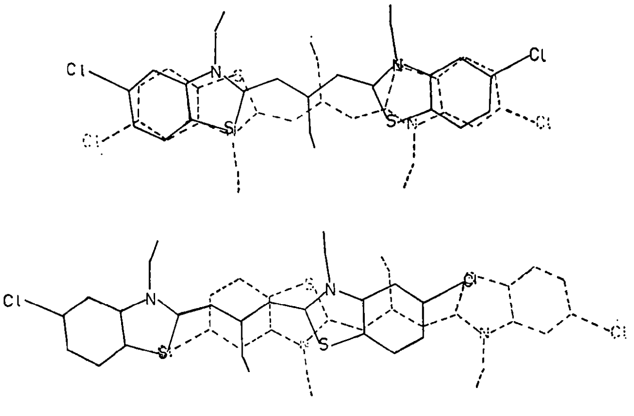

Fig. 3. The two relative orientations of the dye cations in the stacking columns. The view is along the normal to the cation plane in the foreground.

The C(2)–C(3)–C(4) angle [116(1)°] is less than the expected value of 120°, and this is consistent with a bowed structure formed primarily by rotation of each half of the cation about the C(3)– C(22) bond vector. However, since rotation about C(3)–C(22) would not remove either of these atoms from planes 2 and 3, and since C(22) shows rather large deviations from these planes, there must also be some twisting at C(3).

The cation packing arrangement is shown in Fig. 2 which is a view of the structure along **c**.* Adjacent molecules in each column are related by a center of symmetry while every other molecule is related by a cell translation along **a**. Columns are related to each other by unit-cell translations in the **b** and **c** directions. Within a given column, dye cations are stacked in two nonequivalent ways (Fig. 3). One pair is separated by a mean perpendicular distance of 3·63 Å and the two cations are laterally displaced such that the slip angle is 30·4°. To calculate the slip angle, the Cl(1)···Cl(2) vector was used to define the long axis of the cation. The mean perpendicular distance was determined from the cation least-squares planes as the distance from one plane to the center of gravity of the other. The second cation pair shows a mean perpendicular distance of 4·06 Å and the individual cation planes are nearly eclipsed as shown in Fig. 3.

The bromide ions and acetic acid molecules appear to fill holes in the structure and show no unusually short distances to the cations. However, structural evidence strongly supports the presence of a weak hydrogen bond between these two species. In the acetic acid molecule, C=O and C–OH distances are clearly distinguishable (Fig. 1). The hydroxyl oxygen–bromide distance Br–O(2) is short (3·18 Å) while the C(25)–O(2)–Br angle is 119°, placing the bromide ion in a tenable position for hydrogen bonding. Placement of a hydrogen atom 1·0 Å from O(2) on the line between Br and O(2) results in a Br–H distance of 2·18 Å. On the final difference Fourier map, this position showed a positive peak of approximately 0·5 e Å^{-3}.

Discussion

The present structure serves as a model for an important class of sensitizing dyes and may be used to examine possible constraints on the attachment of such dyes to silver halide surfaces. It has been suggested that thiacarbocyanine dyes adsorb edge-on along the [110] rows of {111} and {100} AgBr faces. For the {111} faces, this view is supported by the observation of polarized light absorption due to adsorbing the dye on selectively cut AgBr crystals (Gray, Brewer & Bird, 1970). Thiacarbocyanine adsorption to this surface is relatively strong and this has been attributed to the formation of weak ligand bonds between the dye sulfur atoms and surface silver ions. For the cube faces, weak ligand bonds leading to epitaxic attachment have also been proposed (Bird, 1971; Smith, 1972), although on this surface, the long axes of the dye molecules must be twisted by at least 5° from [110] for the resulting aggregate to pack efficiently. Weak ligand bond formation is supported by the relative resistance of thiacarbocyanines to desorption (Reich, Pandolfe & Bird, 1973), by data on heats of adsorption (Wallace, 1968) and by the selective orientation of dyes along the [110] row. However, this hypothesis has been challenged by Ficken (1973), whose reflectance spectra of adsorbed thiacarbocyanine dyes were interpreted by him to indicate the presence of free-standing aggregates, and by Smith (1974) who suggested that solvent molecules and counterions play an important role in determining the nature of an aggregate. Below, we shall examine the possibility of epitaxically attaching the present dye to the AgBr cube and octahedral faces with the formation of weak ligand bonds.

To consider the detailed contact between the dye and the AgBr substrate, we must first examine the substrate structure. We consider the cube faces of AgBr first; these can be formed with a neutral electrostatic configuration by simply truncating the bulk structure. As a first approximation, we assume that a AgBr cube face is a simple array of interpenetrating Ag^+ and Br^- ions with the same lateral spacing as in the bulk; however, the Ag^+ and Br^- ions may shift upward or downward somewhat in response to peculiar bonding configurations at the surface. Information from low-energy electron diffraction studies would be required to obtain a more detailed picture of this surface.

