

angles involving the hydrogen atoms are known with only approximate accuracy. The values reported are typical of those obtained by X-ray diffraction for other organic molecules.

The packing of the molecules is illustrated by the stereoscopic view of the unit cell shown in Fig. 4. This view shows clearly how one carboxyl oxygen and the sulfoxide oxygen atom point toward the NH_2 group, while the second carboxyl oxygen atom occupies an open part of the structure. The chondrine molecules pack together to form a compact structure which enables the maximum number of intermolecular hydrogen bonds to be formed between the oxygen atoms and the NH_2 group.

The thermal parameters for the heavy atoms are sufficiently small to suggest that the chondrine molecules are rather firmly held in the crystal by the $\text{N-H}\cdots\text{O}$ hydrogen bonds, the electrostatic attraction of the zwitterions, and van der Waals forces. There is no appreciable oscillation about the C(2)–C(5) bond, as verified by the small size of the 50% probability ellipsoids for O(2) and O(3) shown in Fig. 4.

The closest intermolecular approaches between heavy atoms, which are not hydrogen bonded, are 3.117 Å for $\text{O}(1)\cdots\text{C}(3')$, and 3.306 Å for $\text{O}(1)\cdots\text{C}(4')$; these distances are normal. Several additional intermolecular distances occur between 3.38 and 3.50 Å.

The authors thank Dr Alan Zalkin for the use of his computer programs and both Professor David H. Templeton and Dr Zalkin for helpful discussions during the course of this investigation.

References

- CARSON, J. F., BOGGS, L. M. & LUNDIN, R. E. (1970). *J. Org. Chem.* **35**, 1594.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 DE LA CAMP, U. & HOPE, H. (1970). *Acta Cryst.* **B26**, 846.
 HINE, R. (1962). *Acta Cryst.* **15**, 635.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KURIYAMA, M., TAKAGI, M. & MURATA, K. (1960). *Hokkaido Daigaku Suisan Gakubu Kenkyo Iho (Fac. Fish. Bull. Hokkaido Univ.)*, **11**, 58.
 LAMBERT, J. B. & KESKE, R. G. (1966). *J. Org. Chem.* **31**, 3429.
 LAMBERT, J. B., BAILEY, D. S. & MIXAN, C. E. (1972). *J. Org. Chem.* **37**, 377.
 PALMER, K. J. & LEE, K. S. (1966). *Acta Cryst.* **20**, 790.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 TOMINAGA, F. & OKA, K. (1963). *J. Biochem. (Tokyo)*, **54**, 222.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139.

Acta Cryst. (1972). **B28**, 2793

The Crystal Structures of Two Solvates of 5,5',6,6'-Tetrachloro-1,1',3,3'-Tetraethylbenzimidazolocarboyanine Iodide

BY DOUGLAS L. SMITH AND HENRY R. LUSS

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, U.S.A.

(Received 18 February 1972 and in revised form 1 May 1972)

The title compound, $\text{C}_{25}\text{H}_{27}\text{N}_4\text{Cl}_4\text{I}$, DYE, is an efficient spectral sensitizer of silver halide photographic systems and is known to form *J*-aggregates with ease. We have determined the crystal structures of the 2:1 methanol:DYE solvate (DYEM) and the 1:1 acetonitrile:DYE solvate (DYEA) from single-crystal X-ray intensity data collected with an automated diffractometer. DYEM is monoclinic, $P2_1/a$, with $a = 22.547$ (9), $b = 11.036$ (5), $c = 13.375$ (5) Å, $\beta = 107.48$ (1)° and $Z = 4$; DYEA is triclinic, $P1$, with $a = 10.392$ (3), $b = 8.242$ (2), $c = 9.284$ (2) Å, $\alpha = 93.92$ (2), $\beta = 107.81$ (1), $\gamma = 77.71$ (2)° and $Z = 1$. The structures were solved by the heavy-atom technique and refined by block-diagonal least-squares methods. The final *R* values are 0.033 for DYEM and 0.040 for DYEA. The distances and angles for the cations in the two structures agree very well with each other and with the usual accepted values. In spite of the extensive conjugation the cations are only approximately planar. In both structures, the cations pack plane to plane, and end to end on edge in sheets parallel to (100) separated by sheets containing the anions and solute molecules. There is a remarkable similarity of the (100) projections of the cation sheets in the two structures to each other and to the arrangement of ions in (111) faces of AgBr.

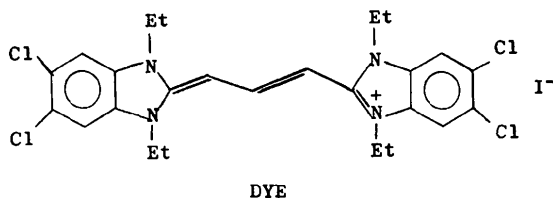
Introduction

Spectral sensitization, the process by which the photographic or photoconductive sensitivity of a material is

extended into spectral regions outside its intrinsic absorption region, was discovered a century ago by Vogel (1873). Since then, the effect, which is indispensable to photographic technology, has been studied intensively

(West, 1970; West & Gilman, 1969; Brooker, 1966; West & Carroll, 1966). Most spectral sensitizers of silver halides have been organic dyes, and the cyanine dyes, with their strong absorption and tendency to form aggregates with close intermolecular spacings and strong coupling, have been studied and used most extensively. A given cyanine dye may simultaneously form several different kinds of aggregates which exhibit spectral shifts of the order of ± 100 nm from the solution monomer spectrum. Red-shifted aggregates with intense sharp absorption maxima were first reported by Jelley (1936) and by Scheibe (Scheibe, Kandler & Ecker, 1937; Scheibe, Mareis & Ecker, 1937)

to form well-ordered, multilayer *J*-aggregates with ease (Zuckerman, 1967). We eventually determined two complete crystal structures, a 2:1 methanol:DYE solvate (DYEM) and a 1:1 acetonitrile:DYE solvate (DYEA).



Crystal data

	DYEM	DYEA
Formula	$C_{25}H_{27}N_4Cl_4I \cdot 2CH_3OH$	$C_{25}H_{27}N_4Cl_4I \cdot CH_3CN$
Molecular weight	716.32	693.29
Color-reflection	Gold	Green
Color-transmission	Red	Red
Habit	Long (<i>c</i>) thick tabular (100)	Chunky
Crystal system	Monoclinic	Triclinic
Wavelength (Mo $K\alpha_1$)	0.70926 Å	0.70926 Å
Unit cell: <i>a</i>	22.547 (9) Å	10.392 (3) Å
<i>b</i>	11.036 (5)	8.242 (2)
<i>c</i>	13.375 (5)	9.284 (2)
α		93.92 (2)°
β	107.48 (1)°	107.81 (1)
γ		77.71 (2)
<i>V</i>	3174.4 (23) Å ³	739.7 (4) Å ³
<i>Z</i>	4	1
<i>D</i> _{obs} (flotation)	1.49 g.cm ⁻³	1.51 g.cm ⁻³
<i>D</i> _{calc}	1.498 g.cm ⁻³	1.556 g.cm ⁻³
μ (Mo $K\alpha$)	13.4 cm ⁻¹	14.9 cm ⁻¹
<i>F</i> (000)	1448	348
Absent spectra	<i>h</i> 0 <i>l</i> , <i>h</i> odd 0 <i>k</i> 0, <i>k</i> odd	none
Space group	$P2_1/a(C_{2h}^5)$	$P1(C_1)$
General positions	$\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, z)$	x, y, z

and are called *J*-aggregates; blue-shifted aggregates are called *H*-aggregates. Current theory indicates that the relatively planar dye molecules in these aggregates pack in an arrangement resembling a slipped deck of cards in which the amount of lateral displacement between adjacent dye molecules determines the absorption region of the aggregate (Norland, Ames & Taylor, 1970). Bird and coworkers (Emerson, Conlin, Rosenoff, Norland, Rodriguez, Chin & Bird, 1967; Bird, Zuckerman & Ames, 1968; Bird, Norland, Rosenoff & Michaud, 1968; Walworth, Rosenoff, and Bird, 1970; Rosenoff, Walworth & Bird, 1970; Gray, Brewer & Bird, 1970; Bird, 1971) have used the slipped deck model, the thiocarbocyanine crystal structures of Wheatley (1959*a, b*), and the arrangement of silver ions in the (111) and (100) planes of AgBr to arrive at a model of aggregation and sensitization in silver halide systems.

Generally, however, because of a lack of firm experimental structure data, our understanding of the structure and packing of these dyes is deficient. We undertook to determine the crystal structure of 5,5', 6,6'-tetrachloro-1,1',3,3'-tetraethylbenzimidazolocarbo-cyanine iodide (DYE), a green-sensitizing dye known

Experimental

Crystals of the dye, obtained by rapid recrystallization from a hot saturated solution in methanol, were provided by E. J. VanLare, of these Laboratories. Optical and X-ray examination indicated these crystals were somewhat bent and distorted and probably disordered. Precession photographs of the long (*c*), thick tabular (100) crystals yielded orthorhombic cell constants: $a = 18.6$, $b = 11.1$ and $c = 13.5$ Å. The observed density of 1.58 g.cm⁻³ compares with 1.55 g.cm⁻³ calculated for four DYE molecules per cell. Systematic absences indicated $P2_12_1$ as the probable space group, but this appears inconsistent with the crystal structure of the methanol solvate, DYEM, which converts directly to this form upon standing in air.

Continued attempts yielded a technique for growing satisfactory single crystals from methanol. A saturated solution of the dye in boiling methanol was rapidly cooled in a dry ice-acetone bath. The cooled solution, which appeared to be clouded with a very fine suspension, was allowed to warm to room temperature, whereupon the cloudiness disappeared. The solution

vessel was sealed to prevent evaporation and allowed to stand undisturbed. Good undistorted crystals grew within two days. These crystals were morphologically very similar to the as-delivered material and deteriorated to this form within a few minutes in air with delamination into (100) plates and preservation of the *b* and *c* lattice dimensions. The crystals could be preserved indefinitely in an air-methanol atmosphere and were sealed in thin-walled glass capillaries for the X-ray analysis. The crystal structure showed the material to be a 2:1 methanol:DYE solvate and this was verified by a subsequent proton count in a high-resolution nuclear magnetic resonance spectrum of a 10^{-3} M solution of the solvate in dimethyl sulfoxide.

Slow evaporation of a solution of the dye in acetonitrile produced good single crystals. These crystals retained their form but developed small branched cracks and pitted surfaces on standing in air for two weeks and these, too, were mounted in thin-walled glass capillaries for the X-ray measurements. The crystal structure showed this material to be a 1:1 acetonitrile:DYE solvate and this was subsequently verified by the nuclear magnetic resonance spectrum.

Space group extinctions and preliminary lattice dimensions were obtained from precession photographs. The unit cell for DYEA is the reduced crystallographic cell (Lawton & Jacobson, 1965); the space group is *P*1 because the DYE molecules cannot contain a center of inversion and there is no evidence of disorder. This unusual case of a symmetrical synthetic material crystallizing in *P*1 was later verified from the statistical averages and distribution of the normalized structure factors (Hauptman & Karle, 1953; Daly, 1966) and, of course, by the ultimate successful refinement of the structure.

