The calculations were performed on the FACOM 230-48 Computer at the Institute for Solid State Physics, University of Tokyo.

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The Structure of 1,1′-Diethyl-2,2′-cyanine Iodide, a Photographic Sensitizing Dye

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The crystal structure of the title compound, $(C_{23}H_{23}N_2)^+I^-$, a well known spectral sensitizing dye in silver halide photography, has been determined by single-crystal X-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$, with four formula units in a cell of dimensions: $a = 10{\cdot}787\,(3)$, $b = 11{\cdot}626\,(2)$, $c = 16{\cdot}484\,(3)$ Å, and $\beta = 107{\cdot}48\,(3)°$. The structure was refined by block-diagonal least-squares calculations to a conventional R of 0·032 for 2177 observed reflexions collected on an automatic diffractometer. The dye cation assumes a skewed conformation with approximate symmetry 2 (C_2); the dihedral angle between the roughly planar quinoline rings is 41°. In the crystals each quinoline ring of the dye cation is stacked in a face-to-face manner with adjacent cations to form a double linear array along [101]. The intense, sharp J absorption band observed on a powder sample is ascribable to the linear array. A charge-transfer interaction between the dye cation and the iodide anion is suggested to be present from an SCF–MO calculation on the dye cation; this is evidenced by the crystal structure.

Introduction

Many photographic sensitizing dyes exhibit striking spectral shifts on aggregation in solution and on the surfaces of silver halide grains, and are interesting from both practical and theoretical points of view. Various one- and two-dimensional packing models of the dyes in the aggregates have been proposed. The actual molecular arrangements in the aggregates, however, have not definitely been established. Since the crystalline state is a three-dimensional aggregate of the constituents, the crystal structures of the dyes, as reviewed by Smith (1974), can provide a reliable structural model for the aggregates.

Of particular interest is 1,1′-diethyl-2,2′-cyanine halide (Fig. 1, hereinafter DYE halide), which is a typical quinocyanine dye exhibiting red- and blue-shifted absorption bands on aggregation (West & Carroll, 1966, a review). The absorption spectrum of a very dilute aqueous solution of the DYE halide shows a maximum near 525 nm (called the M band) (see Fig. 7). On increasing the DYE concentration a new band appears at about 485 nm, and subsequently an intense, remarkably sharp band at 573 nm. These bands, named H and J bands, are ascribed to dimeric and polymeric aggregates, or H and J aggregates respectively. The J band is

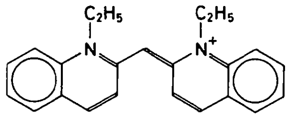

Fig. 1. Chemical structure of 1,1′-diethyl-2,2′-cyanine (DYE) iodide. This nomenclature is the most common (Brooker, 1966). Alternative names are: 1,1′-diethyl-2,2′-quinocyanine, *N,N′*-diethylpseudoisocyanine, bis(1-ethyl-2-quinoline)monomethine cyanine, *etc.*

also observable on the DYE adsorbates on silver halide grains (Tani & Tsuji, 1972; Tani, 1972; Cooper, 1973) and on the aggregates formed in a glassy matrix at 77 K (Cooper, 1970, 1973). Scheibe (1948), Czikkely, Försterling & Kuhn (1970), Cooper (1973), and Daltrozzo, Scheibe, Gschwind & Haimerl (1974) presented several structure models of *J* aggregates of DYE. Very recently, Marchetti, Salzberg & Walker (1976) concluded from their spectroscopic studies of the DYE halide that the *J* and *H* bands are crystal transitions and that the aggregated solutions contain at least two-dimensional microcrystals.

In this report the crystal structure of DYE iodide is described, and the absorption spectrum of the powder specimen is discussed in connexion with the structure.

The DYE chloride and bromide crystallize as monohydrates from methanol–water solutions; they are isomorphous with each other, and the structures have already been determined [chloride: Dammeier & Hoppe (1971), hereinafter DH (1971); bromide: Yoshioka & Nakatsu (1971), hereinafter YN (1971)]. In the analysis of the bromide we missed the water of crystallization but, except for the water environment, the structure was essentially correct. Recently the structure was refined with counter data to $R = 0{\cdot}068$ (Nakatsu, Yoshioka & Tsuji, 1977; hereinafter NYT, 1977).

Experimental

Slow evaporation of an ethanol–acetone solution of DYE iodide yielded dark-red, single crystals. A specimen, approximately 0·18 × 0·28 × 0·29 mm, was used for X-ray data collection on a computer-controlled four-circle diffractometer. The crystal data are given in Table 1.* The cell parameters were determined with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) by a least-squares fit of 11 reflexions in the range $19° < 2\theta < 27°$. The e.s.d.'s of the cell parameters are those from the least-squares calculation. Intensities for the independent reflexions for 2θ less than 50° were measured with the ω–2θ continuous scan mode at a 2θ rate of 2° min^{-1} by use of Zr-filtered Mo $K\alpha$ radiation. The scan width in 2θ was $(1{\cdot}6 + 0{\cdot}7 \tan\theta)°$ with background counts of 10 s on either side of the peak. To check electronic and crystal stability, the intensities of three reflexions were measured after every 50 reflexions. No remarkable variation was observed for these monitoring intensities during the data collection. The intensities were corrected for the Lorentz and polarization factors. Altogether 3618 reflexions were measured and of these 2177 reflexions with $|F_o| > 3\sigma(F)$ were considered observed and used for the structure determination.

