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The Crystal Structures of Three New Solvates of 5,5′,6,6′-Tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine Iodide

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Two solvate crystals of the title dye (DYE), the 2 : 1 methanol : DYE (DYE2M) and the 1 : 1 acetonitrile : DYE (DYEA), were investigated previously [Smith & Luss, *Acta Cryst.* (1972), B**28**, 2793–2806]. Three new solvates, the 1 : 1 ethanol : DYE (DYEE), the 1 : 1 methanol : DYE (DYE1M) and the 2 : 1 dichloromethane : DYE (DYEDC), were studied to find the effect of intermolecular interactions between the dye molecules. The crystal structures were determined from single-crystal X-ray data. DYEE is monoclinic, $P2_1/c$, with a = 16·490 (1), b = 10·990 (1), c = 17·876 (1) Å, β = 108·72 (1)°, and Z = 4; DYE1M is isomorphous with DYEE, with a = 16·262 (1), b = 10·912 (1), c = 17·579 (1) Å, β = 108·04 (1)°, and Z = 4; DYEDC is monoclinic, $P2_1/c$, with a = 14·426 (1), b = 18·237 (1), c = 14·741 (1) Å, β = 118·33 (1)°, and Z = 4. The final R values are 0·096 for DYEE, 0·071 for DYE1M and 0·124 for DYEDC. The bond distances and angles agree with the values reported for DYE2M and DYEA. The crystal structures of five dye solvates are classified into two types; DYE2M, DYEA and DYEDC are grouped into type I, in which the cations pack plane-to-plane in sheets; DYEE and DYE1M belong to type II, in which the cations form dimers and each dimer is linked to another behind it through the overlap of half a dye-cation ring. Close Cl · · · Cl contacts were found, which may indicate a specific interaction between the substituent Cl atoms. The correlation of the crystal structures with the electronic spectra of aggregates is discussed.

Introduction

Cyanine dyes form several different kinds of aggregates which exhibit spectral shifts of the order of ±100 nm from the solution monomer spectrum. Aggregates with red-shifted intense sharp absorption maxima were found by Jelley (1936) and Scheibe (1936) in solution, and were called *J* aggregates. Blue-shifted aggregates were also found in solution, and some of them show intense sharp absorption spectra which were called H^* bands (West, Lovell & Cooper, 1970; Herz, 1974). Molecular and crystal structures of cyanine dyes have been investigated by many investigators and several types of stacking modes were observed (Wheatley, 1959*a*,*b*; Dammeier & Hoppe, 1971; Yoshioka & Nakatsu, 1971; Smith & Barrett, 1971; Nakatsu, Yoshioka & Aoki, 1972; Smith & Luss, 1972, 1975; Potenza & Mastropaolo, 1974).

Scheibe, Muller & Schiffmann (1941) proposed the ladder and staircase models for the *J* aggregate of 2,2′-cyanine dyes, but these models were revised by Daltrozzo, Scheibe, Gschwind & Haimerl (1974) based on the X-ray structural result of Dammeier & Hoppe (1971). Bird and his group (Emerson, Conlin, Rosenoff, Norland, Rodriguez, Chin & Bird, 1967; Bird, Zuckerman & Ames, 1968) proposed the model for the *J* and *H* aggregates of thiacarbocyanine dyes.

The title compound (DYE) is an efficient spectral sensitizer of the silver halide photographic system to green light and the crystal structures of two solvates, the 2 : 1 methanol : DYE (DYE2M)* and the 1 : 1 acetonitrile : DYE (DYEA), were determined by Smith

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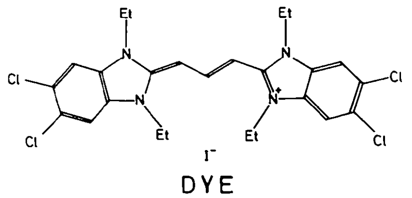
* The crystal was named as DYEM by Smith & Luss, but in this paper it is called DYE2M to distinguish it from the 1 : 1 methanol : DYE solvate (DYE1M).



DYE

& Luss (1972). The crystal structures were considered to conform to the stacking mode of the dyes on AgBr crystals, and this was regarded as a model structure of the J aggregates (Smith, 1974). Actually these crystals were found to show sharp J bands in the single-crystal spectra recently measured by Tanaka, Tanaka, Kaneda & Yoon (1976).

To elucidate further the relation between the structures and the spectral properties of the J and H^* aggregates, we undertook the determination of the crystal structures of three new solvates of the dye. The present solvate crystals, the 1 : 1 ethanol : DYE (DYEE), the 1 : 1 methanol : DYE (DYE1M) and the 2 : 1 dichloromethane : DYE (DYEDC), were shown to have different structures and spectral properties as compared with those previously determined. The structural characteristics of five crystals were clearly demonstrated and their correlation with spectral properties was elucidated. These results will add to both the photosensitizing theory of the cyanine dyes (West, 1974) and the formulation of the mechanism of photosynthesis (Chow, Serlin & Strouse, 1975). They are also important for the quantum-mechanical interpretation of the origin of the J and H^* bands and the excitation transfer mechanism in dye or chlorophyll aggregates.

Experimental

DYE.C_2H_5OH (*DYEE*)

Crystals were obtained by slow evaporation at room temperature from a hot solution in ethanol. They were fairly stable while in air but gradually lost their lustre. They were kept in an air–ethanol atmosphere for preservation. The density measurement showed the crystal to be a 1 : 1 ethanol : DYE solvate; this was verified by proton counting in a high-resolution NMR spectrum of the dyes in CD_3Cl and by the crystal structure analysis.

DYE.CH_3OH (*DYE1M*)

Powdered crystals of the dye were dissolved in a hot methanol–water mixed solution (volume ratio of MeOH : H_2O = 4 : 1), and slow evaporation at about 30°C yielded chunky crystals after two weeks. The density measurement and the crystal structure showed that the crystal was a 1 : 1 methanol : DYE solvate. Although Smith & Luss (1972) reported that the DYE2M crystal was unstable, the DYE1M crystal was considerably stable while in air. However, the crystals were preserved in an air–methanol–water atmosphere.

DYE.$2CH_2Cl_2$ (*DYEDC*)

Powdered crystals were dissolved in warm dichloromethane. Slow evaporation at room temperature yielded chunky crystals just before complete drying. The density measurement and the crystal structure showed the crystals to be a 2 : 1 CH_2Cl_2 : DYE solvate. They were quite unstable while in air, *i.e.* they lost the solvent dichloromethane molecules and developed many cracks within two or three days. They were preserved in an air–dichloromethane atmosphere.