Small chunky crystals of DYEM (0.46 × 0.36 × 0.25 mm) and DYEA (0.38 × 0.25 × 0.23 mm) were chosen for intensity data collection on an automatic Picker four-circle goniostat at 23°C. Twenty reflections for DYEM and eighteen reflections for DYEA, all at moderately high Bragg angles (Mo $K\alpha_1$ radiation), were accurately centered through very narrow vertical and horizontal slits at a take-off angle of 0.5°. These observations were used as input to the computer program *PICK2* (Ibers, 1966) which refined the cell and orientation parameters by the method of least squares and generated the cards to control the automated goniostat.

Intensity data were collected with Zr-filtered Mo radiation at a take-off angle of approximately 2°. A scintillation detector was used and the pulse-height analyzer was set for an approximately 90% window for DYEA but was inoperative for DYEM. All unique reflections with $2\theta < 43^\circ$ for DYEM and $2\theta < 57^\circ$ for DYEA were measured by the θ - 2θ scan technique at a 2θ scan rate of 1.0° per min. The scan ranges varied from 1.2° at low 2θ to 2.0° at high 2θ . Stationary-crystal stationary-counter background counts were taken at each end of the scan for 40 sec for DYEM

and 20 sec for DYEA. For count rates above 13,000 c.p.s., brass attenuators were automatically inserted in the diffracted beam.

To check electronic and crystal stability, the intensities of standard reflections (055 for DYEM, $\bar{2}1\bar{3}$ for DYEA) were measured every 50th reflection. Small systematic decreases (5% for DYEM, 3% for DYEA) in the intensities of the standard reflections were observed over the period of data collection.

The background for a reflection was approximated by a straight line between the two measured background points. The intensities, corrected for background, were scaled by the standard intensities to correct for the slight systematic decrease noted in these intensities. Lorentz and polarization corrections were made. Absorption corrections were not applied because of the low absorption coefficients and the small size and regularity of the crystals. We estimate the maximum error in the structure amplitudes, F_o , caused by absorption, to be $\pm 7\%$ for both crystals. Standard deviations $\sigma(I)$ were based on counting statistics and were corrected to $\sigma(F)$. Those intensities less than $2\sigma(I)$ were considered unobserved and were set equal to $2\sigma(I)$ and corrected to structure amplitudes, F_{lim} . For DYEM the unobserved reflections numbered 695 out of a total of 3666 measured intensities and, for DYEA, 635 out of 3772 were unobserved.

Determination and refinement of the structures

Both structures were solved by the heavy-atom method from Patterson and Fourier maps. Least-squares refinement utilized a local version of the block-diagonal program *NRC-10* (Ahmed, 1970), which minimized $\sum w(F_o - KF_c)^2$. This program employed 4×4 blocks for atoms with isotropic temperature factors and 9×9 blocks for atoms with anisotropic temperature factors and applied Schomaker's correction (Hodgson & Rollett, 1963) for the interaction between thermal and scale factors. A 6×6 block was used for the thermal parameters of the iodide ion which defined the origin of DYEA. Weights were defined (Killean & Lawrence, 1969) as

$$w^{-1} = [\sigma(F_o)]^2 + (rF_o)^2 + s,$$

where *r* and *s* were chosen to make the averages of $\sum w(F_o - KF_c)^2$ approximately constant for groups of increasing F_o 's (Cruickshank, 1965). Unobserved reflections were included in the refinement and the agreement indices if $|F_c| > F_{lim}$. The usual agreement index was defined as $R_1 = \sum |F_o - KF_c| / \sum |F_o|$ and the weighted agreement index as $R_2 = [\sum w(F_o - KF_c)^2 / \sum wF_o^2]^{1/2}$. The atomic scattering factors were obtained from Cromer & Waber (1965) for the iodide ion, Stewart, Davidson & Simpson (1965) for hydrogen, and *International Tables for X-ray Crystallography* (1962) for the other atoms. The anomalous scattering components for chlorine ($\Delta f' = 0.132$, $\Delta f'' = 0.159$) and iodine ($\Delta f' = -0.726$, $\Delta f'' = 1.812$) (Cromer & Liberman, 1970)

Table 1. *Final atomic parameters for the nonhydrogen atoms of DYEM*

Estimated standard deviations are given in parentheses.

The anisotropic thermal parameters are in form $\exp[-0.25(h^2a^*B_{11} + \dots + 2klb^*c^*B_{23})]$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0.23087(2)	0.04513(4)	0.83594(3)	3.87(2)	8.03(2)	4.91(2)	0.18(2)	0.45(1)	0.64(2)
CL(1)	0.4947(1)	0.0577(1)	0.6078(1)	8.08(9)	4.60(7)	3.98(6)	-0.45(6)	3.22(6)	-0.83(5)
CL(2)	0.3568(1)	0.0789(2)	0.6125(1)	6.46(7)	8.09(10)	3.56(6)	-1.94(7)	0.81(5)	-1.22(6)
CL(3)	0.3639(1)	0.4475(2)	1.7255(1)	6.87(7)	7.90(10)	6.02(6)	1.28(8)	3.49(7)	-0.79(7)
CL(4)	0.5022(1)	0.4492(1)	1.8711(1)	8.39(9)	4.88(7)	3.44(6)	0.20(7)	1.88(5)	-0.75(5)
N(1)	0.5522(2)	0.1575(3)	1.0060(3)	3.3(2)	3.5(2)	3.2(2)	0.2(1)	1.2(1)	0.2(1)
N(2)	0.4552(2)	0.1689(3)	1.0086(3)	3.0(2)	4.2(2)	3.0(2)	0.1(1)	1.3(1)	-0.1(1)
N(3)	0.4583(2)	0.3286(3)	1.4303(3)	3.2(2)	3.6(2)	2.7(2)	0.1(1)	0.6(1)	-0.0(1)
N(4)	0.5559(2)	0.3322(3)	1.5306(3)	3.3(2)	3.9(2)	2.9(2)	-0.0(1)	0.6(1)	-0.0(1)
C(1)	0.5143(2)	0.1341(4)	0.9050(3)	3.8(2)	2.8(2)	3.0(2)	-0.0(2)	1.2(2)	0.3(2)
C(2)	0.5289(2)	0.1078(4)	0.8134(4)	4.4(2)	3.0(2)	4.2(2)	0.3(2)	2.0(2)	0.3(2)
C(3)	0.4792(2)	0.0905(4)	0.7246(4)	5.8(3)	2.8(2)	3.4(2)	-0.3(2)	2.5(2)	-0.0(2)
C(4)	0.4180(2)	0.0996(4)	0.7256(3)	5.0(2)	3.8(2)	2.8(2)	-0.9(2)	0.9(2)	-0.1(2)
C(5)	0.4038(2)	0.1249(5)	0.8172(4)	3.7(2)	4.1(2)	3.7(2)	-0.6(2)	1.3(2)	-0.5(2)
C(6)	0.4532(2)	0.1420(4)	0.9059(3)	3.6(2)	3.0(2)	3.1(2)	-0.2(2)	1.5(2)	-0.0(2)
C(7)	0.5155(2)	0.1806(4)	1.0691(3)	3.3(2)	3.1(2)	3.4(2)	0.2(2)	1.3(2)	0.7(2)
C(8)	0.5407(2)	0.2100(4)	1.1748(3)	3.0(2)	4.3(2)	3.2(2)	0.3(2)	0.6(2)	0.3(2)
C(9)	0.5111(2)	0.2441(4)	1.2469(3)	3.2(2)	3.0(2)	3.1(2)	0.1(2)	0.9(2)	0.2(2)
C(10)	0.5424(2)	0.2733(4)	1.3504(3)	3.3(2)	3.9(2)	3.1(2)	0.3(2)	0.8(2)	0.2(2)
C(11)	0.5182(2)	0.3092(4)	1.4303(3)	3.4(2)	3.0(2)	2.9(2)	-0.2(2)	0.4(2)	0.3(2)
C(12)	0.4578(2)	0.3605(4)	1.5302(3)	3.9(2)	2.8(2)	3.2(2)	0.1(2)	0.7(2)	-0.0(2)
C(13)	0.4088(2)	0.3857(4)	1.5691(4)	3.7(2)	3.5(2)	4.3(2)	0.2(2)	1.2(2)	0.3(2)
C(14)	0.4246(2)	0.4136(4)	1.6749(4)	5.6(3)	3.3(2)	4.3(2)	0.6(2)	2.4(2)	-0.4(2)
C(15)	0.4857(2)	0.4158(4)	1.7384(4)	5.8(3)	2.9(2)	3.1(2)	-0.1(2)	1.3(2)	-0.0(2)
C(16)	0.5350(2)	0.3900(4)	1.7003(4)	4.5(2)	2.8(2)	3.5(2)	-0.4(2)	0.8(2)	-0.2(2)
C(17)	0.5193(2)	0.3621(4)	1.5936(3)	4.3(2)	2.5(2)	3.2(2)	-0.2(2)	0.9(2)	-0.1(2)
C(18)	0.6199(2)	0.1614(5)	1.0388(4)	3.6(2)	6.1(3)	4.4(2)	0.8(2)	1.7(2)	0.3(2)
C(19)	0.6452(3)	0.2898(6)	1.0451(5)	4.6(3)	8.2(4)	7.4(4)	-1.9(3)	2.5(3)	0.1(3)
C(20)	0.3986(2)	0.1781(5)	1.0402(4)	3.2(2)	6.1(3)	3.7(2)	-0.8(2)	1.0(2)	-0.8(2)
C(21)	0.3753(3)	0.3045(6)	1.0332(4)	5.8(3)	8.9(4)	5.1(3)	2.7(3)	1.7(2)	-0.2(3)
C(22)	0.4022(2)	0.3184(5)	1.3420(4)	3.2(2)	5.5(3)	3.6(2)	0.6(2)	0.6(2)	-0.4(2)
C(23)	0.3775(3)	0.1921(6)	1.3246(4)	4.6(3)	7.5(4)	5.1(3)	-2.2(3)	0.9(2)	-0.7(3)
C(24)	0.6236(2)	0.3231(5)	1.5668(4)	3.2(2)	6.0(3)	4.1(2)	-0.2(2)	0.4(2)	-0.4(2)
C(25)	0.6471(3)	0.1976(6)	1.5921(5)	4.6(3)	7.2(4)	7.5(4)	0.7(3)	0.6(3)	1.1(3)
C(26)	0.2259(4)	0.2824(10)	0.3684(9)	7.2(5)	15.2(8)	16.6(8)	-3.5(5)	4.6(5)	-1.3(7)
C(27)	0.2323(4)	0.4490(8)	0.8464(6)	7.5(4)	11.1(6)	9.7(5)	1.3(4)	0.7(4)	-1.5(4)
O(1)	0.2666(2)	0.3849(7)	0.3951(4)	6.6(3)	18.7(6)	9.2(3)	2.8(3)	1.3(2)	2.5(4)
O(2)	0.1981(4)	0.5117(10)	0.8901(6)	6.3(4)	12.5(7)	5.2(4)	2.7(5)	2.3(3)	0.9(4)
O(3)	0.1828(4)	0.3639(11)	0.8455(8)	7.3(5)	13.6(8)	8.5(6)	2.4(5)	4.6(4)	2.5(6)

were used in the final cycles of both refinements. All computations were performed on an IBM 360/65 computer.