Table 1. *Crystal data of* 1,1′-*diethyl*-2,2′-*cyanine iodide*

$(C_{23}H_{23}N_2)^+I^-$	FW 454·35
Monoclinic	Space group: $P2_1/c$
$a = 10{\cdot}787\,(3)$ Å	$V = 1971{\cdot}8$ Å^3
$b = 11{\cdot}626\,(2)$	$Z = 4$
$c = 16{\cdot}484\,(3)$	$D_x = 1{\cdot}531$ g cm^{-3}
$\beta = 107{\cdot}48\,(3)°$	μ(Mo $K\alpha$) = 16·6 cm^{-1}

Structure determination and refinement

The structure was solved by the usual combination of Patterson, Fourier, and least-squares methods. In the least-squares calculations the function $\sum w(|F_o| - |F_c|)^2$ was minimized, where w was the weight (see below). Positional and anisotropic thermal parameters of all the non-hydrogen atoms were refined by block-diagonal least-squares calculations to $R = \sum|\Delta F|/\sum|F_o| = 0{\cdot}045$ and $R_w = [\sum w(\Delta F)^2/\sum w(F_o)^2]^{1/2} = 0{\cdot}067$, where $\Delta F = |F_o| - |F_c|$. The weighting scheme used was $1/w = a + |F_o| + b|F_o|^2$, where $a = 2|F_o(\min)|$ and $b = 2/|F_o(\max)|$ (Cruickshank, 1965). A difference Fourier map calculated at this stage revealed all the H atoms; they were refined with isotropic temperature factors. The final residual indices are $R = 0{\cdot}032$ and $R_w = 0{\cdot}046$. In the final refinement cycle no individual parameter shift exceeded the corresponding e.s.d., except a few of the isotropic thermal factors for the H atoms. The subsequent difference map showed no unusual features. The averages of $\sum w(\Delta F)^2$ for several subgroups of increasing $|F_o|$ were reasonably constant.

Atomic scattering factors for C, N, and I$^-$ were taken from *International Tables for X-ray Crystallography* (1974); for H the factors of Stewart, Davidson & Simpson (1965) were used. The anomalous dispersion correction for I$^-$ was taken into account in the least-squares calculations: $\Delta f' = -0{\cdot}726$ and $\Delta f'' = 1{\cdot}812$ (Cromer & Liberman, 1970). All computations were carried out on a FACOM 270/20 computer of this University with the programs developed by the authors, and *DEAM* used for drawing thermal ellipsoids (A. Takenaka, private communication).

The final atomic coordinates of all the atoms and the isotropic thermal factors of the H atoms are given in Table 2.*

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* Throughout this paper the estimated standard deviation (e.s.d.) in the least significant digit of the preceding value is given in parentheses.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32431 (16 pp.). Copies may be obtained from the first author or through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final fractional atomic coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and isotropic thermal parameters* ($\times 10^3$) *for the hydrogen atoms*

The temperature factors are of the form: $\exp[-8\pi^2\overline{u^2}(\sin^2\theta/\lambda^2)]$.