Crystal data are shown in Table 1. Fig. 1 shows the crystal forms of DYEE, DYE1M and DYEDC. The DYEE crystal is a thin tabular plate showing prominent faces {100}, {011} and {101}. The prominent faces of DYE1M are {100}, {011}, {111} and {101} with {001} occasionally developed, and those of DYEDC are {110}, {011} and {010}. The space groups were determined from oscillation and Weissenberg photographs. The densities were measured by the flotation method. The cell dimensions were determined by the least-

Table 1. *Crystal data*

	DYEE	DYE1M	DYEDC
Formula	$C_{25}H_{27}N_4Cl_4I.C_2H_5OH$	$C_{25}H_{27}N_4Cl_4I.CH_3OH$	$C_{25}H_{27}N_4Cl_4I.2CH_2Cl_2$
Molecular weight	698·30	684·27	822·10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell: a	16·490 (1) Å	16·262 (1) Å	14·426 (1) Å
b	10·990 (1)	10·912 (1)	18·237 (1)
c	17·876 (1)	17·579 (1)	14·741 (1)
β	108·72 (1)°	108·04 (1)°	118·33 (1)°
Z	4	4	4
D_m	1·511 g cm^{-3}	1·540 g cm^{-3}	1·595 g cm^{-3}
D_c	1·512	1·532	1·599
μ	15·8 cm^{-1} (for Mo $K\alpha$)	133·4 cm^{-1} (for Cu $K\alpha$)	144·2 cm^{-1} (for Cu $K\alpha$)
Colour reflexion	Gold	Gold	Gold
Colour transmission	Red	Red	Purple

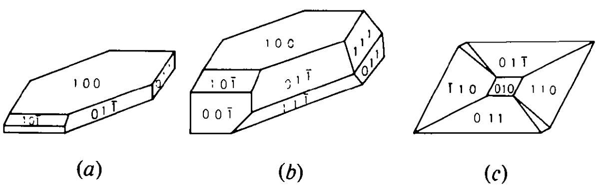


Fig. 1. The crystal habits of (*a*) DYEE, (*b*) DYE1M and (*c*) DYEDC.

squares method, from 12 reflexions measured on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation (λ = 0·71069 Å) for DYEE and with Ni-filtered Cu $K\alpha$ radiation (λ = 1·5418 Å) for DYE1M and DYEDC. Intensity data with $2\theta < 52°$ for DYEE, $2\theta < 130°$ for DYE1M and $2\theta < 114°$ for DYEDC were collected on the diffractometer in a θ–2θ scan mode with the respective radiations mentioned above for each crystal. The crystals were mounted in glass capillaries with a minute drop of solvent for the X-ray measurements. The sizes of the crystals were 0·4 × 0·4 × 0·1 mm for DYEE, 0·4 × 0·3 × 0·2 mm for DYE1M, and 0·3 × 0·3 × 0·3 mm for DYEDC. An absorption correction was applied for DYE1M with the program *INCOR* (Takeda & Irimajiri, 1967) with some modifications. However, the correction was not applied for DYEE because of the smallness of the absorption coefficient and the size of the crystal used for the data collection.

Determination and refinement of the structures

DYEE

The structure was solved by the heavy-atom method. A difference Fourier synthesis revealed the disordered ethyl group attached to N(2), and the disordered sites of the ethanol molecule. The occupancies for the differently oriented ethyl groups were refined as a group by the least-squares method to 0·5 for each. Those for the disordered sites of the ethanol molecule were estimated from the peaks on Fourier and difference Fourier maps. Subsequent block-diagonal least-squares refinement was repeated with anisotropic thermal parameters for all non-hydrogen atoms, and the final *R* index converged to 0·096.

DYE1M

As the crystal is isomorphous with DYEE, the structural parameters were refined with the atomic coordinates of DYEE. Six peaks remained in the Fourier and difference Fourier maps; four of them were assigned to two sites of the disordered ethyl groups attached to N(2) and two other peaks were considered to be a methanol molecule. Subsequently, the coordinates, anisotropic thermal parameters and occupancies of the disordered ethyl groups were refined by the block-diagonal least-squares method, and the final *R* index converged to 0·071.

DYEDC

The structure was solved by the heavy-atom method. As the thermal motion of the solvent molecule was fairly large and the crystal was not very stable, the structure could not be determined with high precision. The final *R* index converged to 0·124.

Total data of 2436, 3295 and 2288 independent reflexions with $|F_o| > 3\sigma$ were used for the least-squares refinement for DYEE, DYE1M and DYEDC respectively, and the calculations were performed with equal weights for the reflexions. The atomic scattering factors were taken from Cromer & Waber (1965) for the iodide ion, and from *International Tables for X-ray Crystallography* (1962) for the other atoms. The anomalous scattering component for the iodide ion was taken from Cromer & Liberman (1970). The program *HBLS*-IV (Ashida, 1967) and *ATLS* coded by A. Furusaki *et al.* and revised by C. Katayama and A. Wada were used for the block-diagonal least-squares refinements, and *RSDA*-4 (Sakurai, 1967) for the calculation of intermolecular distances. All computations were performed on a FACOM 230-60 computer at the Nagoya University Computation Center.

Description of the structures

I. *Molecular structures of DYEE and DYE1M*

The final positional parameters with their estimated standard deviations are listed in Tables 2 and 3 for DYEE and DYE1M respectively.* The atomic labelling, bond distances and angles for the dye cations are shown in Fig. 2. The average e.s.d.'s of the bond distances are 0·026 Å (range 0·019–0·031 Å) for DYEE and 0·014 Å (range 0·010–0·023 Å) for DYE1M, and those of the angles are 1·7° (range 1·3–2·2°) for DYEE and 0·9° (range 0·7–1·1°) for DYE1M. The accuracy for DYE1M is better than that for DYEE.

The bond distances and angles of the cations for both crystals are in good agreement with those found in DYE2M and DYEA (Smith & Luss, 1972). The results show that the conjugated system extends over the whole molecule. The bond distances and angles around the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32388 (48 pp.). Copies may be obtained through the authors or through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final positional parameters* (×10⁴) *for DYEE*

Estimated standard deviations are given in parentheses.