DYEM

The iodide ion was easily located from an ordinary F_0^2 Patterson map. An electron density map, phased by the iodide ion, revealed the positions of the other 33 nonhydrogen atoms of the dye. Several cycles of least-squares refinement, first with isotropic and then with anisotropic thermal parameters, reduced R_1 to 0.13. A difference Fourier map contained five peaks which were interpreted as two molecules of methanol: one ordered and one disordered. The five atoms were assigned carbon scattering factors and equal isotropic temperature factors, and the two end atoms of the three-atom group were given occupancy factors of 0.5. Refinement of the solvate positional and thermal parameters alone yielded thermal parameters that identified three of the atoms as oxygen; this assignment was consistent with the peak heights in the difference Fourier map. With the correct scattering factors, the solvate atoms were refined by full-matrix least-squares calculations (Busing, Martin & Levy, 1962) with the occupancy factor of O(2) allowed to vary [that of O(3) was constrained as 1-O(2)]. The occupancy for O(2)

Table 2. *Atomic parameters for the hydrogen atoms of DYEM* r is the C-H bond length.

	x	y	z	B	r
H(1)	0.575	0.103	0.811	3.72	1.05
H(2)	0.362	0.129	0.825	3.90	0.98
H(3)	0.364	0.383	1.528	3.89	0.99
H(4)	0.582	0.391	1.750	3.68	1.07
H(5)	0.581	0.204	1.205	3.54	0.88
H(6)	0.463	0.242	1.225	3.12	1.04
H(7)	0.588	0.263	1.368	3.39	0.99
H(8)	0.637	0.123	1.104	4.53	0.94
H(9)	0.633	0.120	0.994	4.53	0.87
H(10)	0.633	0.345	1.102	6.53	1.07
H(11)	0.686	0.288	1.067	6.53	0.88
H(12)	0.642	0.308	0.967	6.53	1.04
H(13)	0.368	0.132	0.997	4.31	0.91
H(14)	0.410	0.135	1.117	4.31	1.09
H(15)	0.340	0.313	1.050	6.65	0.89
H(16)	0.406	0.364	1.088	6.65	1.07
H(17)	0.363	0.326	0.963	6.65	0.93
H(18)	0.368	0.144	1.379	5.77	0.98
H(19)	0.410	0.137	1.313	5.77	1.00
H(20)	0.344	0.189	1.279	5.77	0.82
H(21)	0.411	0.356	1.283	4.25	0.96
H(22)	0.371	0.365	1.357	4.25	0.94
H(23)	0.645	0.363	1.523	4.69	0.97
H(24)	0.639	0.396	1.625	4.69	1.10
H(25)	0.625	0.150	1.633	6.87	0.99
H(26)	0.622	0.135	1.533	6.87	1.07
H(27)	0.688	0.200	1.608	6.87	0.88

Table 3. Observed and calculated structure factors for DYEM

The column headings are h , l , $10F_o/K$, $10F_c$ and $10\sigma(F_o)/K$. * denotes unobserved reflections.

h	l	$10F_o/K$	$10F_c$	$10\sigma(F_o)/K$
0	0	0	0	0
0	10	100	100	10
0	20	200	200	20
0	30	300	300	30
0	40	400	400	40
0	50	500	500	50
0	60	600	600	60
0	70	700	700	70
0	80	800	800	80
0	90	900	900	90
0	100	1000	1000	100
0	110	1100	1100	110
0	120	1200	1200	120
0	130	1300	1300	130
0	140	1400	1400	140
0	150	1500	1500	150
0	160	1600	1600	160
0	170	1700	1700	170
0	180	1800	1800	180
0	190	1900	1900	190
0	200	2000	2000	200
0	210	2100	2100	210
0	220	2200	2200	220
0	230	2300	2300	230
0	240	2400	2400	240
0	250	2500	2500	250
0	260	2600	2600	260
0	270	2700	2700	270
0	280	2800	2800	280
0	290	2900	2900	290
0	300	3000	3000	300
0	310	3100	3100	310
0	320	3200	3200	320
0	330	3300	3300	330
0	340	3400	3400	340
0	350	3500	3500	350
0	360	3600	3600	360
0	370	3700	3700	370
0	380	3800	3800	380
0	390	3900	3900	390
0	400	4000	4000	400
0	410	4100	4100	410
0	420	4200	4200	420
0	430	4300	4300	430
0	440	4400	4400	440
0	450	4500	4500	450
0	460	4600	4600	460
0	470	4700	4700	470
0	480	4800	4800	480
0	490	4900	4900	490
0	500	5000	5000	500
0	510	5100	5100	510
0	520	5200	5200	520
0	530	5300	5300	530
0	540	5400	5400	540
0	550	5500	5500	550
0	560	5600	5600	560
0	570	5700	5700	570
0	580	5800	5800	580
0	590	5900	5900	590
0	600	6000	6000	600
0	610	6100	6100	610
0	620	6200	6200	620
0	630	6300	6300	630
0	640	6400	6400	640
0	650	6500	6500	650
0	660	6600	6600	660
0	670	6700	6700	670
0	680	6800	6800	680
0	690	6900	6900	690
0	700	7000	7000	700
0	710	7100	7100	710
0	720	7200	7200	720
0	730	7300	7300	730
0	740	7400	7400	740
0	750	7500	7500	750
0	760	7600	7600	760
0	770	7700	7700	770
0	780	7800	7800	780
0	790	7900	7900	790
0	800	8000	8000	800
0	810	8100	8100	810
0	820	8200	8200	820
0	830	8300	8300	830
0	840	8400	8400	840
0	850	8500	8500	850
0	860	8600	8600	860
0	870	8700	8700	870
0	880	8800	8800	880
0	890	8900	8900	890
0	900	9000	9000	900
0	910	9100	9100	910
0	920	9200	9200	920
0	930	9300	9300	930
0	940	9400	9400	940
0	950	9500	9500	950
0	960	9600	9600	960
0	970	9700	9700	970
0	980	9800	9800	980
0	990	9900	9900	990
0	1000	10000	10000	1000
0	1010	10100	10100	1010
0	1020	10200	10200	1020
0	1030	10300	10300	1030
0	1040	10400	10400	1040
0	1050	10500	10500	1050
0	1060	10600	10600	1060
0	1070	10700	10700	1070
0	1080	10800	10800	1080
0	1090	10900	10900	1090
0	1100	11000	11000	1100
0	1110	11100	11100	1110
0	1120	11200	11200	1120
0	1130	11300	11300	1130
0	1140	11400	11400	1140
0	1150	11500	11500	1150
0	1160	11600	11600	1160
0	1170	11700	11700	1170
0	1180	11800	11800	1180
0	1190	11900	11900	1190
0	1200	12000	12000	1200
0	1210	12100	12100	1210
0	1220	12200	12200	1220
0	1230	12300	12300	1230
0	1240	12400	12400	1240
0	1250	12500	12500	1250
0	1260	12600	12600	1260
0	1270	12700	12700	1270
0	1280	12800	12800	1280
0	1290	12900	12900	1290
0	1300	13000	13000	1300
0	1310	13100	13100	1310
0	1320	13200	13200	1320
0	1330	13300	13300	1330
0	1340	13400	13400	1340
0	1350	13500	13500	1350
0	1360	13600	13600	1360
0	1370	13700	13700	1370
0	1380	13800	13800	1380
0	1390	13900	13900	1390
0	1400	14000	14000	1400
0	1410	14100	14100	1410
0	1420	14200	14200	1420
0	1430	14300	14300	1430
0	1440	14400	14400	1440
0	1450	14500	14500	1450
0	1460	14600	14600	1460
0	1470	14700	14700	1470
0	1480	14800	14800	1480
0	1490	14900	14900	1490
0	1500	15000	15000	1500
0	1510	15100	15100	1510
0	1520	15200	15200	1520
0	1530	15300	15300	1530
0	1540	15400	15400	1540
0	1550	15500	15500	1550
0	1560	15600	15600	1560
0	1570	15700	15700	1570
0	1580	15800	15800	1580
0	1590	15900	15900	1590
0	1600	16000	16000	1600
0	1610	16100	16100	1610
0	1620	16200	16200	1620
0	1630	16300	16300	1630
0	1640	16400	16400	1640
0	1650	16500	16500	1650
0	1660	16600	16600	1660
0	1670	16700	16700	1670
0	1680	16800	16800	1680
0	1690	16900	16900	1690
0	1700	17000	17000	1700
0	1710	17100	17100	1710
0	1720	17200	17200	1720
0	1730	17300	17300	1730
0	1740	17400	17400	1740
0	1750	17500	17500	1750
0	1760	17600	17600	1760
0	1770	17700	17700	1770
0	1780	17800	17800	1780
0	1790	17900	17900	1790
0	1800	18000	18000	1800
0	1810	18100	18100	1810
0	1820	18200	18200	1820
0	1830	18300	18300	1830
0	1840	18400	18400	1840
0	1850	18500	18500	1850
0	1860	18600	18600	1860
0	1870	18700	18700	1870
0	1880	18800	18800	1880
0	1890	18900	18900	1890
0	1900	19000	19000	1900
0	1910	19100	19100	1910
0	1920	19200	19200	1920
0	1930	19300	19300	1930
0	1940	19400	19400	1940
0	1950	19500	19500	1950
0	1960	19600	19600	1960
0	1970	19700	19700	1970
0	1980	19800	19800	1980
0	1990	19900	19900	1990
0	2000	20000	20000	2000
0	2010	20100	20100	2010
0	2020	20200	20200	2020
0	2030	20300	20300	2030
0	2040	20400	20400	2040
0	2050	20500	20500	2050
0	2060	20600	20600	2060
0	2070	20700	20700	2070
0	2080	20800	20800	2080
0	2090	20900	20900	2090
0	2100	21000	21000	2100
0	2110	21100	21100	2110
0	2120	21200	21200	2120
0	2130	21300	21300	2130
0	2140	21400	21400	2140
0	2150	21500	21500	2150
0	2160	21600	21600	2160
0	2170	21700	21700	2170
0	2180	21800	21800	2180
0	2190	21900	21900	2190
0	2200	22000	22000	2200
0	2210	22100	22100	2210
0	2220	22200	22200	2220
0	2230	22300	22300	2230
0	2240	22400	22400	2240
0	2250	22500	22500	2250
0	2260	22600	22600	2260
0	2270	22700	22700	2270
0	2280	22800	22800	2280
0	2290	22900	22900	2290
0	2300	23000	23000	2300
0	2310	23100	23100	2310
0	2320	23200	23200	2320
0	2330	23300	23300	2330
0	2340	23400	23400	2340
0	2350	23500	23500	2350
0	2360	23600	23600	2360
0	2370	23700	23700	2370
0	2380	23800	23800	2380
0	2390	23900	23900	2390
0	2400	24000	24000	2400
0	2410	24100	24100	2410
0	2420	24200	24200	2420
0	2430	24300	24300	2430
0	2440	24400	24400	2440
0	2450	24500	24500	2450
0	2460	24600	24600	2460
0	2470	24700	24700	2470
0	2480	24800	24800	2480
0	2490	24900	24900	2490
0	2500	25000	25000	2500
0	2510	25100	25100	2510
0	2520	25200	25200	2520
0	2530	25300	25300	2530
0	2540	25400	25400	2540

Table 3 compares the observed and calculated structure factors and the standard deviations based on counting statistics.