	x	y	z		x	y	z	$\overline{u^2}$
I	2998·6 (4)	8594·5 (3)	3128·5 (2)	H(3)	408 (6)	459 (5)	137 (4)	38 (17)
N(1)	1414 (4)	3178 (4)	1197 (3)	H(4)	299 (6)	524 (5)	−5 (3)	35 (17)
C(2)	2580 (5)	3679 (4)	1597 (3)	H(5)	105 (6)	488 (5)	−135 (4)	42 (17)
C(3)	3134 (5)	4426 (4)	1103 (3)	H(6)	−88 (6)	378 (5)	−198 (4)	40 (18)
C(4)	2498 (5)	4649 (4)	277 (3)	H(7)	−163 (6)	239 (5)	−123 (4)	37 (17)
C(5)	676 (6)	4235 (5)	−1019 (3)	H(8)	−69 (6)	195 (5)	19 (3)	32 (16)
C(6)	−418 (6)	3617 (6)	−1407 (4)	H^1(12)	−23 (5)	258 (5)	152 (3)	30 (16)
C(7)	−910 (6)	2832 (6)	−949 (4)	H^2(12)	107 (6)	278 (5)	230 (4)	38 (17)
C(8)	−322 (5)	2684 (5)	−82 (3)	H^1(13)	67 (7)	63 (6)	203 (4)	66 (22)
C(10)	1310 (5)	4084 (5)	−133 (3)	H^2(13)	196 (6)	101 (7)	189 (4)	60 (22)
C(11)	772 (5)	3307 (5)	326 (3)	H^3(13)	86 (6)	86 (6)	114 (4)	58 (20)
C(12)	756 (5)	2483 (5)	1698 (3)	H(9)	303 (5)	259 (5)	264 (3)	29 (16)
C(13)	1095 (7)	1203 (6)	1708 (4)	H(3′)	355 (5)	564 (5)	253 (3)	24 (15)
C(9)	3255 (5)	3386 (5)	2442 (3)	H(4′)	515 (7)	674 (6)	337 (4)	54 (20)
N(1′)	5107 (4)	3578 (3)	3689 (2)	H(5′)	696 (7)	692 (7)	469 (5)	77 (23)
C(2′)	4229 (5)	4070 (5)	3005 (3)	H(6′)	846 (6)	593 (6)	600 (4)	43 (18)
C(3′)	4285 (6)	5291 (5)	2926 (3)	H(7′)	815 (6)	391 (5)	624 (4)	41 (18)
C(4′)	5168 (6)	5927 (4)	3487 (3)	H(8′)	664 (6)	291 (5)	521 (4)	43 (18)
C(5′)	6965 (6)	6046 (5)	4831 (4)	H^1(12′)	625 (5)	207 (5)	399 (3)	28 (16)
C(6′)	7745 (6)	5549 (6)	5560 (4)	H^2(12′)	499 (5)	205 (4)	318 (3)	6 (13)
C(7′)	7601 (6)	4395 (5)	5686 (4)	H^1(13′)	427 (7)	90 (7)	418 (5)	80 (17)
C(8′)	6748 (5)	3716 (4)	5083 (3)	H^2(13′)	345 (6)	202 (5)	400 (4)	41 (14)
C(10′)	6057 (5)	5416 (4)	4209 (3)	H^3(13′)	469 (5)	194 (5)	485 (3)	18 (23)
C(11′)	5970 (5)	4216 (4)	4325 (3)					
C(12′)	5211 (5)	2309 (4)	3736 (3)					
C(13′)	4395 (6)	1730 (5)	4228 (4)					

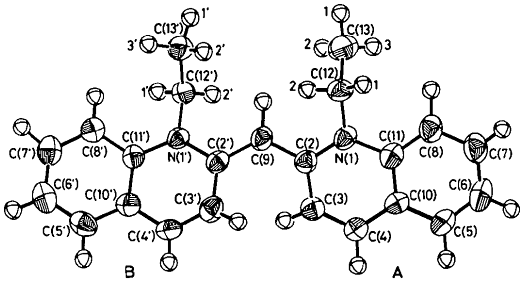


Fig. 2. Structure of 1,1′-diethyl-2,2′-cyanine cation projected on the plane *M* defined by the C(2), C(9), and C(2′) atoms. Thermal ellipsoids are scaled to include 50% probability except those for the H atoms, which are represented by spheres of a fixed arbitrary radius.

Description of the structure and discussion

Molecular structure

Fig. 2 shows the structure of DYE displayed by the thermal ellipsoids. Interatomic distances and bond angles are given in Fig. 3. Table 3 describes the relevant planes, deviations of atoms from the planes and the dihedral angles. The numbering system of the non-hydrogen atoms is the same as that adopted by DH (1971). The overall geometry of DYE is almost the same as that found in the chloride (DH, 1971) and the bromide (YN, 1971; NYT, 1977). DYE has an approximate twofold axis of rotation passing through the C(9) atom and bisecting the C(2)–C(9)–C(2′) angle. The two quinoline rings, *A* and *B*, are twisted almost symmetrically around the C(9)–C(2) and C(9)–C(2′) bonds, and, moreover, bent in such a way that the C(10) atom moves downward and the C(10′) atom upward from the C(2)–C(9)–C(2′) plane (plane *M*, see Table 3). Thus, the dihedral angles between the mean planes *A* and *B*, *A* and *M*, and *B* and *M* are 41, 21, and 20° respectively. On close examination, however, both quinoline rings are significantly non-planar: the pyridine and benzene rings in either quinoline are folded along the C(10)–C(11) and C(10′)–C(11′) bonds to give dihedral angles of 5·2 and 5·5°. Hence, the dihedral angles are 43·9° for the planes *A*-Py and *B*-Py, 23·7° for the planes *M* and *A*-Py and 22·8° for the planes *M* and *B*-Py. Most of these angles are less than those in the chloride (DH, 1971) (50·6, 26·2, and 24·0° respectively) and also in the bromide (NYT, 1977) (50, 28, and 22° respectively).