	x	*y*	*z*
I	3491 (1)	4122 (1)	3206 (1)
Cl(1)	9144 (5)	3114 (6)	7188 (4)
Cl(2)	9495 (6)	372 (6)	6957 (5)
Cl(3)	1221 (5)	−4778 (5)	749 (4)
Cl(4)	285 (5)	−2516 (6)	−210 (4)
N(1)	6231 (11)	2362 (12)	4977 (7)
N(2)	6487 (14)	399 (14)	4852 (11)
N(3)	3299 (12)	−1601 (12)	2537 (9)
N(4)	2568 (12)	−2 (13)	1902 (9)
C(1)	7044 (13)	2112 (14)	5510 (9)
C(2)	7634 (14)	2820 (17)	6044 (11)
C(3)	8375 (14)	2262 (17)	6480 (11)
C(4)	8527 (16)	1029 (22)	6400 (12)
C(5)	7935 (17)	281 (19)	5872 (13)
C(6)	7205 (16)	855 (18)	5445 (12)
C(7)	5900 (14)	1290 (15)	4568 (10)
C(8)	5059 (16)	1300 (15)	4014 (11)
C(9)	4625 (16)	311 (16)	3553 (12)
C(10)	3800 (14)	519 (14)	3022 (10)
C(11)	3292 (16)	−353 (16)	2524 (13)
C(12)	2602 (16)	−2047 (16)	1905 (11)
C(13)	2343 (16)	−3232 (18)	1689 (11)
C(14)	1619 (18)	−3319 (17)	1043 (12)
C(15)	1173 (17)	−2281 (19)	614 (12)
C(16)	1401 (16)	−1133 (20)	857 (13)
C(17)	2154 (16)	−1018 (17)	1519 (12)
C(18)	5834 (14)	3575 (15)	4900 (12)
C(19)	6121 (19)	4351 (18)	4306 (14)
C(20*A*)	6210 (32)	−1035 (34)	4820 (24)
C(20*B*)	6527 (29)	−790 (32)	4410 (23)
C(21*A*)	6603 (36)	−1293 (41)	4138 (28)
C(21*B*)	6197 (45)	−1786 (34)	4737 (30)
C(22)	3939 (14)	−2396 (16)	3088 (10)
C(23)	4670 (16)	−2723 (21)	2772 (13)
C(24)	2302 (18)	1298 (18)	1634 (14)
C(25)	1629 (24)	1685 (23)	1970 (19)
O(1*E*)*	2135 (28)	2160 (31)	9144 (22)
O(2*E*)*	2164 (50)	1036 (73)	9482 (33)
C(26*E*)	1203 (33)	1875 (36)	8819 (25)
C(27*E*)*	901 (44)	961 (51)	9120 (32)
C(28*E*)*	1356 (87)	956 (102)	8898 (74)

* The occupancy for O(1*E*) and C(27*E*) is 0·65; for O(2*E*) and C(28*E*) it is 0·35.

disordered ethyl groups and the values for the solvent ethanol molecules listed in Table 4 show abnormal values because of the disordered structures.

The equations of the least-squares planes for the benzimidazole *A* plane [C(1)–C(7), N(1) and N(2)], *B* plane [C(11)–C(17), N(3) and N(4)], and *C* plane (trimethine bridge) are listed in Table 5 with the deviations of the atoms from these planes. Cl(3) deviates −0·11 Å in DYEE and −0·12 Å in DYE1M from the *B* plane. The molecule is not perfectly planar in spite of the extensive conjugation and the good planarity of each half of the molecule. The *A* and *C* planes are almost coplanar but the *B* plane is not coplanar with them. The *A* and *B* planes are twisted 15·2° in DYEE and 14·4° in DYE1M.

Table 3. *Final positional parameters* (×10⁴) *for DYE1M*

Estimated standard deviations are given in parentheses.

	x	*y*	*z*
I	3435 (1)	4116 (1)	3243 (1)
Cl(1)	9210 (2)	3147 (3)	7147 (2)
Cl(2)	9553 (2)	386 (4)	6938 (3)
Cl(3)	1119 (2)	−4725 (3)	721 (2)
Cl(4)	155 (2)	−2421 (4)	−194 (2)
N(1)	6257 (5)	2351 (7)	4971 (5)
N(2)	6496 (6)	397 (8)	4829 (6)
N(3)	3248 (5)	−1570 (7)	2513 (5)
N(4)	2526 (6)	46 (7)	1909 (6)
C(1)	7096 (6)	2104 (9)	5493 (6)
C(2)	7691 (6)	2863 (10)	6013 (6)
C(3)	8433 (7)	2284 (11)	6468 (7)
C(4)	8580 (6)	1041 (11)	6384 (7)
C(5)	7989 (7)	281 (11)	5850 (8)
C(6)	7240 (7)	864 (10)	5412 (7)
C(7)	5901 (6)	1319 (9)	4575 (6)
C(8)	5080 (6)	1296 (9)	4010 (6)
C(9)	4615 (7)	325 (9)	3566 (6)
C(10)	3790 (6)	529 (9)	3030 (6)
C(11)	3236 (7)	−302 (9)	2520 (7)
C(12)	2539 (6)	−1989 (9)	1890 (6)
C(13)	2268 (7)	−3183 (10)	1664 (7)
C(14)	1531 (7)	−3265 (10)	1008 (7)
C(15)	1070 (7)	−2245 (11)	625 (6)
C(16)	1336 (7)	−1060 (11)	858 (7)
C(17)	2073 (7)	−976 (10)	1516 (7)
C(18)	5844 (7)	3581 (9)	4900 (6)
C(19)	6128 (9)	4365 (11)	4292 (8)
C(20*A*)	6330 (12)	−936 (17)	4752 (13)
C(20*B*)	6652 (15)	−825 (21)	4300 (12)
C(21*A*)	6639 (16)	−1460 (22)	4101 (15)
C(21*B*)	6192 (17)	−1695 (22)	4742 (16)
C(22)	3870 (6)	−2380 (9)	3070 (6)
C(23)	4631 (7)	−2738 (11)	2760 (8)
C(24)	2264 (8)	1350 (10)	1653 (8)
C(25)	1576 (9)	1756 (13)	2041 (10)
O(1*M*)	2010 (9)	3230 (18)	4338 (9)
C(26*M*)	1171 (12)	3530 (20)	3881 (12)

II. *Crystal structures of DYEE and DYE1M*

Fig. 3 shows a stereoscopic view (Johnson, 1965) of the crystal structure viewed along **b** for DYE1M. The molecular long axes are inclined either +21° or −21° to the *ac* plane. The most interesting feature is the dimer pair formed by two cations related by a centre of symmetry. The cations form double-layered zigzag walls along [101]. In Fig. 4 the stacking pattern of the dimer is shown in projection on the *B* ring of the cation. The dye cations in the dimer overlap each other extensively and the interplanar distance estimated by mean perpendicular separation is 3·85 Å for DYEE and 3·86 Å for DYE1M. The mean perpendicular distance is determined from the centre of gravity of the benzimidazole *A* ring to the least-squares plane of the *B* ring of the facing cation. Intermolecular distances are listed in Table 6. The shortest Cl···C contact in the