DYEA

The iodide ion was chosen at (0,0,0) to fix the origin. A sharpened ($E^2 - 1$) Patterson map revealed the four chlorine atoms, and two subsequent Fourier maps yielded all remaining atoms of the dye. Several cycles of least-squares refinement, first with isotropic and then with anisotropic thermal parameters, reduced R_1 to 0.078. A difference Fourier map revealed the three nonhydrogen atoms of a molecule of acetonitrile and 15 hydrogen atoms of the dye, representing all but the methyl hydrogen atoms. Refinement was continued with the dye heavy atoms being varied anisotropically, the solvate atoms varied isotropically, and the hydrogen atoms held constant, until $R_1 = 0.044$. At this point, the real and imaginary parts of the anomalous scattering factors were first applied to iodine and chlorine and the structure was tested for absolute configuration. The configuration reported here gave $R_2 = 0.057$ and the inverted configuration gave $R_2 = 0.063$. In addition, the intensities of 46 Friedel pairs of reflections for which the calculated structure factors differed by more than 10% were measured. In all but one case, the ratios of the observed structure factors agreed with the

ratios of the calculated structure factors. These two tests indicate that the configuration reported here is the correct one for this particular crystal.

A difference Fourier did not produce suitable methyl hydrogen atoms and refinement was continued as before to $R_1 = 0.037$. Another difference Fourier map failed to produce satisfactory methyl hydrogen atom positions. The other 15 hydrogen atoms had such unreasonable distances and angles that it was decided to exclude them from the calculations completely. Refinement was continued with anisotropic thermal parameters for all atoms and was terminated when all shifts were less than 0.3σ . The final agreement indices for the 3137 observed reflections plus the 95 unobserved reflections with $|F_c| > F_{lim}$ are $R_1 = 0.040$ and $R_2 = 0.048$. Of the unobserved reflections with $|F_c| > F_{lim}$, none had $|F_c| > 1.5 F_{lim}$. The final weighting scheme had $r = 0.025$ and $s = 0$. The standard deviation of an observation of unit weight was 1.32. A final difference Fourier map contained residual electron densities between -0.32 and $+0.61 \text{ e.}\text{\AA}^{-3}$ with all detail beyond $\pm 0.32 \text{ e.}\text{\AA}^{-3}$ attributable to either hydrogen or iodine.

The final positional and thermal parameters, with standard deviations estimated from the least-squares process, are given in Table 4. The average standard deviations of the positional parameters expressed in \AA are 0.0019 for chlorine, 0.0047 for nitrogen, 0.0057 for

Table 4. Final atomic parameters for DYEA

Estimated standard deviations are given in parentheses.

The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^2B_{11} + \dots 2klb^*c^*B_{23})]$.

I	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
CL(1)	0.5745(2)	1.3104(2)	-0.1256(2)	5.80(8)	5.37(8)	3.35(6)	-1.68(6)	1.66(6)	1.20(5)
CL(2)	0.2672(2)	1.3169(2)	-0.1443(2)	4.71(7)	4.68(7)	3.83(6)	-0.47(6)	0.05(5)	1.42(5)
CL(3)	0.2393(2)	0.5638(2)	1.3130(2)	4.08(6)	5.50(8)	5.02(8)	-1.37(6)	2.01(6)	1.16(6)
CL(4)	0.5453(2)	0.4472(2)	1.5170(2)	5.19(8)	5.04(8)	3.34(6)	3.34(6)	1.44(5)	1.57(5)
N(1)	0.6895(5)	1.0203(6)	0.3917(5)	2.9(2)	3.5(2)	3.2(2)	-0.6(1)	1.0(1)	0.9(2)
N(2)	0.4727(5)	1.0199(6)	0.3737(5)	3.0(2)	3.9(2)	3.1(2)	-1.1(1)	1.0(1)	0.5(2)
N(3)	0.4605(5)	0.7725(5)	0.9481(5)	3.0(2)	2.8(2)	2.9(2)	-0.7(1)	0.9(1)	0.4(1)
N(4)	0.6740(4)	0.6973(6)	1.0939(5)	2.5(2)	3.3(2)	2.7(2)	-0.6(1)	0.4(1)	0.7(1)
N(5)	0.9954(13)	0.5375(13)	0.5247(10)	9.2(5)	8.7(7)	6.8(5)	-3.9(5)	-0.9(4)	1.8(4)
C(1)	0.6096(5)	1.0907(6)	0.2536(6)	3.1(2)	2.9(2)	2.8(2)	-0.9(2)	1.0(2)	0.1(2)
C(2)	0.6452(6)	1.1556(7)	0.1404(6)	3.3(2)	3.0(2)	3.3(2)	-0.9(2)	1.3(2)	0.0(2)
C(3)	0.5375(6)	1.2247(7)	0.0201(6)	4.3(3)	3.1(2)	2.5(2)	-0.9(2)	1.1(2)	0.2(2)
C(4)	0.3990(6)	1.2279(7)	0.0102(6)	4.0(2)	2.8(2)	2.9(2)	-0.8(2)	0.4(2)	0.7(2)
C(5)	0.3641(6)	1.1616(7)	0.1218(7)	3.3(2)	3.3(2)	3.2(2)	-0.9(2)	0.6(2)	0.1(2)
C(6)	0.4734(6)	1.0924(7)	0.2444(6)	3.6(2)	2.9(2)	2.7(2)	-1.0(2)	0.9(2)	0.3(2)
C(7)	0.6062(6)	0.9809(7)	0.4680(6)	3.2(2)	3.4(2)	2.8(2)	-1.1(2)	1.1(2)	0.0(2)
C(8)	0.6585(6)	0.9206(8)	0.6172(6)	3.0(2)	4.0(2)	3.2(2)	-0.6(2)	0.7(2)	1.3(2)
C(9)	0.5870(6)	0.8697(7)	0.7056(6)	3.7(2)	2.7(2)	2.9(2)	-1.1(2)	0.9(2)	-0.1(2)
C(10)	0.6515(6)	0.8261(7)	0.8557(6)	3.0(2)	3.5(2)	3.1(2)	-0.8(2)	0.8(2)	0.7(2)
C(11)	0.5946(5)	0.7694(6)	0.9578(6)	2.8(2)	2.8(2)	2.6(2)	-0.7(1)	0.6(2)	0.2(2)
C(12)	0.4553(5)	0.7006(6)	1.0756(6)	2.8(2)	2.6(2)	2.7(2)	-0.5(1)	0.6(2)	0.4(2)
C(13)	0.3429(6)	0.6730(7)	1.1168(6)	3.1(2)	3.1(2)	3.1(2)	-0.6(2)	1.1(2)	0.2(2)
C(14)	0.3744(6)	0.5957(7)	1.2548(7)	3.3(2)	3.0(2)	3.6(2)	-0.7(2)	1.5(2)	-0.2(2)
C(15)	0.5113(6)	0.5485(7)	1.3466(6)	4.1(2)	2.8(2)	2.7(2)	-0.7(2)	1.3(2)	0.4(2)
C(16)	0.6223(6)	0.5747(7)	1.3062(6)	3.6(2)	2.8(2)	2.8(2)	-0.8(2)	0.8(2)	0.3(2)
C(17)	0.5903(5)	0.6532(6)	1.1671(6)	3.0(2)	2.4(2)	2.7(2)	-0.6(2)	0.8(2)	0.1(2)
C(18)	0.8418(6)	0.9945(8)	0.4470(8)	2.8(2)	4.5(3)	4.4(3)	-0.6(2)	1.0(2)	1.0(2)
C(19)	0.8866(8)	1.1438(12)	0.5345(11)	4.1(3)	6.4(4)	7.4(5)	-2.5(3)	0.3(3)	-0.7(3)
C(20)	0.3459(6)	0.9961(9)	0.4021(8)	3.1(2)	4.8(3)	4.4(3)	-1.0(3)	1.1(2)	0.8(2)
C(21)	0.2892(10)	1.1383(11)	0.4885(10)	6.4(4)	5.3(4)	6.7(4)	-0.5(3)	3.5(4)	1.0(3)
C(22)	0.3355(6)	0.8578(7)	0.8335(6)	3.1(2)	3.5(2)	3.0(2)	-0.1(2)	0.5(2)	0.8(2)
C(23)	0.2771(8)	0.7379(9)	0.7107(7)	4.6(3)	5.4(3)	3.6(3)	-2.1(3)	-0.2(2)	0.5(2)
C(24)	0.8265(6)	0.6549(8)	1.1504(7)	2.8(2)	4.0(3)	3.6(2)	-1.0(2)	0.4(2)	0.9(2)
C(25)	0.8808(8)	0.4723(10)	1.1246(10)	3.6(3)	5.2(4)	6.5(4)	-0.1(2)	0.9(3)	-0.5(3)
C(26)	0.9299(12)	0.5271(16)	0.7714(14)	6.2(5)	9.5(7)	8.6(6)	0.4(5)	2.7(5)	-0.9(5)
C(27)	0.9672(9)	0.5356(11)	0.6304(11)	4.6(3)	5.2(4)	7.1(5)	-0.4(3)	-1.5(3)	0.2(3)

Table 5. Observed and calculated structure factors for DYEA

The column headings are h, l, 10F_o/K, 10F_c and 10σ(F_o)/K. * denotes unobserved reflections.