This finding is explained primarily by the location of the C(12) and C(12′) atoms, which are displaced out of the parent pyridine ring planes by +0·17 Å (upward in Fig. 2) and −0·25 Å (downward) respectively. A similar deviation of the *N*-methylene C atom from the parent *N*-hetero-ring plane is sometimes found: 0·30 and 0·23 Å in 1,1′,3,3′-tetraethylimidazo[4,5-*b*]-

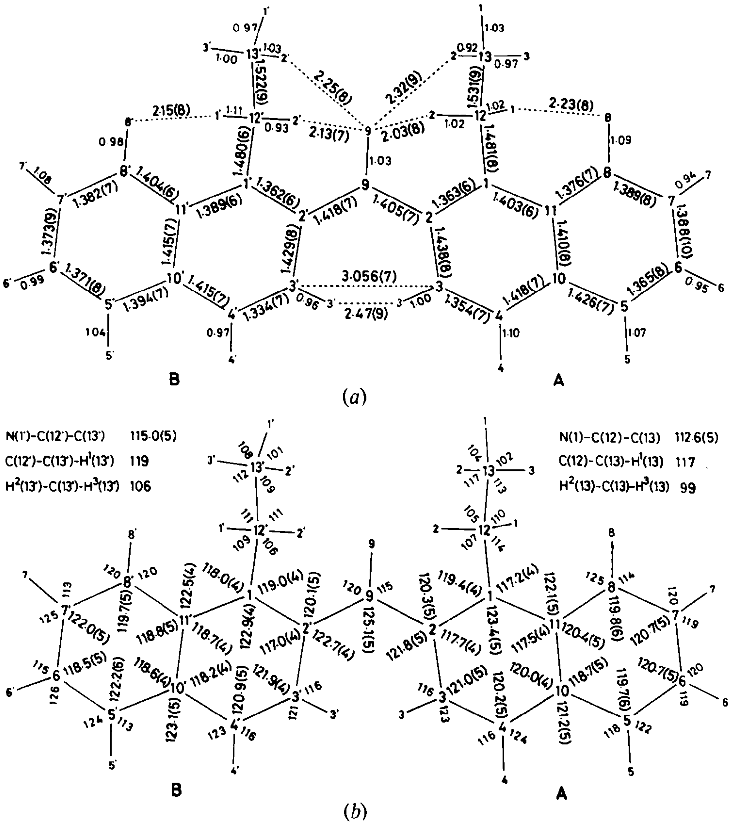


Fig. 3. (*a*) Bond lengths and some intramolecular short contacts (Å). E.s.d.'s for the C–H distances range from 0·05 to 0·08 Å. (*b*) Bond angles (°). E.s.d.'s for the angles including the H atoms are 3–5° for C–C–H, and 5–6° for H–C–H.

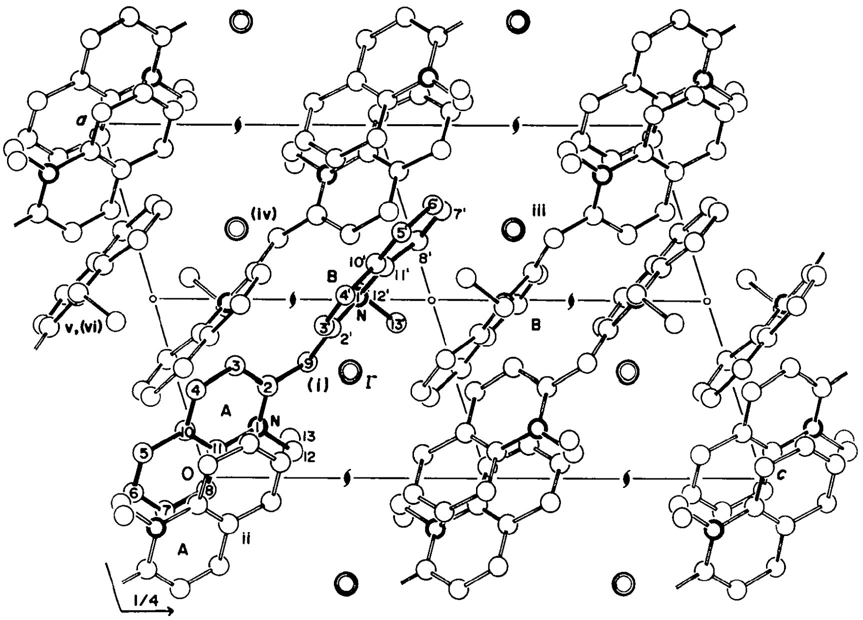


Fig. 4. Crystal structure viewed along **b**. DYE drawn with thick lines indicates the asymmetric cation whose atomic coordinates are given in Table 2. The lower-case roman numerals refer to different asymmetric cations and anions, and the numerals within parentheses show the **b**-translated species (see Table 5).

Table 3. *Description of planes*

(*a*) Equations of planes. Orthogonal coordinates (in Å), X, Y and Z, are taken along **a**, **b** and **c*** respectively.