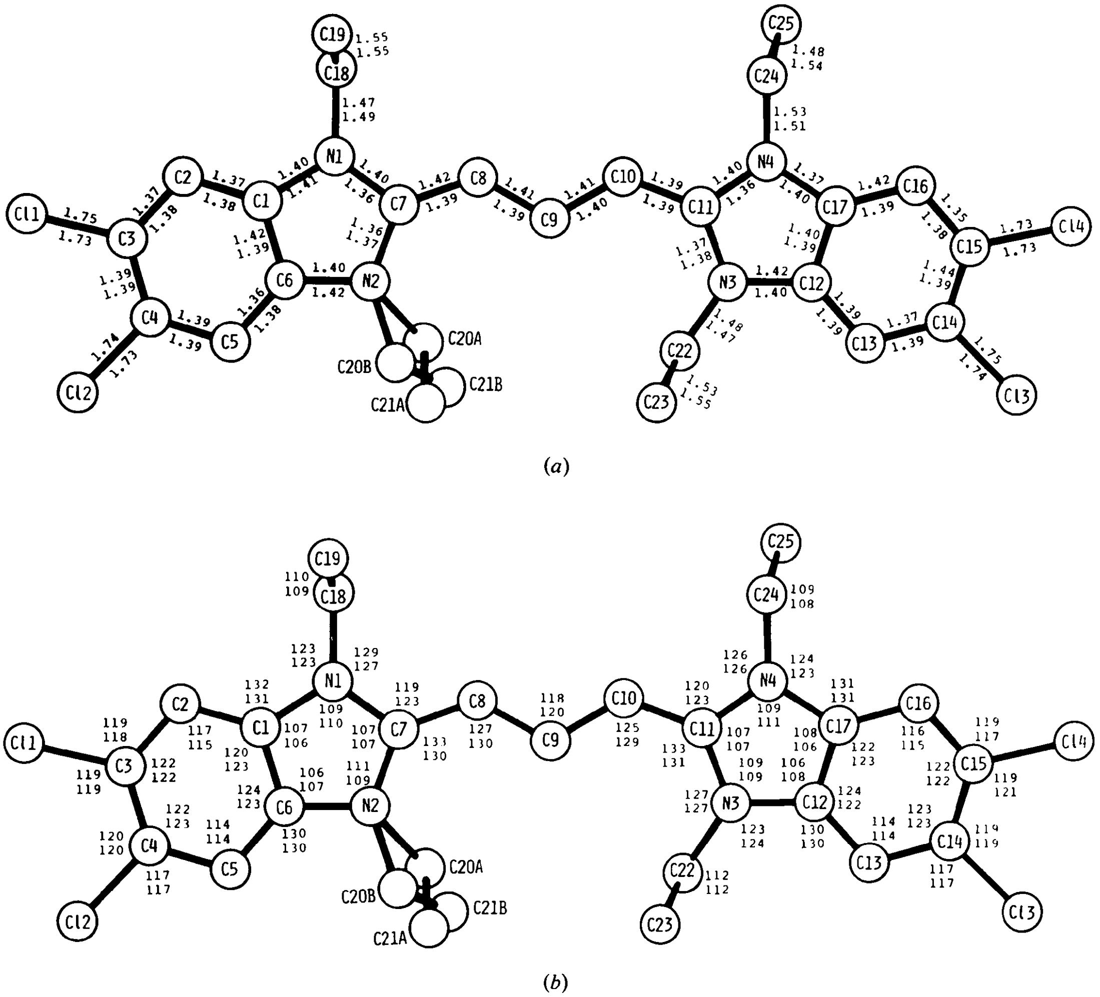

Fig. 2. Atomic labelling, (*a*) bond distances (Å) and (*b*) bond angles (°) for the dye cations. The upper values are for DYEE and the lower ones for DYE1M.

Table 4. *Bond lengths* (Å) *and angles* (°) *around the disordered ethyl groups and solvent molecules of DYEE, DYE1M and DYEDC*

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

	DYEE	DYE1M
N(2)–C(20*A*)	1·64 (4)	1·48 (2)
N(2)–C(20*B*)	1·54 (4)	1·69 (3)
C(20*A*)–C(21*A*)	1·58 (8)	1·50 (4)
C(20*B*)–C(21*B*)	1·43 (7)	1·56 (4)
C(6)–N(2)–C(20*A*)	122 (2)	121 (1)
C(6)–N(2)–C(20*B*)	122 (2)	116 (1)
C(7)–N(2)–C(20*A*)	122 (2)	127 (1)
C(7)–N(2)–C(20*B*)	124 (2)	128 (1)
N(2)–C(20*A*)–C(21*A*)	91 (3)	111 (2)
N(2)–C(20*B*)–C(21*B*)	111 (4)	92 (2)

C(26*E*)–O(1*E*)	1·49 (6)
C(26*E*)–C(27*E*)	1·32 (7)
C(28*E*)–O(2*E*)	1·4 (1)
C(26*E*)–C(28*E*)	1·1 (1)
O(1*E*)–C(26*E*)–C(27*E*)	118 (4)
O(2*E*)–C(28*E*)–C(26*E*)	100 (10)
C(26*M*)–O(1*M*)	1·39 (2)
C(26*D*)–Cl(5*D*)	1·75 (4)
C(26*D*)–Cl(6*D*)	1·76 (5)
C(27*D*)–Cl(7*D*)	1·89 (6)
C(27*D*)–Cl(8*D*)	1·63 (8)
Cl(5*D*)–C(26*D*)–Cl(6*D*)	105 (3)
Cl(7*D*)–C(27*D*)–Cl(8*D*)	111 (5)

dimer, Cl(1)···C(13), is 3·64 Å for both crystals, and the shortest C···C (skeletal) contact, C(3)···C(12), is 3·74 Å for DYEE and 3·71 Å for DYE1M.

Two dyes in the dimer are laterally displaced, so that the slip angle is 54·6° for DYEE and 54·4° for DYE1M. The molecular long axis was chosen along the trimethine bridge, C(7)—C(11), and the aggregate axis was taken as the vector connecting the centres of two dyes, C(9)—C(9)′, related by an inversion centre.

Overlap of the benzimidazole rings is also found as a zigzag chain structure, which is made of dimers related by a twofold screw axis. The mean perpendicular distance between the rings is 4·42 Å for DYEE and 4·35 Å for DYE1M. The shortest Cl···C contact between the rings is 3·60 Å for DYEE and 3·49 Å for DYE1M for Cl(3)···C(5).

Table 5. *Deviations of atoms* (Å) *from the least-squares planes*

X, *Y*, and *Z*′ are the coordinates along **a**, **b**, and **c***.

(1) Trimethine bridge plane[a]

	DYEE	DYE1M	DYEDC		DYEE	DYE1M	DYEDC
C(8)	0·00	0·00	0·00	N(3)[d]	0·33	0·20	0·05
C(9)	0·00	0·00	0·00	N(4)[d]	−0·30	−0·31	−0·07
C(10)	0·00	0·00	0·00	C(7)[d]	−0·03	0·00	0·00
N(1)[d]	−0·03	0·03	0·17	C(11)[d]	−0·01	−0·04	−0·01
N(2)[d]	0·01	−0·04	−0·14				

(2) Benzimidazole ring *A* plane[b]

	DYEE	DYE1M	DYEDC		DYEE	DYE1M	DYEDC
C(1)	−0·01	−0·02	0·00	C(8)[d]	0·06	−0·01	0·05
C(2)	0·01	−0·02	−0·02	C(9)[d]	0·06	0·03	0·23
C(3)	−0·01	0·02	0·00	C(10)[d]	0·10	0·07	0·25
C(4)	−0·01	0·02	0·05	C(18)[d]	0·04	0·07	0·10
C(5)	0·01	0·00	−0·02	C(20*A*)[d]	0·60	0·36	0·08
C(6)	0·01	−0·01	−0·06	C(20*B*)[d]	−0·46	−0·73	—
C(7)	−0·01	0·02	0·02	Cl(1)[d]	0·04	0·04	−0·14
N(1)	0·01	0·02	0·01	Cl(2)[d]	−0·06	−0·02	0·15
N(2)	−0·01	−0·01	0·01				