Our results suggest that, without substantial readjustment of surface silver ions, it would be virtually impossible to pack the present thiacarbocyanine dye edge-on along a completely occupied [110] row with the formation of even weak $Ag^+\cdots S$ bonds. For appreciable bonding to occur, $Ag^+\cdots S$ distances should be less than 3·0 Å, the sum of the van der Waals radius of sulfur (1·85 Å) and the ionic radius of silver (1·15 Å, Shannon & Prewitt, 1968). Silver–sulfur distances in the range 2·6–2·8 Å have been observed in several silver complexes (Gasparri, Mangia, Musatti & Nardelli, 1968), and we take this range as representing that expected for weak interactions. Fig. 4 shows a model of the dye cation placed along a [110] row of AgBr in such a way as to form weak ligand bonds. For this geometry, the 7,7′ hydrogen atoms [crystallographic atoms H(C8) and H(C16)] interfere strongly with Ag^+ ions at site *B*; the calculated $Ag^+\cdots H$ distance is 1·22 Å. Removal of this steric interference by raising the dye from the surface would give a $Ag^+\cdots S$ (site *A*) distance of 3·8 Å, which is far too large to imply a ligand bond. To maintain weak bonds, Ag^+ ions on site *A* would have to be raised approximately 1 Å from the surface. We therefore conclude that weak ligand bonding of the type proposed cannot occur on an *ideal* AgBr cube face.

Treatment of a {111} AgBr surface is more complex. If an octahedral face were formed by truncation, it would consist exclusively of a sheet of Ag^+ or Br^- ions. An electrically neutral crystal would contain equal areas of Ag^+ and Br^- faces, each with an extremely large potential. The potential may be reduced either by the presence of large concentrations of silver ion interstitials in the first few lattice spacings (Berry & Skillman, 1964) or by randomly positioning a half-sheet of Ag^+ ions over a full Br^- layer (Hamilton & Brady, 1970). Half-layer models have been used to interpret highly ordered metallic nuclei deposits on AgBr {111} faces. The true surface probably lies somewhere between these extreme possibilities and contains somewhat less than a half-layer of Ag^+ ions. For the purpose of discussion, we shall consider ideal {111} AgBr half-layer faces.

Epitaxic attachment of thiacarbocyanines along [110] is possible if the initially random Ag^+ ions are shifted into a geometry compatible with that of the dye. With the present cationic dye, six Ag^+ positions are covered by one dye molecule (the $Ag^+\cdots Ag^+$ spacing along [110] is 4·083 Å while the $Cl\cdots Cl$ distance in the dye, augmented by two Cl van der Waals radii, is 21·1 Å). Thus, allowing for the positive charge of this particular dye molecule, a maximum of four of the six Ag^+ sites could be vacant and electrical neutrality maintained. In Fig. 4, this would correspond to sites *A* occupied, and sites *B* and *C* vacant. The exact occupancy of site *C* will depend on the nature of the counter-ion layer and the number of interstitial Ag^+ ions. Fig. 5 shows one possibility for the surface

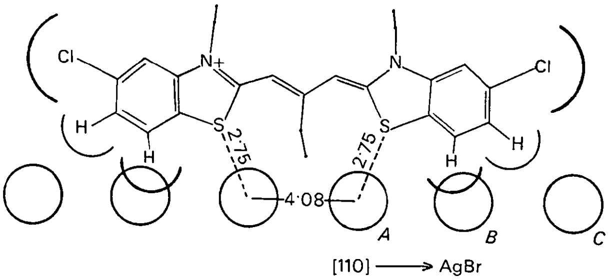

Fig. 4. The dye cation placed along an ideal [110] row of AgBr. Full circles represent the ionic radius of silver; arcs represent chlorine and hydrogen van der Waals radii.

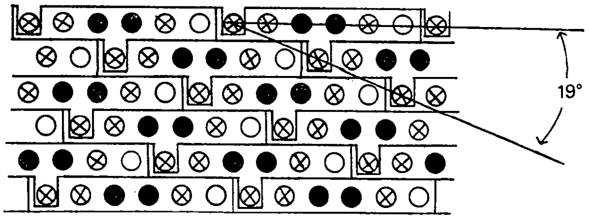

Fig. 5. Sketch of a portion of a {111} AgBr surface showing monolayer coverage by a cationic 9-ethylthiacarbocyanine dye which occupies six lattice positions. Tabs indicate protruding methyl groups. Filled, crossed and open circles represent occupied, vacant and partically occupied silver sites respectively. The 19° aggregate with one molecule per unit cell is shown.