Plane *M*: C(2), C(9), C(2′)
$-0{\cdot}832X + 0{\cdot}460Y + 0{\cdot}312Z = 1{\cdot}093$

Plane *A*-Py: N(1), C(2), C(3), C(4), C(10), C(11)
$-0{\cdot}595X + 0{\cdot}766Y + 0{\cdot}242Z = 2{\cdot}702$

Plane *A*-Bz: C(5), C(6), C(7), C(8), C(10), C(11)
$-0{\cdot}659X + 0{\cdot}726Y + 0{\cdot}199Z = 2{\cdot}440$

Plane *A*-Et: N(1), C(12), C(13)
$0{\cdot}554X + 0{\cdot}143Y + 0{\cdot}820Z = 2{\cdot}589$

Plane *B*-Py: N(1′), C(2′), C(3′), C(4′), C(10′), C(11′)
$-0{\cdot}851X + 0{\cdot}118Y + 0{\cdot}511Z = 0{\cdot}353$

Plane *B*-Bz: C(5′), C(6′), C(7′), C(8′), C(10′), C(11′)
$-0{\cdot}877X + 0{\cdot}181Y + 0{\cdot}445Z = 0{\cdot}157$

Plane *B*-Et: N(1′), C(12′), C(13′)
$0{\cdot}535X + 0{\cdot}075Y + 0{\cdot}842Z = 7{\cdot}162$

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

	A-Py	*A*-Bz		*B*-Py	*B*-Bz
N(1)	31*	2	N(1′)	−34*	−57
C(2)	−2*	−148	C(2′)	2*	102
C(3)	−26*	−228	C(3′)	22*	216
C(4)	23*	−115	C(4′)	−14*	150
C(10)	5*	−10*	C(10′)	−17*	19*
C(11)	−32*	9*	C(11′)	41*	−19*
C(5)	−51	1*	C(5′)	−2	−2*
C(6)	−162	9*	C(6′)	107	−18*
C(7)	−235	−10*	C(7′)	235	19*
C(8)	−159	1*	C(8′)	186	0*
C(12)	172	203	C(12′)	−245	−368
C(9)	−125	−335	C(9)	113	242
H(3)	−310	−590	H(3′)	260	530
d†	23	8		25	15

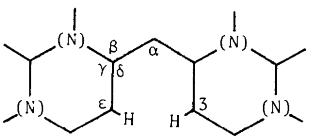
(*c*) Dihedral angles (°) between the planes

M–*A*-Py	22·7	*M*–*B*-Py	19·4
A-Py–*A*-Bz	5·0	*B*-Py–*B*-Bz	5·4
A-Py–*A*-Et	88·8	*B*-Py–*B*-Et	89·1
A-Py–*B*-Py	43·9		

† Root-mean-square deviation from the plane.

Table 4. *Comparison of distances* (Å) *and mean angles* (°) *related to the overcrowding around* C(3) *and* C(3′)

The compound and reference notations are: (2,2′) 1,1′-diethyl-2,2′-cyanine, (2,4′) 1,1′-diethyl-2,4′-cyanine, (4,4′) 1,1′-diethyl-4,4′-cyanine; NYT Nakatsu, Yoshioka & Tsuji (1977), DH Dammeier & Hoppe (1971), NYM Nakatsu, Yoshioka & Morishita (unpublished work), YN Yoshioka & Nakatsu (1971). Key for the angles:



	(2,2′)I	(2,2′)Br. H_2O	(2,2′)Cl. H_2O	(2,4′)I. $2H_2O$	(4,4′)Br
C(3)···C(3′)	3·056 (7)	3·11 (2)	3·106 (5)	3·08 (2)	3·15 (3)
H(3)···H(3′)	2·47 (9)	2·4 (2)	2·37 (6)	2·2 (2)	–
α	125·1 (5)	125 (1)	125·3 (4)	125 (1)	129 (2)
β	120·2 (5)	119 (1)	118·9 (5)	121 (1)	122 (2)
γ	117·4 (4)	118 (1)	117·6 (3)	116 (1)	115 (2)
δ	122·3 (5)	123 (1)	123·2 (4)	125 (1)	124 (2)
ε	121·5 (5)	121 (1)	122·3 (4)	122 (1)	122 (2)
φ*	43·9	50	50·6	40	40
Reference	This work	NYT	DH	NYM	YN