(3) Benzimidazole ring *B* plane[c]

	DYEE	DYE1M	DYEDC		DYEE	DYE1M	DYEDC
C(11)	0·02	0·00	0·00	C(8)[d]	0·15	0·18	−0·09
C(12)	0·01	0·01	0·00	C(9)[d]	0·26	0·23	−0·08
C(13)	−0·01	−0·02	0·03	C(10)[d]	−0·05	−0·03	0·00
C(14)	−0·02	0·01	−0·02	C(22)[d]	0·03	−0·03	0·20
C(15)	0·04	0·00	0·03	C(24)[d]	0·03	0·06	−0·11
C(16)	−0·02	0·01	0·00	Cl(3)[d]	−0·11	−0·12	−0·13
C(17)	0·00	−0·02	−0·05	Cl(4)[d]	0·08	0·03	0·00
N(3)	0·00	0·01	0·00				
N(4)	−0·02	0·00	0·03				

(*a*) The equations of the planes are:

$-0{\cdot}6590X - 0{\cdot}2386Y + 0{\cdot}7133Z' - 0{\cdot}5263 = 0$ (for DYEE)
$-0{\cdot}6598X - 0{\cdot}1892Y + 0{\cdot}7272Z' - 0{\cdot}5965 = 0$ (for DYE1M)
$-0{\cdot}1898X - 0{\cdot}1801Y + 0{\cdot}9652Z' - 4{\cdot}3173 = 0$ (for DYEDC)

(*b*) The equations of the planes are:

$-0{\cdot}6801X - 0{\cdot}2184Y + 0{\cdot}6999Z' - 0{\cdot}2775 = 0$ (for DYEE)
$-0{\cdot}6637X - 0{\cdot}2118Y + 0{\cdot}7174Z' - 0{\cdot}4461 = 0$ (for DYE1M)
$-0{\cdot}2330X - 0{\cdot}0009Y + 0{\cdot}9725Z' - 5{\cdot}5263 = 0$ (for DYEDC)

(*c*) The equations of the planes are:

$0{\cdot}7990X + 0{\cdot}0041Y - 0{\cdot}6013Z' - 0{\cdot}5929 = 0$ (for DYEE)
$0{\cdot}7823X + 0{\cdot}0127Y - 0{\cdot}6228Z' - 0{\cdot}4161 = 0$ (for DYE1M)
$-0{\cdot}2687X - 0{\cdot}0583Y + 0{\cdot}9615Z' - 5{\cdot}1061 = 0$ (for DYEDC)

(*d*) Atom not included in the least-squares calculation.

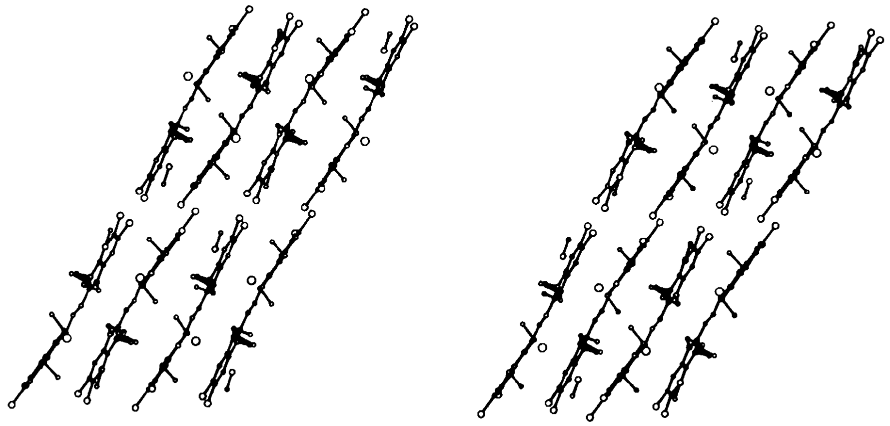

Fig. 3. A stereoscopic view of the crystal structure of DYE1M viewed along **b**. The *c* axis is horizontal, left to right.

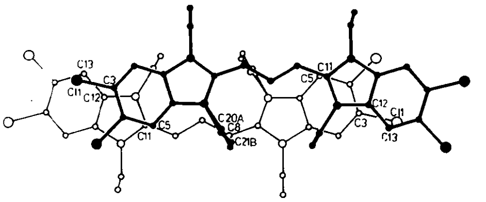

Fig. 4. Stacking pattern of the dimer of the dye cations related by a centre of symmetry in DYE1M.

Almost all the intermolecular distances are consistent with normal van der Waals contacts, but Cl(1)···Cl(2) ($2-x, \frac{1}{2}+y, \frac{3}{2}-z$) is 3·37 Å for DYEE and 3·26 Å for DYE1M. The same trend was noticed by Smith & Luss (1972). The I^- ions and the solvent molecules are packed in the gaps between the dye cations. The interatomic distances of O(1*E*)···I^-, O(2*E*)···I^- and O(1*M*)···I^- show that the hydrogen bond may connect the solvent molecule with the I^- ion. The contacts C(8)···I^-, 4·00 Å, in DYEE and C(10)···I^-, 3·99 Å, in DYE1M are the shortest between the I^- ions and the skeletal atoms of the cation.

Table 6. *Van der Waals contacts less than* 3·7 Å *and their estimated standard deviations for DYEE and DYE*1*M*

	DYEE	DYE1M
(1) Between facing dye molecules		
Cl(1)···C(13^{i})	3·64 (3)	3·64 (1)
N(1)···C(22^{i})	3·56 (2)	3·51 (1)
N(3)···C(2^{i})	3·62 (3)	3·67 (2)
C(1)···C(22^{i})	3·41 (3)	3·38 (2)
C(2)···C(22^{i})	3·45 (3)	3·44 (2)
C(8)···C(20A^{i})	3·41 (6)	3·64 (3)
C(8)···C(21B^{i})	3·54 (8)	3·48 (3)
(2) In the zigzag chain		
Cl(3)···C(5^{ii})	3·60 (3)	3·49 (2)
Cl(4)···C(3^{ii})	3·65 (3)	3·69 (1)
Cl(4)···C(4^{ii})	3·69 (3)	3·75 (1)
N(4)···C(19^{iii})	3·58 (4)	3·56 (2)
C(8)···C(23^{iii})	3·53 (3)	3·45 (2)
C(21*A*)···C(24^{ii})	3·71 (6)	3·48 (3)
(3) Other contacts		
I···O(1E^{iv})	3·49 (5)	—
I···O(2E^{iv})	3·64 (8)	—
I···O(1M^{iv})	—	3·57 (2)
Cl(1)···Cl(2^{ix})	3·37 (1)	3·26 (1)
Cl(1)···C(28E^{vi})	3·63 (11)	—
Cl(4)···C(25^{vii})	3·78 (3)	3·65 (1)
Cl(4)···C(27E^{viii})	3·60 (7)	—
C(5)···O(1E^{v})	3·43 (4)	—
C(21*B*)···O(1M^{v})	—	3·32 (3)