h	l	10F _o /K	10F _c	10σ(F _o)/K
0 0 1	0 0 1	140	140	140
0 0 2	0 0 2	280	280	280
0 0 3	0 0 3	420	420	420
0 0 4	0 0 4	560	560	560
0 0 5	0 0 5	700	700	700
0 0 6	0 0 6	840	840	840
0 0 7	0 0 7	980	980	980
0 0 8	0 0 8	1120	1120	1120
0 0 9	0 0 9	1260	1260	1260
0 0 10	0 0 10	1400	1400	1400
0 0 11	0 0 11	1540	1540	1540
0 0 12	0 0 12	1680	1680	1680
0 0 13	0 0 13	1820	1820	1820
0 0 14	0 0 14	1960	1960	1960
0 0 15	0 0 15	2100	2100	2100
0 0 16	0 0 16	2240	2240	2240
0 0 17	0 0 17	2380	2380	2380
0 0 18	0 0 18	2520	2520	2520
0 0 19	0 0 19	2660	2660	2660
0 0 20	0 0 20	2800	2800	2800
0 0 21	0 0 21	2940	2940	2940
0 0 22	0 0 22	3080	3080	3080
0 0 23	0 0 23	3220	3220	3220
0 0 24	0 0 24	3360	3360	3360
0 0 25	0 0 25	3500	3500	3500
0 0 26	0 0 26	3640	3640	3640
0 0 27	0 0 27	3780	3780	3780
0 0 28	0 0 28	3920	3920	3920
0 0 29	0 0 29	4060	4060	4060
0 0 30	0 0 30	4200	4200	4200
0 0 31	0 0 31	4340	4340	4340
0 0 32	0 0 32	4480	4480	4480
0 0 33	0 0 33	4620	4620	4620
0 0 34	0 0 34	4760	4760	4760
0 0 35	0 0 35	4900	4900	4900
0 0 36	0 0 36	5040	5040	5040
0 0 37	0 0 37	5180	5180	5180
0 0 38	0 0 38	5320	5320	5320
0 0 39	0 0 39	5460	5460	5460
0 0 40	0 0 40	5600	5600	5600
0 0 41	0 0 41	5740	5740	5740
0 0 42	0 0 42	5880	5880	5880
0 0 43	0 0 43	6020	6020	6020
0 0 44	0 0 44	6160	6160	6160
0 0 45	0 0 45	6300	6300	6300
0 0 46	0 0 46	6440	6440	6440
0 0 47	0 0 47	6580	6580	6580
0 0 48	0 0 48	6720	6720	6720
0 0 49	0 0 49	6860	6860	6860
0 0 50	0 0 50	7000	7000	7000
0 0 51	0 0 51	7140	7140	7140
0 0 52	0 0 52	7280	7280	7280
0 0 53	0 0 53	7420	7420	7420
0 0 54	0 0 54	7560	7560	7560
0 0 55	0 0 55	7700	7700	7700
0 0 56	0 0 56	7840	7840	7840
0 0 57	0 0 57	7980	7980	7980
0 0 58	0 0 58	8120	8120	8120
0 0 59	0 0 59	8260	8260	8260
0 0 60	0 0 60	8400	8400	8400
0 0 61	0 0 61	8540	8540	8540
0 0 62	0 0 62	8680	8680	8680
0 0 63	0 0 63	8820	8820	8820
0 0 64	0 0 64	8960	8960	8960
0 0 65	0 0 65	9100	9100	9100
0 0 66	0 0 66	9240	9240	9240
0 0 67	0 0 67	9380	9380	9380
0 0 68	0 0 68	9520	9520	9520
0 0 69	0 0 69	9660	9660	9660
0 0 70	0 0 70	9800	9800	9800
0 0 71	0 0 71	9940	9940	9940
0 0 72	0 0 72	10080	10080	10080
0 0 73	0 0 73	10220	10220	10220
0 0 74	0 0 74	10360	10360	10360
0 0 75	0 0 75	10500	10500	10500
0 0 76	0 0 76	10640	10640	10640
0 0 77	0 0 77	10780	10780	10780
0 0 78	0 0 78	10920	10920	10920
0 0 79	0 0 79	11060	11060	11060
0 0 80	0 0 80	11200	11200	11200
0 0 81	0 0 81	11340	11340	11340
0 0 82	0 0 82	11480	11480	11480
0 0 83	0 0 83	11620	11620	11620
0 0 84	0 0 84	11760	11760	11760
0 0 85	0 0 85	11900	11900	11900
0 0 86	0 0 86	12040	12040	12040
0 0 87	0 0 87	12180	12180	12180
0 0 88	0 0 88	12320	12320	12320
0 0 89	0 0 89	12460	12460	12460
0 0 90	0 0 90	12600	12600	12600
0 0 91	0 0 91	12740	12740	12740
0 0 92	0 0 92	12880	12880	12880
0 0 93	0 0 93	13020	13020	13020
0 0 94	0 0 94	13160	13160	13160
0 0 95	0 0 95	13300	13300	13300
0 0 96	0 0 96	13440	13440	13440
0 0 97	0 0 97	13580	13580	13580
0 0 98	0 0 98	13720	13720	13720
0 0 99	0 0 99	13860	13860	13860
0 0 100	0 0 100	14000	14000	14000
0 0 101	0 0 101	14140	14140	14140
0 0 102	0 0 102	14280	14280	14280
0 0 103	0 0 103	14420	14420	14420
0 0 104	0 0 104	14560	14560	14560
0 0 105	0 0 105	14700	14700	14700
0 0 106	0 0 106	14840	14840	14840
0 0 107	0 0 107	14980	14980	14980
0 0 108	0 0 108	15120	15120	15120
0 0 109	0 0 109	15260	15260	15260
0 0 110	0 0 110	15400	15400	15400
0 0 111	0 0 111	15540	15540	15540
0 0 112	0 0 112	15680	15680	15680
0 0 113	0 0 113	15820	15820	15820
0 0 114	0 0 114	15960	15960	15960
0 0 115	0 0 115	16100	16100	16100
0 0 116	0 0 116	16240	16240	16240
0 0 117	0 0 117	16380	16380	16380
0 0 118	0 0 118	16520	16520	16520
0 0 119	0 0 119	16660	16660	16660
0 0 120	0 0 120	16800	16800	16800
0 0 121	0 0 121	16940	16940	16940
0 0 122	0 0 122	17080	17080	17080
0 0 123	0 0 123	17220	17220	17220
0 0 124	0 0 124	17360	17360	17360
0 0 125	0 0 125	17500	17500	17500
0 0 126	0 0 126	17640	17640	17640
0 0 127	0 0 127	17780	17780	17780
0 0 128	0 0 128	17920	17920	17920
0 0 129	0 0 129	18060	18060	18060
0 0 130	0 0 130	18200	18200	18200
0 0 131	0 0 131	18340	18340	18340
0 0 132	0 0 132	18480	18480	18480
0 0 133	0 0 133	18620	18620	18620
0 0 134	0 0 134	18760	18760	18760
0 0 135	0 0 135	18900	18900	18900
0 0 136	0 0 136	19040	19040	19040
0 0 137	0 0 137	19180	19180	19180
0 0 138	0 0 138	19320	19320	19320
0 0 139	0 0 139	19460	19460	19460
0 0 140	0 0 140	19600	19600	19600
0 0 141	0 0 141	19740	19740	19740
0 0 142	0 0 142	19880	19880	19880
0 0 143	0 0 143	20020	20020	20020
0 0 144	0 0 144	20160	20160	20160
0 0 145	0 0 145	20300	20300	20300
0 0 146	0 0 146	20440	20440	20440
0 0 147	0 0 147	20580	20580	20580
0 0 148	0 0 148	20720	20720	20720
0 0 149	0 0 149	20860	20860	20860
0 0 150	0 0 150	21000	21000	21000
0 0 151	0 0 151	21140	21140	21140
0 0 152	0 0 152	21280	21280	21280
0 0 153	0 0 153	21420	21420	21420
0 0 154	0 0 154	21560	21560	21560
0 0 155	0 0 155	21700	21700	21700
0 0 156	0 0 156	21840	21840	21840
0 0 157	0 0 157	21980	21980	21980
0 0 158	0 0 158	22120	22120	22120
0 0 159	0 0 159	22260	22260	22260
0 0 160	0 0 160	22400	22400	22400
0 0 161	0 0 161	22540	22540	22540
0 0 162	0 0 162	22680	22680	22680
0 0 163	0 0 163	22820	22820	22820
0 0 164	0 0 164	22960	22960	22960
0 0 165	0 0 165	23100	23100	23100
0 0 166	0 0 166	23240	23240	23240
0 0 167	0 0 167	23380	23380	23380
0 0 168	0 0 168	23520	23520	23520
0 0 169	0 0 169	23660	23660	23660
0 0 170	0 0 170	23800	23800	23800
0 0 171	0 0 171	23940	23940	23940
0 0 172	0 0 172	24080	24080	24080
0 0 173	0 0 173	24220	24220	24220
0 0 174	0 0 174	24360	24360	24360
0 0 175	0 0 175	24500	24500	24500
0 0 176	0 0 176	24640	24640	24640
0 0 177	0 0 177	24780	24780	24780
0 0 178	0 0 178	24920	24920	24920
0 0 179	0 0 179	25060	25060	25060
0 0 180	0 0 180	25200	25200	25200
0 0 181	0 0 181	25340	25340	25340
0 0 182	0 0 182	25480	25480	25480
0 0 183	0 0 183	25620	25620	25620
0 0 184	0 0 184	25760	25760	25760
0 0 185	0 0 185	25900	25900	25900
0 0 186	0 0 186	26040	26040	26040
0 0 187	0 0 187	26180	26180	26180
0 0 188	0 0 188	26320	26320	26320
0 0 189	0 0 189	26460	26460	26460
0 0 190	0 0 190	26600	26600	26600
0 0 191	0 0 191	26740	26740	26740
0 0 192	0 0 192	26880	26880	26880
0 0 193	0 0 193	27020	27020	27020
0 0 194	0 0 194	27160	27160	27160
0 0 195	0 0 195	27300	27300	27300
0 0 196	0 0 196	27440	27440	27440
0 0 197	0 0 197	27580	27580	27580
0 0 198	0 0 198	27720	27720	27720
0 0 199	0 0 199	27860	27860	27860
0 0 200	0 0 200	28000	28000	28000

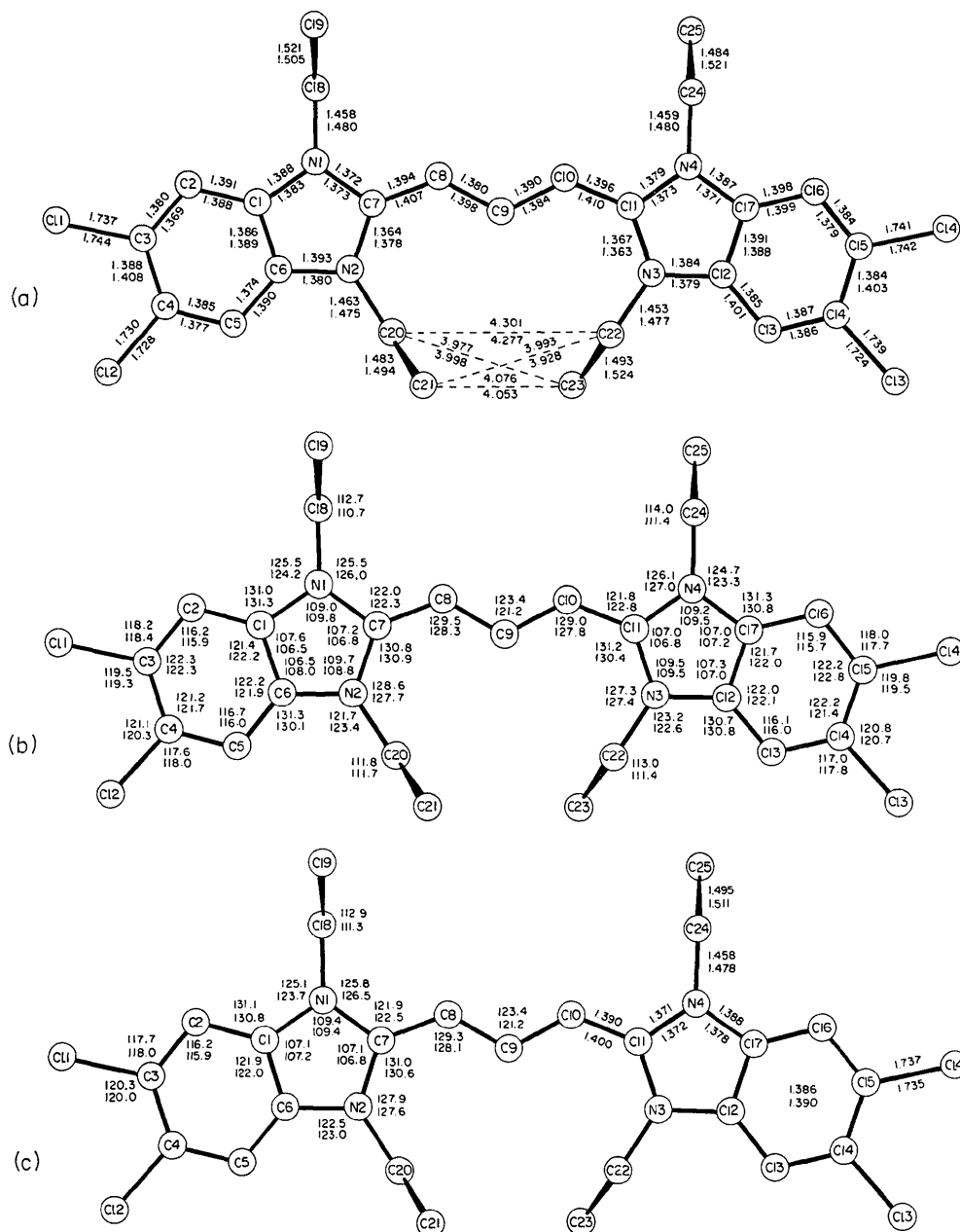
Table 5 (cont.)