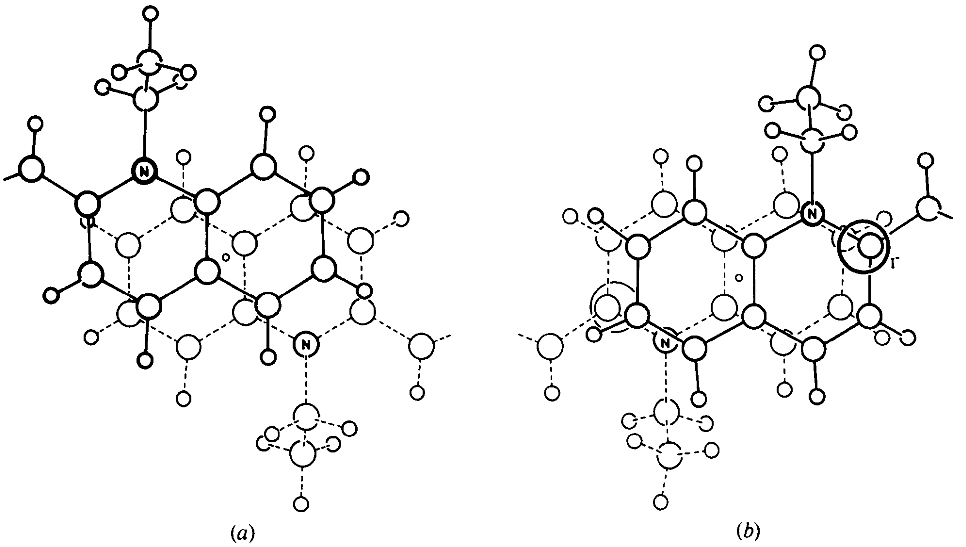
* Dihedral angle between the quinoline rings, except in (2,2′)I between pyridine rings.

quinoxalinocyanine dye (Smith & Barrett, 1971) and 0·18 Å in 1,1′-diethyl-2,4′-cyanine dye (Morishita & Nakatsu, unpublished). In the chloride (DH, 1971) the corresponding deviations are only +0·03 and −0·02 Å. The out-of-plane shifts of C(12) and C(12′) resolve the severe overcrowding which otherwise exists around H(9) (see Fig. 3*a*), and hence cause the dihedral angle between the quinoline rings to decrease. In the chloride or bromide the overcrowding is resolved by the large twisting of the quinoline rings about the plane *M*.

Owing to the small dihedral angle between the planes *A*-Py and *B*-Py, the C(3) and C(3′) atoms approach each other to give a shorter distance, 3·054 (7) Å, than the 3·106 (5) Å in the chloride and 3·11 (2) Å in the bromide (NYT, 1977). The resulting conflict between H(3) and H(3′) is relieved by the deviations of these atoms by −0·31 and +0·26 Å out of the planes of *A*-Py and *B*-Py respectively. Thus all the intramolecular non-bonded H···H contacts are preserved in the range of the usual van der Waals approach. Previously, the twisting of the quinoline rings was ascribed to the steric hindrance between H(3) and H(3′) (YN, 1971). The present DYE structure shows, however, that the non-bonded interatomic contacts between H(9) and the ethyl H atoms are important as well.

Table 4 compares the distances and angles of the C(3)–C(2)–C(9)–C(2′)–C(3′) fragment with those of similar dyes. The deviations of the bond angles from 120° show a common tendency among the dyes cited: the deviations of α are largest, while the β's are kept almost to 120°. The endocyclic bond angles, γ, are less than 120°: this is commonly found in pyridine derivatives. The angle C(2)–C(3)–H(3) and its equivalent in *B* are somewhat less than C(4)–C(3)–H(3): this tendency is seemingly contrary to what is expected in order to relieve the steric hindrance between H(3) and H(3′). In the chloride no significant difference has been found.

No adequate explanation was found here for the cause of the deviations of the C(12) and C(12′) atoms from the pyridine ring planes. Smith & Barrett (1971) attributed similar deviations in the structure of



(*a*) (*b*)

Fig. 5. The relative orientation of the quinoline rings viewed perpendicular to the mean ring plane. (*a*) Ring *A* (broken lines) and ring A^{ii} (solid lines) related by $\bar{1}$ at $(0,\frac{1}{2},0)$. (*b*) Ring *B* (broken lines) and ring B^{iii} (solid lines) related by $\bar{1}$ at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

Table 5. *Short intermolecular distances* (Å)

(*a*) H···H < 2·6 Å, e.s.d. = 0·08–0·10 Å

$H(5')\cdots H^3(13'^{iii})$	2·51	$H(7)\cdots H^1(12'^{vii})$	2·50
$H^2(12')\cdots H(4'^{iv})$	2·53	$H^1(12)\cdots H(7'^{vii})$	2·41
$H(4)\cdots H^1(13'^{v})$	2·51		

(*b*) H···I < 3·4 Å, e.s.d. = 0·05–0·08 Å

$H(4')\cdots I$	3·11	$H(3)\cdots I^{iv}$	3·23
$H^1(13')\cdots I^{i}$	3·27	$H(4)\cdots I^{vi}$	3·30
$H(7)\cdots I^{ii}$	3·24	$H(5)\cdots I^{vi}$	3·06
$H(8')\cdots I^{iii}$	3·18		

(*c*) C···I < 4·1 Å, e.s.d. = 0·004–0·007 Å

$C(4')\cdots I$	3·823	$C(3)\cdots I^{iv}$	4·095
$C(13')\cdots I^{i}$	4·001	$C(2')\cdots I^{iv}$	4·012
$C(7)\cdots I^{ii}$	3·984	$N(1')\cdots I^{iv}$	4·102
$C(8')\cdots I^{iii}$	3·938	$C(5)\cdots I^{vi}$	4·091