Symmetry code

(i) $1-x, -y, 1-z$;
(ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$;
(iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$;
(iv) $x, \frac{1}{2}-y, -\frac{1}{2}+z$;
(v) $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$;
(vi) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$
(vii) $-x, -y, -z$
(viii) $-x, -y, 1-z$
(ix) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$

III. *Molecular and crystal structures of DYEDC*

The final positional parameters with their estimated standard deviations are listed in Table 7.* Bond distances and angles for the cation are shown in Fig. 5. They are in agreement with those found in four other crystals within the range of ±3σ. The average e.s.d.'s of the bond distances and the angles are 0·05 Å and 2° respectively. The bond distances and angles for the solvent dichloromethane molecules are listed in Table 4. The planarity of each half of the cation is fairly good but Cl(1) and Cl(2) deviate respectively by −0·14 and 0·15 Å from the *A* plane and Cl(3) deviates by −0·13 Å from the *B* plane (Table 5). The *A* and *B* planes are respectively inclined by 8·3 and 3·9° to the *C* plane and they make an angle of 10·6° to each other.

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* See previous footnote.

Table 7. *Final positional parameters* ($\times 10^4$) *for DYEDC*

Estimated standard deviations are given in parentheses.

	x	*y*	*z*
I	−2205 (3)	4860 (1)	5741 (2)
Cl(1)	−4449 (10)	2435 (5)	2717 (8)
Cl(2)	−3718 (11)	810 (5)	2682 (8)
Cl(3)	7923 (12)	701 (5)	5660 (9)
Cl(4)	8770 (11)	2294 (5)	5950 (8)
N(1)	−609 (30)	3114 (10)	3740 (23)
N(2)	−143 (26)	1975 (12)	3565 (21)
N(3)	4344 (28)	1898 (11)	4904 (21)
N(4)	4969 (27)	3083 (12)	5077 (20)
C(1)	−1467 (36)	2673 (15)	3463 (26)
C(2)	−2460 (42)	2853 (22)	3293 (33)
C(3)	−3182 (32)	2235 (15)	3019 (21)
C(4)	−2852 (30)	1523 (14)	2949 (24)
C(5)	−1864 (31)	1391 (13)	3066 (22)
C(6)	−1174 (32)	1957 (14)	3308 (25)
C(7)	280 (35)	2712 (13)	3832 (24)
C(8)	1240 (34)	3014 (17)	4115 (25)
C(9)	2131 (36)	2614 (15)	4326 (23)
C(10)	3047 (33)	2960 (13)	4599 (25)
C(11)	4064 (34)	2613 (18)	4838 (22)
C(12)	5439 (30)	1876 (14)	5161 (22)
C(13)	6056 (37)	1261 (17)	5326 (27)
C(14)	7027 (34)	1439 (15)	5521 (25)
C(15)	7469 (32)	2123 (17)	5661 (26)
C(16)	6798 (27)	2760 (14)	5482 (19)
C(17)	5748 (27)	2600 (12)	5203 (19)
C(18)	−529 (44)	3869 (19)	4003 (39)
C(19*A*)*	−53 (71)	4010 (27)	4952 (55)
C(19*B*)*	−864 (105)	4368 (38)	3276 (78)
C(20)	499 (50)	1285 (24)	3577 (42)
C(21)	545 (53)	1283 (26)	2678 (35)
C(22)	3788 (31)	1262 (17)	4912 (22)
C(23)	3657 (39)	1186 (22)	5868 (27)
C(24)	5047 (47)	3832 (17)	4995 (37)
C(25)	4683 (44)	4076 (18)	3813 (28)
Cl(5*D*)	881 (21)	519 (7)	6024 (12)
Cl(6*D*)	1496 (14)	1982 (5)	6512 (10)
Cl(7*D*)	3734 (18)	5018 (7)	7769 (11)
Cl(8*D*)	2899 (19)	3553 (8)	7116 (12)
C(26*D*)	1234 (50)	1173 (18)	7005 (32)
C(27*D*)	3384 (67)	4251 (27)	6796 (48)

* The occupancies for C(19*A*) and C(19*B*) are 0·5

A stereoscopic view of the cation sheets viewed along **b** is shown in Fig. 6. The cations pack plane-to-plane, on edge in sheets parallel to (010). The molecular long axis is elongated along [104]. The stacking of the cations resembles those found in DYE2M and DYEA but the extent of the overlapping is considerably less than found previously. The overlapping pattern is shown in Fig. 7 with those of DYE2M and DYEA. Two overlapping modes are found: the greater one with a plane separation of 3·52 Å is found in column *B*, which is composed of the cations related by the glide symmetry; and the lesser one with a separation of 3·60 Å is observed in another column, *A*, which is made of the cations related by translation along **a**. A slip angle of 15·5° is found in each pair.

Intermolecular distances less than 3·70 Å are listed in Table 8. The shortest Cl···C (skeletal) contact, Cl(1)···C(17), is 3·55 Å and the shortest C···C, C(3)···C(15), is 3·55 Å; these are found in the column of translationally equivalent cations. The $\mathrm{I^-}$ ions are packed in the space between the cations. Two dichloromethane molecules are inserted between two cations in the sheet as is shown in Fig. 8. This situation is quite different from the case of other crystals where the solvent molecules are not involved in the cation sheet. The interatomic distance Cl(6*D*)···Cl(8*D*) is 3·37 Å. It is interesting that a specific affinity exists between Cl atoms in the crystal. It is also noticed that $\mathrm{I^-}$···C(26*D*) and $\mathrm{I^-}$···C(27*D*) distances are fairly short, which may indicate the presence of hydrogen-bonding of $\mathrm{I^-}$···H—C type.

Discussion

The present results on three solvate crystals, DYEE, DYE1M and DYEDC, add a new view of the structures of the dye crystals: they may be classified into two types. In type I crystals, DYE2M, DYEA and DYEDC, the cations are packed plane-to-plane with small slip angles. In type II crystals, DYEE and DYE1M, the cations form a dimeric unit with a large slip angle.

Bird *et al.* (1968) discussed the structures of thiacarbocyanine dye aggregates and their relation to spectral properties; the aggregates with slip angles of 19 and 30° were considered to give the *J* band and that with 60° was thought to show the *H* band. Norland, Ames & Taylor (1970) confirmed this result by a theoretical calculation. According to their results, type I crystals may exhibit the *J* band and type II crystals may show the *H* band. The slip angles found in the type I crystals were 15·4 and 24·2° for DYE2M, 16·6 and 23·3° for DYEA and 15·5° for DYEDC. Although the spectra found by us showed a prominent *J* band in DYE2M and a medium-strong one in DYEA, only a broad red-shifted band was found in DYEDC, which was difficult to explain as a *J* band. It suggests that an arrangement of the dyes with small slip angles may be a necessary condition but is not sufficient for the appearance of the *J* band. Following our results, a good overlap and a short interplanar distance are more important than the arrangement of the dyes to give the *J* band.