h	k	l	F _o	F _c	σ(F _o)	σ(F _c)	h	k	l	F _o	F _c	σ(F _o)	σ(F _c)
12	-2	-2	46	4			12	-2	-2	46	4		
12	-2	2	46	4			12	-2	2	46	4		
12	2	-2	46	4			12	2	-2	46	4		
12	2	2	46	4			12	2	2	46	4		
12	-4	0	46	4			12	-4	0	46	4		
12	0	0	46	4			12	0	0	46	4		
12	0	4	46	4			12	0	4	46	4		
12	0	-4	46	4			12	0	-4	46	4		
12	4	0	46	4			12	4	0	46	4		
12	-4	4	46	4			12	-4	4	46	4		
12	4	4	46	4			12	4	4	46	4		
12	-4	-4	46	4			12	-4	-4	46	4		
12	4	-4	46	4			12	4	-4	46	4		
12	-8	0	46	4			12	-8	0	46	4		
12	0	8	46	4			12	0	8	46	4		
12	8	0	46	4			12	8	0	46	4		
12	-8	8	46	4			12	-8	8	46	4		
12	8	8	46	4			12	8	8	46	4		
12	-8	-8	46	4			12	-8	-8	46	4		
12	8	-8	46	4			12	8	-8	46	4		
12	-16	0	46	4			12	-16	0	46	4		
12	0	16	46	4			12	0	16	46	4		
12	16	0	46	4			12	16	0	46	4		
12	-16	16	46	4			12	-16	16	46	4		
12	16	16	46	4			12	16	16	46	4		
12	-16	-16	46	4			12	-16	-16	46	4		
12	16	-16	46	4			12	16	-16	46	4		
12	-32	0	46	4			12	-32	0	46	4		
12	0	32	46	4			12	0	32	46	4		
12	32	0	46	4			12	32	0	46	4		
12	-32	32	46	4			12	-32	32	46	4		
12	32	32	46	4			12	32	32	46	4		
12	-32	-32	46	4			12	-32	-32	46	4		
12	32	-32	46	4			12	32	-32	46	4		
12	-64	0	46	4			12	-64	0	46	4		
12	0	64	46	4			12	0	64	46	4		
12	64	0	46	4			12	64	0	46	4		
12	-64	64	46	4			12	-64	64	46	4		
12	64	64	46	4			12	64	64	46	4		
12	-64	-64	46	4			12	-64	-64	46	4		
12	64	-64	46	4			12	64	-64	46	4		
12	-128	0	46	4			12	-128	0	46	4		
12	0	128	46	4			12	0	128	46	4		
12	128	0	46	4			12	128	0	46	4		
12	-128	128	46	4			12	-128	128	46	4		
12	128	128	46	4			12	128	128	46	4		
12	-128	-128	46	4			12	-128	-128	46	4		
12	128	-128	46	4			12	128	-128	46	4		
12	-256	0	46	4			12	-256	0	46	4		
12	0	256	46	4			12	0	256	46	4		
12	256	0	46	4			12	256	0	46	4		
12	-256	256	46	4			12	-256	256	46	4		
12	256	256	46	4			12	256	256	46	4		
12	-256	-256	46	4			12	-256	-256	46	4		
12	256	-256	46	4			12	256	-256	46	4		
12	-512	0	46	4			12	-512	0	46	4		
12	0	512	46	4			12	0	512	46	4		
12	512	0	46	4			12	512	0	46	4		
12	-512	512	46	4			12	-512	512	46	4		
12	512	512	46	4			12	512	512	46	4		
12	-512	-512	46	4			12	-512	-512	46	4		
12	512	-512	46	4			12	512	-512	46	4		
12	-1024	0	46	4			12	-1024	0	46	4		
12	0	1024	46	4			12	0	1024	46	4		
12	1024	0	46	4			12	1024	0	46	4		
12	-1024	1024	46	4			12	-1024	1024	46	4		
12	1024	1024	46	4			12	1024	1024	46	4		
12	-1024	-1024	46	4			12	-1024	-1024	46	4		
12	1024	-1024	46	4			12	1024	-1024	46	4		
12	-2048	0	46	4			12	-2048	0	46	4		
12	0	2048	46	4			12	0	2048	46	4		
12	2048	0	46	4			12	2048	0	46	4		
12	-2048	2048	46	4			12	-2048	2048	46	4		
12	2048	2048	46	4			12	2048	2048	46	4		
12	-2048	-2048	46	4			12	-2048	-2048	46	4		
12	2048	-2048	46	4			12	2048	-2048	46	4		
12	-4096	0	46	4			12	-4096	0	46	4		
12	0	4096	46	4			12	0	4096	46	4		
12	4096	0	46	4			12	4096	0	46	4		
12	-4096	4096	46	4			12	-4096	4096	46	4		
12	4096	4096	46	4			12	4096	4096	46	4		
12	-4096	-4096	46	4			12	-4096	-4096	46	4		
12	4096	-4096	46	4			12	4096	-4096	46	4		
12	-8192	0	46	4			12	-8192	0	46	4		
12	0	8192	46	4			12	0	8192	46	4		
12	8192	0	46	4			12	8192	0	46	4		
12	-8192	8192	46	4			12	-8192	8192	46	4		
12	8192	8192	46	4			12	8192	8192	46	4		
12	-8192	-8192	46	4			12	-8192	-8192	46	4		
12	8192	-8192	46	4			12	8192	-8192	46	4		
12	-16384	0	46	4			12	-16384	0	46	4		
12	0	16384	46	4			12	0	16384	46	4		
12	16384	0	46	4			12	16384	0	46	4		
12	-16384	16384	46	4			12	-16384	16384	46	4		
12	16384	16384	46	4			12	16384	16384	46	4		
12	-16384	-16384	46	4			12	-16384	-16384	46	4		
12	16384	-16384	46	4			12	16384	-16384	46	4		
12	-32768	0	46	4			12	-32768	0	46	4		
12	0	32768	46	4			12	0	32768	46	4		
12	32768	0	46	4			12	32768	0	46	4		
12	-32768	32768	46	4			12	-32768	32768	46	4		
12	32768	32768	46	4			12	32768	32768	46	4		
12	-32768	-32768	46	4			12	-32768	-32768	46	4		
12	32768	-32768	46	4			12	32768	-32768	46	4		
12	-65536	0	46	4			12	-65536	0	46	4		
12	0	65536	46	4			12	0	65536	46	4		
12	65536	0	46	4			12	65536	0	46	4		
12	-65536	65536	46	4			12	-65536	65536	46	4		
12	65536	65536	46	4			12	65536	65536	46	4		
12	-65536	-65536	46	4			12	-65536	-65536	46	4		
12	65536	-65536	46	4			12	65536	-65536	46	4		
12	-131072	0	46	4			12	-131072	0	46	4		
12	0	131072	46	4			12	0	131072	46	4		
12	131072	0	46	4			12	131072	0	46	4		
12	-131072	131072	46	4			12	-131072	131072	46	4		
12	131072	131072	46	4			12	131072	131072	46	4		
12	-131072	-131072	46	4			12	-131072	-131072	46	4		
12	131072	-131072	46	4			12	131072	-131072	46	4		
12	-262144	0	46	4			12	-262144	0	46	4		
12	0	262144	46	4			12	0	262144	46	4		
12	262144	0	46	4			12	262144	0	46	4		
12	-262144	262144	46	4			12	-262144	262144	46	4		
12	262144	262144	46	4			12	262144	262144	46	4		
12	-262144	-262144	46	4			12	-262144	-262144	46	4		
12	262144	-262144	46	4			12	262144	-262144	46	4		
12	-524288	0	46	4			12	-524288	0	46	4		
12	0	524288	46	4			12	0	524288	46	4		
12	524288	0	46	4			12	524288	0	46	4		
12	-524288	524288	46	4			12	-524288	524288	46	4		
12	524288	524288	46	4			12	524288	524288	46	4		
12</													

matic C–C bonds. The N–C bonds of the cations average 1.371 Å for the conjugated N(1)–C(7)-type bonds, 1.383 Å for N(1)–C(1)-type bonds, and 1.468 Å for the unconjugated N(1)–C(18)-type bonds. These values compare with the well known 1.34 Å for aromatic N–C bonds and 1.47 Å for unconjugated N–C bonds. The C–C bonds of the ethyl groups average a short 1.503 Å, probably due to neglect of the thermal motion. The apparent lengthening of the C–C and N–C bonds of the ethyl groups of DYEA compared to those of DYEM is probably caused by the neglect of hydrogen

atoms in the refinement of the DYEA structure. The C–Cl distance of 1.736 Å agrees well with the 1.737 Å obtained from a tabulation of aromatic C–Cl bonds by Palenik, Donohue & Trueblood (1968), but is longer than the 1.709 Å claimed by Rudman (1971) for aromatic compounds with *ortho* chlorine atoms.

As is evident from the stereoscopic views (Johnson, 1965) in Fig. 3, the cations are only approximately planar, in spite of the high degree of conjugation. Atomic deviations from least-squares planes fitted to atoms C(1)⋯C(17) and N(1)⋯N(4) are as much as 0.14 Å



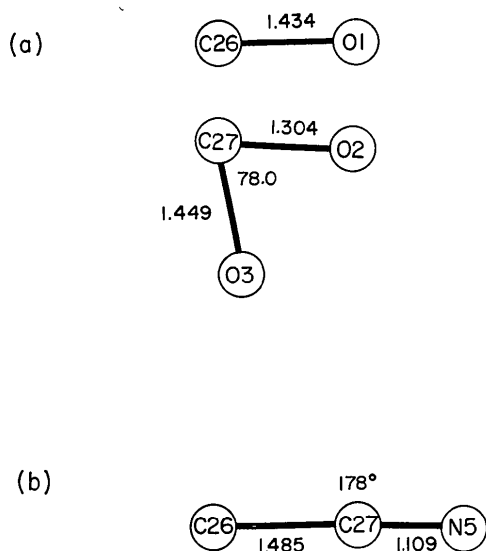


Fig. 2. Labeling and distances and angles for the solvent molecules in (a) DYEM and (b) DYEA.