Symmetry code

None	$x,$	$y,$	z	(iv)	$1-x,$	$-\frac{1}{2}+y,$	$\frac{1}{2}-z$
(i)	$x,$	$-1+y,$	z	(v)	$x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$
(ii)	$-x$	$1-y,$	$-z$	(vi)	$x,$	$\frac{3}{2}-y,$	$-\frac{1}{2}+z$
(iii)	$1-x,$	$1-y,$	$1-z$	(vii)	$-1+x,$	$\frac{1}{2}-y,$	$-\frac{1}{2}+z$

1,1',3,3'-tetraethylimidazo[4,5-*b*]quinoxalinocyanine dye to the intramolecular steric hindrance between the crowded *N*-methylene groups. This view is not accepted here, because no deviation is found in the DYE structures in the chloride and bromide. Crystal packing may influence the methylene atoms, but no clear evidence is found from the crystal structure. Another suggestion is that the DYE structure may be slightly changed due to a charge-transfer interaction between the DYE cation and the I^- ion in the crystals. Some evidence for this is found from the crystal structure as described in the following section.

The bond lengths and angles in the two halves of DYE are in near agreement with each other – within three times their e.s.d.'s except for a few. Therefore, in spite of the skewed conformation a high conjugation is attained almost completely. Averaged bond lengths and angles involving only the non-hydrogen atoms agree well with those found in the chloride (DH, 1971) and in the bromide (NYT, 1977). The only significant difference in the lengths appears for the C(2)—C(3) bond and its equivalent in *B*: the average distance of 1·434 Å is longer than that of 1·416 Å found in the chloride. For bond angles, C(2)—N(1)—C(11) angles (average 123·2°) are somewhat greater than those found in the chloride (average 121·8°).

Crystal structure

The crystal structure consists of the DYE cations and the I^- anions, as shown in Fig. 4. DYE's are stacked face-to-face by each quinoline ring: ring *A* of DYE, drawn with thick lines in Fig. 4, is related to ring A^{ii} by the centre of symmetry at $(0,\frac{1}{2},0)$, the interplanar spacing being 3·65 Å; similarly, ring *B* faces parallel to ring B^{iii} with a separation of 3·60 Å across the centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$. These interplanar separations are greater than the usual graphitic separation of about 3·4 Å because of the stacking of the 1-ethylquinoline rings, where the H atoms of the ethyl groups prevent a closer mutual approach of the quinoline rings. The successive stacking of DYE's extends along [101]. This linear arrangement or quasi-one-dimensional thread of DYE's is different from the DYE stacking found in the DYE chloride (DH, 1971) and the bromide (YN, 1971), in which the DYE array is somewhat similar to the stair-

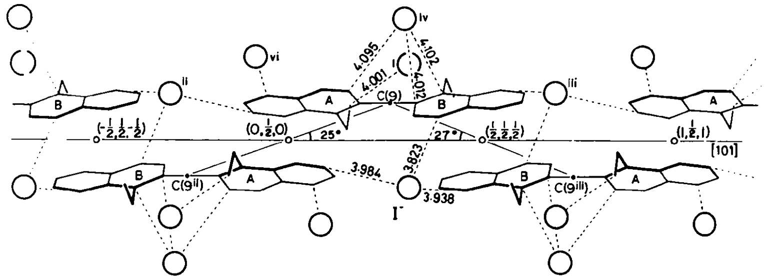


Fig. 6. Double linear array extracted from the crystal structure. The [101] direction is horizontal. Small circles represent centres of symmetry and large circles iodide ions. The lower-case roman numerals indicate different asymmetric units (see Table 5).

case type (Czikkely, Försterling & Kuhn, 1970) or the slipped-deck-of-cards type (Reich, Pandolfe & Bird, 1973) and has been discussed by Smith (1974). The present DYE arrangement is described below in detail. Fig. 5 illustrates the overlap orientations of the quinoline rings related by the centres of symmetry; these may be compared with those shown in Fig. 5 of the previous paper (YN, 1971).

Interatomic distances between the DYE cations and the I^- anions are given in Table 5. Several close contacts less than the sum of the van der Waals radius and the ionic radius are found. The shortest contact of 3·823 (5) Å between I^- and C(4′) is considerably less than the expected value of about 4·2 Å. The I^{iv} ion is located on top of the ring *B* at the C(2′) atom (Fig. 5*b*).