The overlapping modes of the cations in type I crystals are shown in Fig. 7; three modes (*A*, *B* and *C*) are found in the DYE2M columns and two each (*A* and *B*) in DYEA and DYEDC. It is clearly seen that the extent of the overlapping of the cations is largest in DYE2M, while it is smallest in DYEDC. The plane separations tabulated in Table 9 show that the values for DYE2M are smaller than those found for DYEA

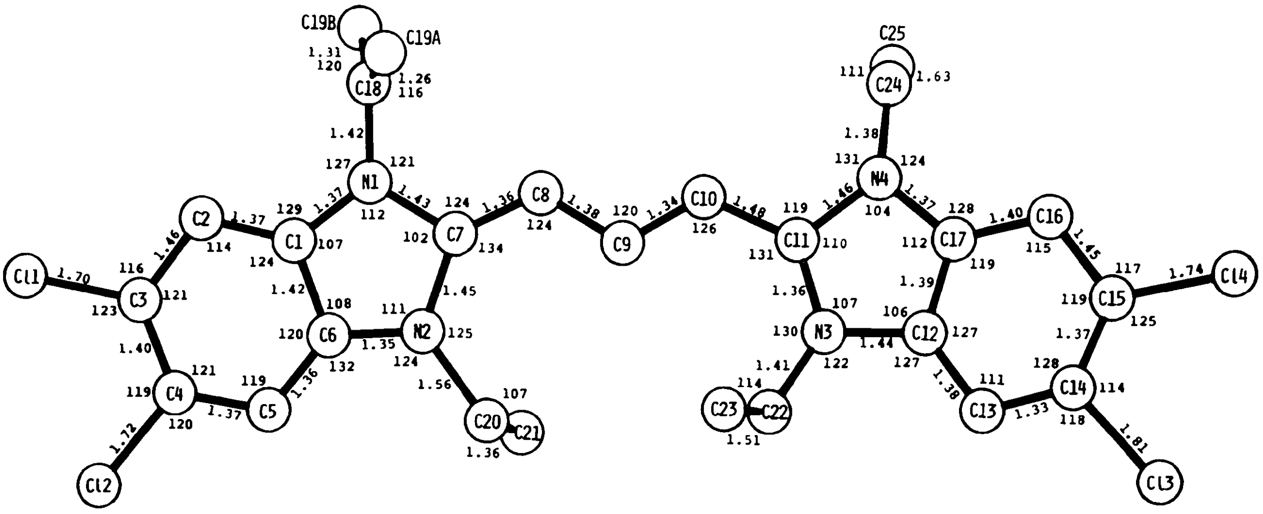

Fig. 5. Atomic labelling, bond distances (Å) and bond angles (°) for the dye cation in DYEDC.

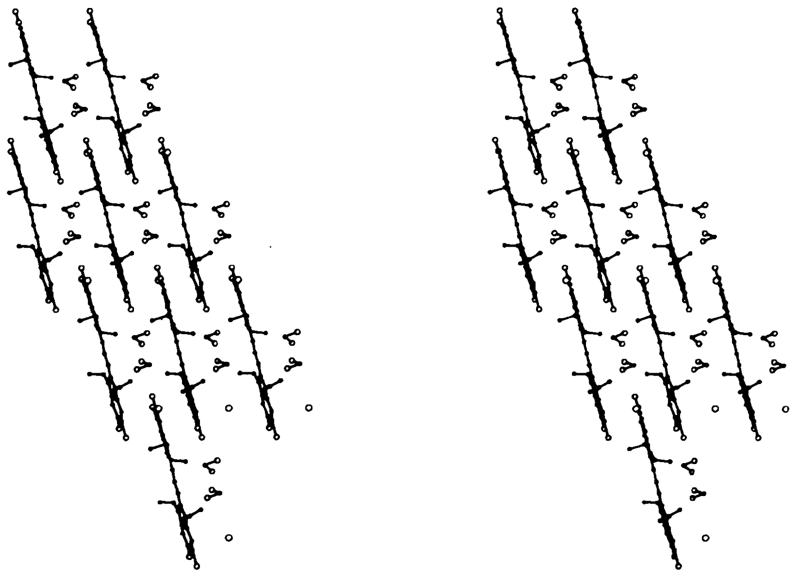

Fig. 6. A stereoscopic view of the cation sheets in DYEDC. The view is along **b** with the *c* axis is horizontal, left to right.

and DYEDC, hence the electron overlap will be largest in DYE2M. The plane separations for DYEA and DYEDC are almost the same, but the overlapping of the dyes is more extensive for DYEA than for DYEDC. Thus the sharpness of the *J* band, which is a measure of the energy transfer (Sumi, 1975), is correlated with the extent of the electron overlap.

The type II crystal is composed of a dimer unit, which is a typical mode for the *H* aggregate. Moreover, one molecule in the dimer makes contact with the molecules in the column behind. From spectral studies it was found that the H^* band appears more sharply for DYE1M than for DYEE, and this result may be correlated with the strength of the interactions between the molecules in the dimer or those between the dimers. It appears that a polymer, or at least several-dimer aggregates, must be formed for the appearance of the H^* band. In the DYE1M and DYEE crystals the dimer units overlap along **c**, and the H^* band was actually observed in this direction.

Consideration of intermolecular forces

Most cyanine dyes, including the present dye, crystallize in such a way that the dye cations adopt a face-to-face conformation which excludes the anions outside the packed column. The positive charge on the cation may be delocalized over the whole molecule. However, from a primary view of the electrostatic forces between the cations, such a conformation may not be stable unless other forces stabilize the paired structure. The electrostatic repulsive forces between the cations should be compensated by the attractive forces between the cation and anions. Actually, several anions surround one cation and the locations of the anions are reasonable for stabilizing the dimer pair. In order to estimate quantitatively the electrostatic forces in the crystal, an elaborate calculation of the Madelung energy may be needed; such an attempt we postpone for further investigation.

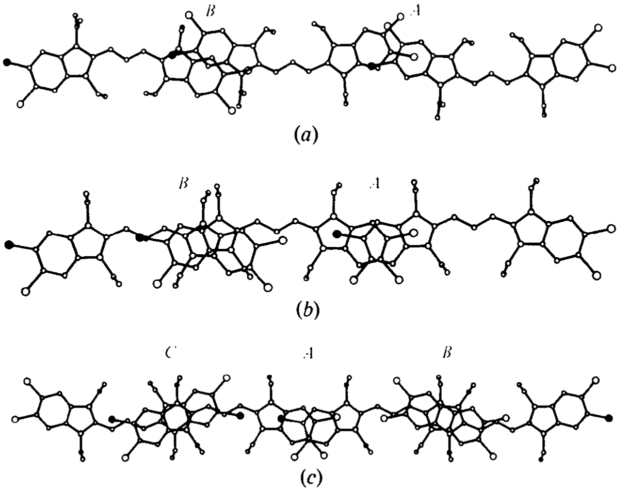

Fig. 7. Stacking patterns of dye cations in type I crystals for (*a*) DYEDC, (*b*) DYEA and (*c*) DYE2M. Cl(1) is depicted as a filled circle for ease of identification. Symbols *A*, *B* and *C* indicate overlapping modes of columns in the sequence of increasing overlap. The interplanar distances are given in Table 9.