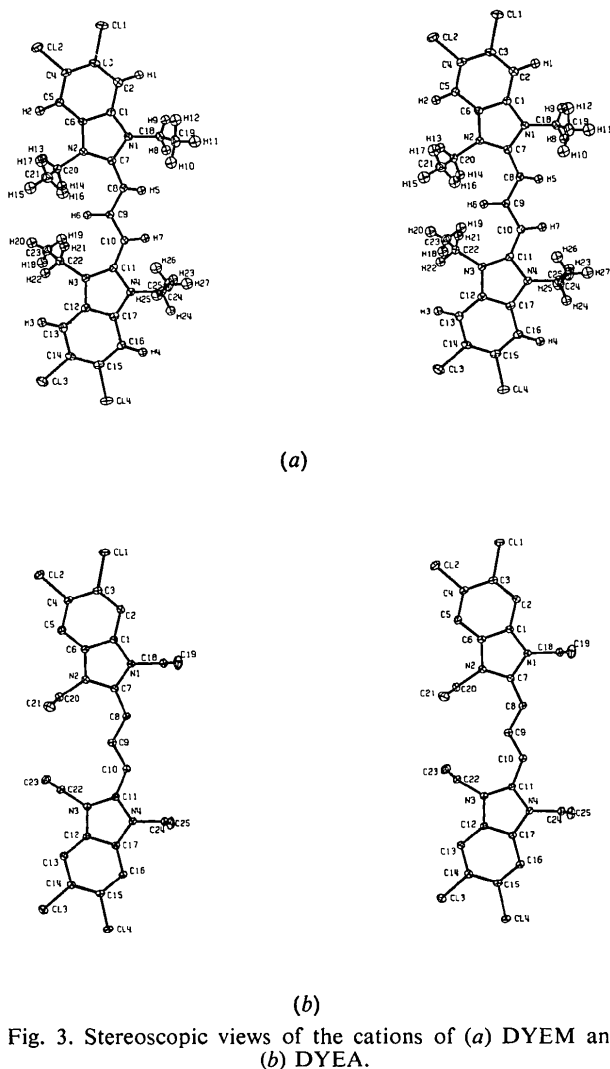


Fig. 3. Stereoscopic views of the cations of (a) DYEM and (b) DYEA.

for N(2) of DYEM and 0.16 Å for C(10) of DYEA, and the peripheral substituents show even larger deviations. The two cations, though distorted somewhat differently overall by the molecular packing, exhibit similar bond angle distortions caused by intramolecular overcrowding between H(6), the ethyl group at N(2) and the ethyl group at N(3). The average contacts between the groups are 3.97 Å for methylene...methyl C...C, 4.06 Å for methyl...methyl C...C, 4.29 Å for methylene...methylene C...C and 2.54 Å for methylene...hydrogen C...H(6). To achieve these separations, which are consistent with van der Waals distances (Pauling, 1960), and to minimize strain, the angles at N(2), C(7), C(8), C(9), C(10), C(11) and N(3) are distorted by as much as 4° from expected symmetrical values and the trimethine bridges have twisted somewhat. Thus, the only truly planar parts of the cations are the benzo groups with their adjacent nitrogens. These planes are essentially parallel but displaced by 0.5 Å for DYEA; for DYEM they are inclined at 4.3°.

The C-C-Cl angles show a slight overcrowding of the chlorine atoms. The benzo angles at C(2), C(5), C(13) and C(16) average 116.1°, and the remaining benzo angles average 122.0°. Similar distortions have been noted (Luss & Smith, 1972) for 9-fluorenone and other compounds in which the benzo ring is fused to a four- or five-membered ring. The angular strain imposed by the smaller rings causes the benzo angles at the point of fusion to become larger than 120° and the angles at C(2)-type positions are reduced below 120°.

The methanol molecules in the DYEM structure have high thermal parameters and a partial disorder, but the C-O distances compare fairly well with the accepted value of 1.43 Å. For the acetonitrile molecule in DYEA, the C-C distance is somewhat longer and the C-N distance somewhat shorter than normal, but not significantly so.

All intermolecular contacts are consistent with van der Waals radii, but the Cl(1)...Cl(1) (1-x, -y, 1-z) separation of 3.23 Å in DYEM implies that the effective van der Waals radius of chlorine is somewhat less than the 1.80 Å tabulated by Pauling (1960). Molecular packing diagrams are shown stereoscopically in Fig. 4. In both structures the dye cations pack plane to plane and end to end on edge in sheets parallel to (100). The mean cation planes make angles of 87.6 and 85.8° with these sheets for DYEM and DYEA respectively. The sheets, which correspond to $d_{100} = 9.69$ Å in DYEA and $d_{200} = 10.75$ Å in DYEM, are separated by sheets containing the iodide ions and the solute molecules. In DYEA all the cations are related by unit-cell translations and hence all are oriented identically with the result that they also lie flat in (021) layers ($d_{021} = 3.66$ Å). In DYEM adjacent cation sheets are related by the glide planes and screw axes, which results in an angle of 30.8° between the long axes of the molecules of adjacent sheets. Within a DYEM sheet, the cations in columns along c are related by

the c translation and are oriented identically, but the adjacent columns are related by centers of symmetry so these cations are inverted. Nevertheless, as shown in Fig. 5, there is a remarkable similarity of the (100) projections of the cation sheets in the two structures. The lines of end-to-end cations ($[013]$ in DYEM, $[0\bar{1}2]$ in DYEA), apart from the inversion of every other DYEM cation, superimpose very closely. The separation from a given atom to a translationally equivalent atom two molecules farther along the line is 41.62 \AA in DYEM and 41.65 \AA in DYEA so that each cation occupies approximately 20.8 \AA of linear space. For reference, the intramolecular $Cl(2) \cdots Cl(3)$ and $Cl(1) \cdots Cl(4)$ distances are 15.39 and 17.39 \AA in DYEM and 15.37 and 17.37 \AA in DYEA. Adjacent lines are separated by 3.55 \AA in DYEM but are somewhat farther apart at 3.67 \AA in DYEA so that DYEM cations cover 73.8 \AA^2 and DYEA cations cover 76.3 \AA^2 in the (100) projection.

The cation lines are shifted laterally relative to each other by 12.90 \AA in DYEM and 12.29 \AA in DYEA to form a tilted brickwork of cations in which the methyl groups, which project from the mean cation planes, are directed toward the gaps between the ends of cations in adjacent lines. In DYEM, methyl groups related by centers of symmetry form planar, almost rectangular arrays around the gaps; in DYEA the arrangement resembles a very distorted tetrahedron. The lateral shifts of the cation lines result in two types of tilted columns of cations stacked plane to plane. The axes of the columns with the greater amount of plane-to-plane overlap are $[011]$ for DYEM and $[001]$ for DYEA and make angles of 24.2 and 23.3° respectively, with the lines of end-to-end cations. The axes of the columns with the lesser overlap are $[001]$ for DYEM and $[0\bar{1}1]$ for DYEA and make angles of 15.4 and 16.6° respectively with the cation lines. The extent of plane-to-plane overlap is shown stereoscopically in Fig. 6. Both dyes have one type of lesser overlap. It involves opposite ends of translationally equivalent cations and looks very similar in the projections. However, the plane separation is 3.45 \AA in DYEM and 3.64 \AA in DYEA, a difference probably caused by the different arrangements of the methyl groups around the gaps. The greater overlaps are different for the two dyes, but involve similar plane separations, probably because the methyl groups are directed away from this overlap. DYEA has one type of greater overlap with a plane separation of 3.49 \AA between opposite ends of translationally equivalent molecules. DYEM has two very similar cases of greater overlap between centrosymmetrically related ends of molecules. The planes of the $Cl(1)$ ends are separated by 3.48 \AA and those of the $Cl(4)$ ends by 3.45 \AA .

Discussion

Of primary importance here is the extrapolation of the single-crystal structure results reported above to the

structures of sensitizing dye aggregates adsorbed on silver halide grains in photographic emulsions. The intermolecular separations in the (100) cation sheets of DYEM and DYEA bear a striking similarity to the spacings of ions in the predominant (111) octahedral faces of AgBr, a material which crystallizes in the NaCl arrangement with $a = 5.775 \text{ \AA}$ (Wyckoff, 1960). Ideally, the (111) faces of AgBr contain ions of one type lying in $[110]$ rows with each ion surrounded by six nearest neighbors at 4.083 \AA . The $[110]$ rows are separated by 3.536 \AA , which closely resembles the plane separation involved in the natural graphitic packing of planar aromatic molecules and the spacings between cation rows in DYEA (3.67 \AA) and DYEM (3.55 \AA).

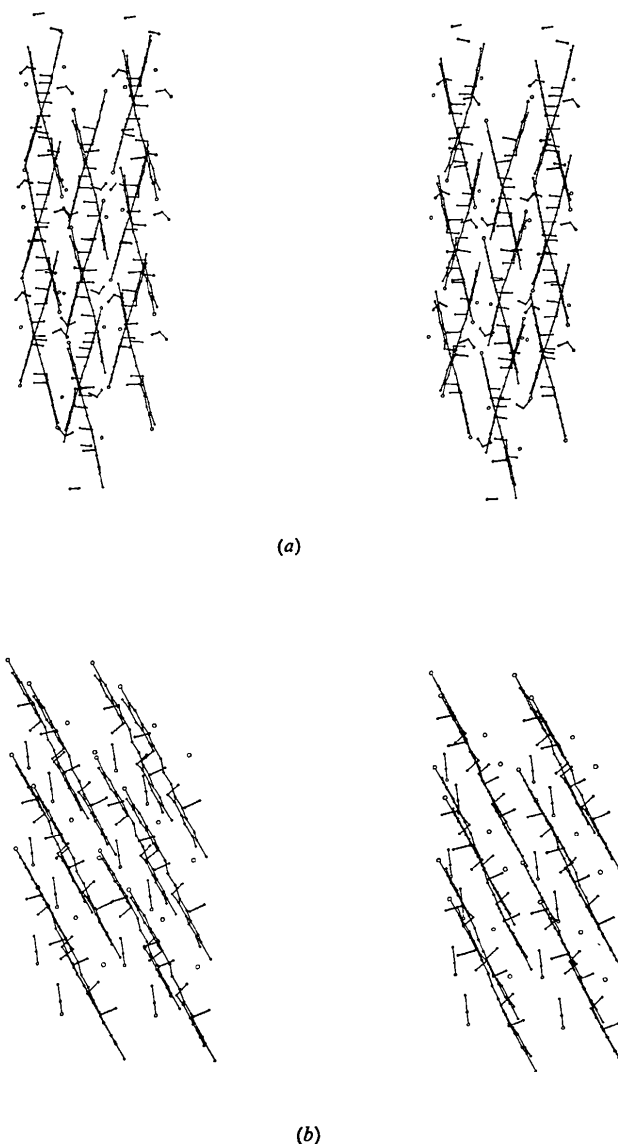


Fig. 4. Stereoscopic views of the molecular packing of (a) DYEM and (b) DYEA. In both cases b is horizontal, left to right, and the view is from positive a^* . Atoms $Cl(4)$, $O(1)$, $O(2)$, and $N(5)$ are drawn larger for identification purposes.