An SCF–MO calculation on the DYE cation with the π-approximation (K. Nishimoto, personal communication) shows that the energy of the lowest vacant MO is 2·70 eV, which is close to the negative of the electron affinity of the I atom, 3·063 ± 0·003 eV (Berry & Reimann, 1963). On the other hand, the frontier electron densities, f_r^-, for the lowest vacant MO, defined by $f_r^- = c_r^2$, where c_r is the coefficient of the *r*th AO, are calculated to be 0·128 (the largest) on C(2), 0·123 (the second largest) on C(4), 0·079 on N(1), and less than 0·054 on the other skeleton atoms. These results suggest that some charge-transfer interaction between the DYE cation and the I^- anion is possibly present at the C(2) and C(4) atoms. This is evidenced by the fact that the I^- ion is located near those atoms (see below). In view of the skewed conformation of DYE the $C(2)\cdots I^{iv}$ contact seems to be the closest possible. It should be noted that the largest positive net charge is assigned to the C(2) atom by several MO calculations: +0·122 (π-approximation) by Nishimoto, +0·189 ($\sigma + \pi$) by Ferré, Larivé & Vincent (1974), and +0·40 ($\sigma + \pi$) by Hada & Honda (1975).

The arrangement of the I^- ions around the DYE cation is somewhat similar to those found in several ionic charge-transfer compounds: in *N*-methylacridinium iodide (Nakamura, Yasuoka, Kasai, Mikawa & Kakudo, 1970) the I^- ion is located approximately above the midpoint of an endocyclic N–C bond with the distances $N\cdots I^- = 3{\cdot}78\,(2)$ and $C\cdots I^- = 3{\cdot}75\,(2)$ Å, while in 1-ethyl-2-methylquinolinium iodide (Sakanoue, Kai, Yasuoka, Kasai, Kakudo & Mikawa, 1969; Sakanoue, Kai, Yasuoka, Kasai & Kakudo, 1970) the I^- ion is almost coplanar with the quinoline ring, the shortest distance between C and I^- being 3·95 (2) Å.

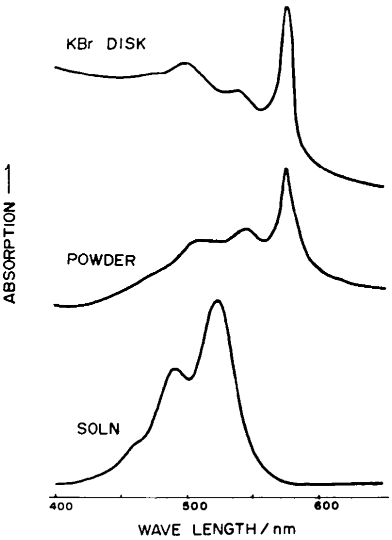


Fig. 7. Absorption spectra of the DYE iodide recorded on a Cary 14 spectrophotometer. KBr DISK: spectrum measured from a KBr disk sample. POWDER: spectrum of powder sample suspended on a quartz-glass plate. SOLN: spectrum measured from an ethanol solution of 10^{-5} mol dm^{-3}. The ordinate is on an arbitrary linear scale, and the three curves are not to the same scale.

Fig. 6 illustrates a portion of the crystal structure viewed parallel to the plane *M* and perpendicular to [101], showing a double linear array of DYE cations together with the I^- ions surrounding it. The lower DYE's are related to the upper DYE's by centres of inversion, so that a unit cell of the array contains two DYE's. The adjacent arrays are produced by the operations of the 2_1 axes or the *c* glide planes to give the whole crystal structure. The angles between [101] and the lines connecting the C(9) atom of a DYE to those of facing DYE's are 25 and 27°, which correspond to the 'slip angle' or 'tilt angle' used to describe the mutual orientation of dyes in aggregate of the slipped-deck-of-cards type (Smith, 1974). The long molecular axis, taken as the line joining N(1) and N(1′), is inclined 12° to [101]. According to Norland, Ames & Taylor (1970) this crystal should show a red-shifted absorption band, since the slip angles are less than 32°. In fact, a powder specimen of these crystals exhibits a sharp, red-shifted *J* band at 575 nm (Fig. 7), which is almost in agreement with that observed by Jelley (1936) and Scheibe (1948) from a concentrated solution, and also with that observed by Marchetti, Salzberg & Walker (1976) from the DYE iodide crystals. Hence, the linear array, shown in Fig. 6, should be taken as a *J* aggregate. This array resembles apparently the brickstone model of Czikkely, Försterling & Kuhn (1970) and closely the model *A*-1 of Daltrozzo, Scheibe, Gschwind & Haimerl (1974), but not the model by Scheibe, Haimerl & Hoppe (1970).

In epitaxically adsorbed aggregates on the surfaces of silver halide crystals or of some other solids, DYE's would necessarily be arranged such that they all keep a particular orientation with respect to the solid surface. Therefore, the centrosymmetric arrangement found in the present crystal structure may not be accommodated for such adsorbates, and the model proposed by Scheibe, Haimerl & Hoppe (1970) or some other polar model might be more plausible. Nevertheless, the fact that the *J* band has been observed from the present crystal implies that a centrosymmetric model should also be considered.

It should be noted that in the aggregate model so far proposed no participation of the anions on aggregation has been considered seriously. It is unlikely that the anions are not associated with the formation and the stabilization of the aggregates. The crystal structure could provide a useful model for the role and the arrangement of the anions around the cationic aggregates.

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