obtained. Tabs in the figure indicate the locations of the 9-ethyl substituents [C(22), C(23)] which protrude from the cationic plane. These protruding groups have been shown to be a crucial structural feature which hinders the formation of undesirable 60° aggregates (Rosenoff, Walworth & Bird, 1970). Steric requirements are such that $Ag^+\cdots S$ distances of approximately 2·75 Å can be maintained only if the silver site below the ethyl group is vacant. With this proviso, there are no unusually short contacts between dye atoms and silver or halide ions. The ethyl groups may be placed above vacant Ag^+ sites *B* or *C*, leading to dye aggregates with slip angles of 30° or 19°06′ respectively. With the present dye, the 19° aggregate is expected to be most stable from steric considerations alone since the least hindered site (*C*) is vacant. However, there appears to be no great hindrance to the formation of the 30° aggregate, and either could form. On bare AgBr {111} faces, the 19° aggregate appeared to be most stable, while with crystals coated with gelatin, the 30° aggregate exhibited increased stability (Reich, Pandolfe & Bird, 1973). With the present dye, no evidence for a 60° aggregate was found.

Overall, these results suggest that epitaxic attachment of thiacarbocyanine dyes along [110] with the formation of weak ligand bonds is possible on the {111} faces of AgBr. The detailed nature of attachment of individual dyes should be affected by (1) their charge and the nature of the counterion layer, since these would affect the fraction of silver sites occupied, (2) the size and electronic characteristics of the 6,6′ substituents, since these could interact with silver ions at sites *C*, (3) solvent effects and (4) the lateral forces between dye molecules. Using the basic carbon skeleton from the present structure, we have calculated packing lengths and related parameters for a variety of 5,5′ and 6,6′-disubstituted dyes. The results of these calculations, which may be used to evaluate the above model, will be presented in a more specialized journal (Mastropaolo, Potenza & Bird, 1974).

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References

Berry, C. R. & Skillman, D. C. (1964). *J. Appl. Phys.* **35**, 2165–2169.

Bird, G. R. (1971). *Photogr. Sci. Eng.* **15**, 134–137.

Bird, G. R., Norland, K. S., Rosenoff, A. E. & Michaud, H. B. (1968). *Photogr. Sci. Eng.* **12**, 196–206.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE*. Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Ficken, G. E. (1973). *J. Photogr. Sci.* **21**, 11–17.

Gasparri, G. F., Mangia, A., Musatti, A. & Nardelli, M. (1968). *Acta Cryst.* B**24**, 367–374.

Gray, W. E., Brewer, W. R. & Bird, G. R. (1970). *Photogr. Sci. Eng.* **14**, 316–320.

Hamilton, J. F. & Brady, L. E. (1970). *Surf. Sci.* **23**, 389–402.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 201–209, 213–216. Birmingham: Kynoch Press.

Mastropaolo, D., Potenza, J. & Bird, G. R. (1974). *Photogr. Sci. Eng.* In the press.

Mees, C. E. K. & James, T. H. (1966). *The Theory of the Photographic Process*, chap. 11 and 12, pp. 198–277. New York: Macmillan.

Norland, K., Ames, A. E. & Taylor, T. (1970). *Photogr. Sci. Eng.* **14**, 295–307.

Reich, C., Pandolfe, W. D. & Bird, G. R. (1973). *Photogr. Sci. Eng.* **17**, 334–342.

Ricci, J. S., Eggers, C. A. & Bernal, I. (1972). *Inorg. Chim. Acta*, **6**, 97–105.

Rosenoff, A. E., Walworth, V. K. & Bird, G. R. (1970). *Photogr. Sci. Eng.* **14**, 328–335.

Shannon, R. D. & Prewitt, C. T. (1969). *Acta Cryst.* B**25**, 925–946.

Sheppard, S. E., Lambert, R. H. & Walker, R. D. (1939). *J. Chem. Phys.* **7**, 265–273.

Sheppard, S. E., Lambert, R. H. & Walker, R. D. (1941). *J. Chem. Phys.* **9**, 96–113.

Smith, D. L. (1972). *Photogr. Sci. Eng.* **16**, 329–333.

Smith, D. L. (1974). *Photogr. Sci. Eng.* In the press.

Smith, D. L. & Luss, H. R. (1972). *Acta Cryst.* B**28**, 2793–2806.

Wallace, F. (1968). Private communication quoted in Bird, G. R., Zuckerman, B. & Ames, A. E. (1968). *Photochem. Photobiol.* **8**, 393–410.

West, W., Carroll, B. H. & Whitcomb, D. H. (1952). *J. Phys. Chem.* **56**, 1054–1067.

Wheatley, P. J. (1959). *J. Chem. Soc.* pp. 3245–3250, 4096–4100.