In both dye structures a cation occupies 20.8 Å along a row, 2% longer than the 20.4 Å for five $\text{Ag}^+ \cdots \text{Ag}^+$ spacings along [110]. The projected area per cation (76.3 Å² for DYEA, 73.8 Å² for DYEM) compares with 72.2 Å² for the area occupied by five silver ions in (111) in AgBr. Thus, if DYE adsorbs to AgBr with a definite epitaxial relationship, the cation sheets must be packed somewhat more tightly than in the solvate crystals; the energy of adsorption might provide the means to do this. Alternatively, the dye monolayers could relax somewhat to cover six silver ions per DYE cation along [110] which would presumably make it easier to decrease the spacings between adjacent rows of cations. This relaxation could be even more important if one considers that aggregates also form on AgCl which has a smaller lattice ($a = 5.547$ Å; Wyckoff, 1960) than AgBr.

The long and short lateral displacements of adjacent rows of DYE cations are 12.9 and 7.9 Å in DYEM and 12.3 and 8.5 Å in DYEA, which compare to three and two $\text{Ag}^+ \cdots \text{Ag}^+$ spacings. This indicates that the cations are more likely to be associated with the holes between silver or halide ions rather than directly with the silver ions as was suggested by Bird *et al.* (1968) for benzothiazolocarbo-cyanine dyes. Bird used lateral displacements of odd integral multiples of half spacings to arrive at postulated tilt angles of 60, 30, or 19.1° for the cation stacks, but lateral displace-

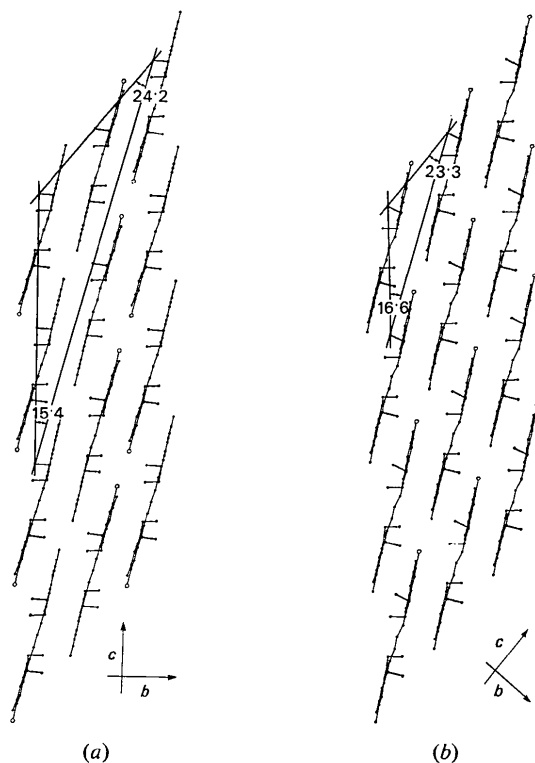


Fig. 5. (100) projections of a cation sheet of (a) DYEM and (b) DYEA. Cl(4) is drawn larger for identification. Stacking angles have been drawn in.

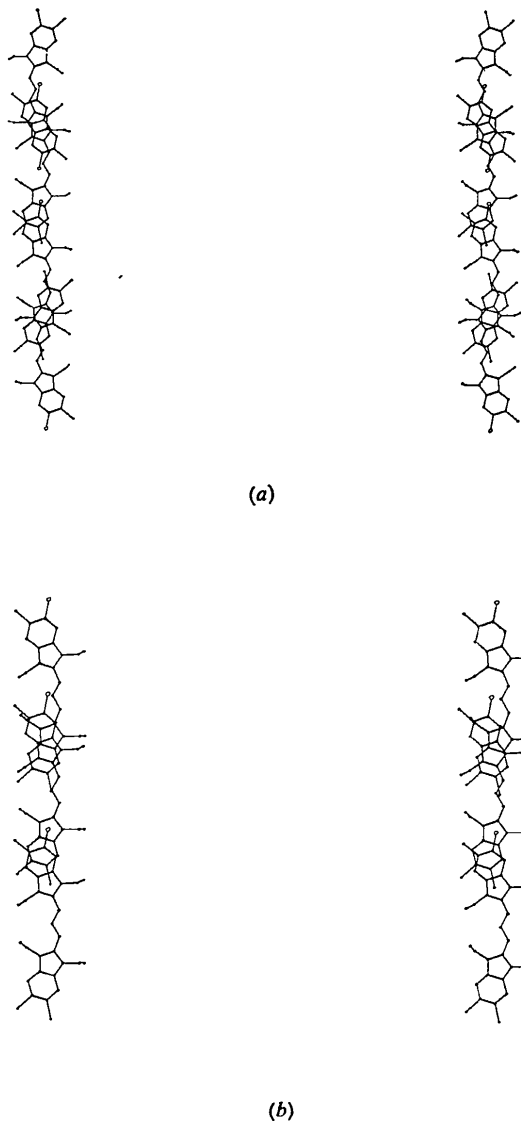


Fig. 6. Stereoscopic views of the cation overlap in (a) DYEM and (b) DYEA. a^* is horizontal. The vertical axis is [013] in DYEM and [012] in DYEA. Cl(4) is drawn larger for identification.

ments of 0, 1, 2 or 3 $\text{Ag}^+ \cdots \text{Ag}^+$ separations would yield stacking angles of 90, 40.9, 23.4 or 16.1° respectively. The latter two angles are approached in DYEA and DYEM. Norland *et al.* (1970) have used the model of Bird *et al.* (1968) to make quantum mechanical calculations based on the theory of simple electrostatic coupling of molecular transition densities to describe the spectral shifts of aggregates. For linear aggregates of 3,3'-diethylthiacarbocyanine cations, the calculations predict blue-shifted (*H*) spectra for tilt angles greater than 32° and red-shifted (*J*) spectra for tilt angles less than 32°. The calculations were extended to other dyes and to sheets of linear aggregates stacked side by side with little change in the results. Dichroism measurements (Gray *et al.* 1970) have suggested that DYE and

benzothiazolocarbo-cyanine dyes take up identical structures on AgBr. For the *J*-aggregate of DYE adsorbed on AgBr, the sharpness of the absorption bands and the absence of doublet bands indicate a simple aggregate structure of one molecule per cell (Gray *et al.*, 1970; Hochstrasser & Kasha, 1964) such as occurs in DYEA. However, it should be noted that although the unit cell of a DYEM monolayer contains two molecules, these molecules are related by a center of symmetry. Consequently, the transition moments for the cations are parallel and a sharp absorption spectrum would be expected for a DYEM-like monolayer as well as for DYEA.

It is possible that the striking correlations of structural parameters between silver halides and DYE could be coincidental. Additional spectroscopic and crystallographic studies are clearly necessary before a definitive model of dye aggregation on silver halides will emerge.

We are indebted to P. B. Gilman for suggesting the problem and for subsequent discussion, to E. J. VanLare for furnishing samples, to S. J. Marino for initial crystallization of DYEA, to P. I. Rose for nuclear magnetic resonance spectra and to A. P. Marchetti and R. L. Griffith for discussion.

References

- AHMED, F. R. (1970). Private communication.
 BIRD, G. R. (1971). *Photogr. Sci. Eng.* **15**, 134.
 BIRD, G. R., NORLAND, K. S., ROSENOFF, A. E. & MICHAUD, H. B. (1968). *Photogr. Sci. Eng.* **12**, 196.
 BIRD, G. R., ZUCKERMAN, B. & AMES, A. E. (1968). *Photochem. Photobiol.* **8**, 393.
 BROOKER, L. G. S. (1966). In *Theory of the Photographic Process*. 3rd Ed. Edited by C. E. K. MEES and T. H. JAMES, chap. 11. New York: Macmillan.
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
 CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*. Edited by J. S. ROLLETT. Oxford: Pergamon Press.
 DALY, J. J. (1966). *J. Chem. Soc. (A)*, p. 1020.
 EMERSON, E. S., CONLIN, M. A., ROSENOFF, A. E., NORLAND, K. S., RODRIGUEZ, H., CHIN, D. & BIRD, G. R. (1967). *J. Phys. Chem.* **71**, 2396.
 GRAY, W. E., BREWER, W. R. & BIRD, G. R. (1970). *Photogr. Sci. Eng.* **14**, 316.
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
 HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem*. I. *The Centrosymmetric Crystal*. A.C.A. Monograph No. 3. Pittsburgh: Polycrystal Book Service.
 HOCHSTRASSER, R. M. & KASHA, M. (1964). *Photochem. Photobiol.* **3**, 317.
 HODGSON, L. I. & ROLLETT, J. S. (1963). *Acta Cryst.* **16**, 329.
 IBERS, J. A. (1966). Private communication.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
 JELLEY, E. E. (1936). *Nature, Lond.* **138**, 1009.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
 KILLEAN, R. C. G. & LAWRENCE, J. L. (1969). *Acta Cryst.* **B25**, 1750.
 LAWTON, S. L. & JACOBSON, R. A. (1965). *The Reduced Cell and Its Crystallographic Applications*. Report IS-1141, Ames Laboratory, Iowa State University, Ames, Iowa.
 LIDE, D. R. (1962). *Tetrahedron*, **17**, 125.
 LUSS, H. R. & SMITH, D. L. (1972). *Acta Cryst.* **B28**, 884.
 NORLAND, K., AMES, A. & TAYLOR, T. (1970). *Photogr. Sci. Eng.* **14**, 295.
 PALENIK, G. J., DONOHUE, J. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 1139.
 PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd Ed. Ithaca: Cornell Univ. Press.
 ROSENOFF, A. E., WALWORTH, V. K. & BIRD, G. R. (1970). *Photogr. Sci. Eng.* **14**, 328.
 RUDMAN, R. (1971). *Acta Cryst.* **B27**, 262.
 SCHEIBE, G., KANDLER, L. & ECKER, H. (1937). *Naturwiss.* **25**, 75.
 SCHEIBE, G., MAREIS, A. & ECKER, H. (1937). *Naturwiss.* **25**, 474.
 SMITH, D. L. & BARRETT, E. K. (1971). *Acta Cryst.* **B27**, 969.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175.
 SUTTON, L. E. (1965). *Interatomic Distances and Configuration in Molecules and Ions*, Supplement. Special Publication No. 18. London: The Chemical Society.
 VOGEL, H. (1873). *Ber. dtsh. chem. Gesell.* **6**, 1302.
 WALWORTH, V. K., ROSENOFF, A. E. & BIRD, G. R. (1970). *Photogr. Sci. Eng.* **14**, 321.
 WEST, W. (1970). *Dye Sensitization: Symposium Bressanone*. pp. 105–135. New York: Focal Press.
 WEST, W. & GILMAN, P. B. (1969). *Photogr. Sci. Eng.* **13**, 221.
 WEST, W. & CARROLL, B. H. (1966). In *Theory of the Photographic Process*. 3rd Ed. Edited by C. E. K. MEES and T. H. JAMES, chap. 12. New York: Macmillan.
 WHEATLEY, P. J. (1959a). *J. Chem. Soc.* p. 3245.
 WHEATLEY, P. J. (1959b). *J. Chem. Soc.* p. 4096.
 WYCKOFF, R. W. G. (1960). *Crystal Structures*. 2nd Ed., Vol. 1. New York: Interscience.
 ZUCKERMAN, B. (1967). *Photogr. Sci. Eng.* **11**, 156.