Table 8. *Van der Waals contacts less than* 3·7 Å *and their estimated standard deviations for DYEDC*

(1) In column *A*

$Cl(1)\cdots C(16^{iii})$	3·64 (3)
$Cl(1)\cdots C(17^{iii})$	3·55 (3)
$Cl(4)\cdots C(1^{ii})$	3·58 (4)
$Cl(4)\cdots C(2^{ii})$	3·60 (4)
$C(3)\cdots C(15^{iii})$	3·55 (5)
$C(1)\cdots C(15^{vi})$	3·68 (5)
$C(3)\cdots C(17^{vi})$	3·69 (4)
$C(4)\cdots C(16^{vi})$	3·67 (5)
$C(5)\cdots C(16^{vi})$	3·70 (4)
$C(8)\cdots C(26D^{ix})$	3·44 (7)

(2) In column *B*

$Cl(1)\cdots N(4^{vi})$	3·69 (3)
$Cl(2)\cdots C(24^{vi})$	3·55 (5)
$Cl(3)\cdots C(19B^{vii})$	3·40 (10)
$Cl(4)\cdots N(2^{vii})$	3·66 (3)
$Cl(4)\cdots C(6^{vii})$	3·70 (4)
$Cl(4)\cdots C(21^{vii})$	3·69 (5)

(3) Other contacts

$I\cdots C(27D^{v})$	3·67 (6)
$Cl(4)\cdots Cl(6D^{ii})$	3·66 (3)
$Cl(6D)\cdots Cl(8D^{i})$	3·37 (2)
$C(13)\cdots Cl(7D^{viii})$	3·51 (4)
$C(19A)\cdots C(19A^{v})$	3·61 (7)
$C(20)\cdots Cl(5D^{i})$	3·66 (7)
$Cl(5D)\cdots Cl(5D^{iv})$	3·45 (2)

Symmetry code

(i)	$x,y,z;$	(vi)	$-1+x,\frac{1}{2}-y,-\frac{1}{2}+z$
(ii)	$1+x,y,z;$	(vii)	$1+x,\frac{1}{2}-y,\frac{1}{2}+z$
(iii)	$-1+x,y,z;$	(viii)	$1-x,-\frac{1}{2}+y,\frac{3}{2}-z$
(iv)	$-x,-y,1-z;$	(ix)	$x,\frac{1}{2}-y,-\frac{1}{2}+z$
(v)	$-x,1-y,1-z;$		

Table 9. *Interplanar separations* (Å) *in DYEDC, DYEA and DYE2M*

	Stacking *A*	Stacking *B*	Stacking *C*
DYEDC	3·60	3·52	—
DYEA	3·64	3·49	—
DYE2M	3·45	3·45	3·48

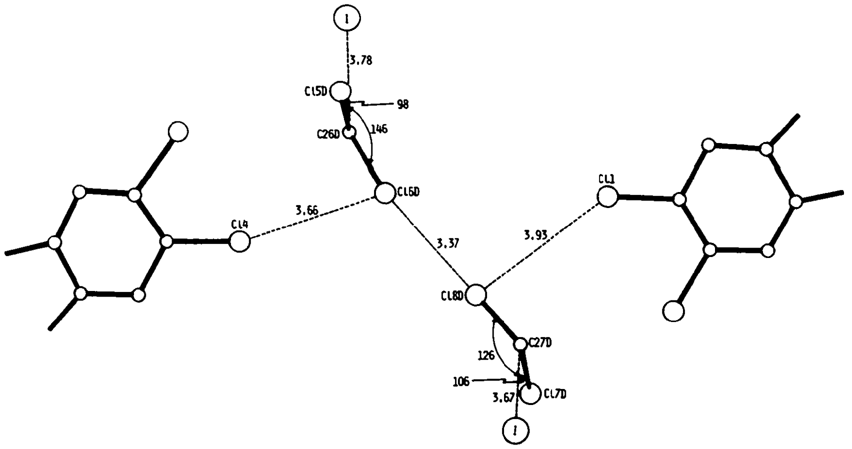

Fig. 8. Intermolecular Cl···Cl and I···C contacts, distances (Å) and angles (°) in the cavity formed by dye cations in DYEDC.

The paired conformation may be favoured by the dispersion force between the dye cations, and it may be roughly estimated by the perturbation theory as

$$\varDelta E = \sum_{n_1} \sum_{n_2} \frac{\langle 0_1 0_2 | V | n_1 n_2 \rangle \langle n_1 n_2 | V | 0_1 0_2 \rangle}{E_{n_1} + E_{n_2} - E_{0_1} - E_{0_2}}$$

where E_{n_1} is the nth transition energy of the dye 1, E_{n_2} is that of the dye 2, $|0\rangle$ and $|n\rangle$ represent the wavefunctions of the ground and the nth excited states, and V is the intermolecular potential. The matrix element may be semi-empirically estimated from the spectral shift of the aggregate. If we estimate the value numerically by taking only the first $\pi\pi^*$ transition of the dye, then the value of $\varDelta E$ is evaluated as -1175 cal mol^{-1}. If we consider higher transitions, this value may be increased to give a so-called van der Waals force.

These dye cations form dimers or higher aggregates in solution at high concentration. For instance, Herz (1974) investigated the equilibrium of the association between the J and M states of 1,1′-dibutylsulphonyl–DYE in aqueous solution, and found that a tetramer may be formed at high concentration. In aqueous solution, the hydrophobic force may be more important than other forces (Sinanoglu, 1968). It is also interesting that the present dye forms several quite different crystals, including different kinds of solvent molecules. This is because of the capability of this dye to dimerize or polymerize in two different ways, type I and type II, in solution. Actually, a low-temperature spectrum of the dye in a mixed solution of methanol and ethanol exhibits both the red-shifted and blue-shifted bands. This may mean that both types of aggregates are comparable in energy. A similar situation is conceivable in methanol and methanol–water solutions. For this reason, two different crystalline forms might be obtained from these solutions.

Finally, the role of the Cl · · · Cl contact may be examined. In the DYE2M and DYEA crystals, the Cl atoms are close to each other between the dye molecules in the cation sheets, which enhances the intermolecular overlap between the cation rings. In the DYEDC crystal, the dichloromethane molecules are connected to the Cl atoms of substituents of the dyes; hence the intermolecular overlap between the dye cations is diminished. In DYEE and DYE1M crystals, a short Cl · · · Cl contact was also observed, which may be correlated with the sharpness of the H^* band.

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