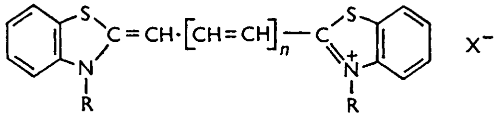
659. *The Crystallography of Some Cyanine Dyes.*

By P. J. WHEATLEY.

The cell constants and space groups of some cyanine dyes and their solvates have been determined. The structure of the unsolvated dye 3,3'-diethylthiacarbocyanine bromide has been elucidated from two projections. The cation is planar with the conjugated chain in the extended form. The sulphur atoms are *cis* with respect to this chain. Some curious properties of the crystals are described. The results of the structure determination are correlated with other properties of cyanine dyes.

THIACARBOCYANINES (I; $n = 1$) are typical of the cyanine dyes used for the sensitization of photographic films.[1] Sensitization consists of two main processes. First, the dye must absorb light in the appropriate region of the spectrum. Secondly, the energy acquired by the dye must be transferred in some way to the photographic emulsion. The first of these processes is well understood. The second is not. On theoretical grounds the cation shown in (I) would be expected to be planar. The planarity of the cation can be destroyed by the introduction of bulky substituents into the central conjugated chain. It has been established that non-planar cyanines are non-sensitizers.[2] Apart from this fact, there seem to be few generalizations in the theory of photographic sensitization. For instance, examples are known in which a diethyl-cyanine (R = Et) is an excellent sensitizer, whereas the corresponding dimethyl compound is valueless.[3] Moreover, there appears to be no correlation between the degree of adsorption of the dye on the photographic emulsion and the degree of sensitization conferred.[4] Some dyes that are adsorbed strongly are poor sensitizers; others that are but weakly adsorbed are amongst the best. Finally, most cyanine dyes in solution have the property of forming J-aggregates in which a number of the flat cations are stacked like a pack of cards. But again there is no correlation between the sensitizing power and the capacity to form J-aggregates.



(I)

(II)

(III)

The present investigation was undertaken to establish the molecular configuration of a typical cyanine dye and, possibly, to throw some light on the mechanism of photographic sensitization. The substance finally selected for an *X*-ray structural determination was 3,3'-diethylthiacarbocyanine bromide (I; $n = 1$, R = Et, X = Br). Although there could be little doubt that, except for the methyl groups of the ethyl substituents, the cation would be planar, various conformations were possible. The conjugated chain could be extended (II) or folded (III), and the sulphur atoms could be either on the same side or on opposite sides of either of these chains. Consideration of the non-bonded radii of the atoms suggested that the extended form of the chain was more probable, but the sulphur atoms could still be *cis* or *trans* with respect to this chain.

EXPERIMENTAL

It was difficult to obtain crystals suitable for diffraction purposes. Crystals that had lain for several weeks in a stoppered bottle were apparently perfect with well-defined faces and

---

[1] Doja, *Chem. Rev.*, 1932, **11**, 273.

[2] Sheppard, Lambert, and Walker, *J. Chem. Phys.*, 1941, **9**, 96.

[3] Brooker, White, Heseltine, Keyes, Dent, and van Lare, *J. Photog. Sci.*, 1953, **5**, 173.

[4] Carroll and West, in " Photographic Sensitivity," ed. Mitchell, Butterworths Scientific Publications, London, 1951, p. 166.

measurable interfacial angles. However, they showed no extinction in polarized light, and *X*-ray photographs confirmed almost total structural disorder. Finally, it was found that relatively good photographs could be obtained if the crystals were grown in the dark and transferred rapidly to the diffraction apparatus with a minimum exposure to light. The crystals would remain ordered in the dark indefinitely. As it was not possible to mount the crystals without some exposure to light, however, all *X*-ray photographs showed some evidence of disorder. The incidence of *X*-rays appeared to accelerate the disordering process that had already started. Some crystals became disordered so rapidly that little useful crystal information could be obtained. Others could be used to obtain cell dimensions and space groups. A few gave photographs sufficiently good for a structural analysis to be attempted. The useful information obtained is summarized in Table 1. An additional complicating feature is that the dyes crystallize solvated from a wide variety of solvents. The crystals of 3,3′-dimethylthiacyanine bromide and iodide obtained from aniline appear to contain a non-integral number of solvent molecules. The figures 1·7 and 1·2 in Table 1 are rough values and are the mean of the *X*-ray and microanalytical results. The fourth entry in Table 1 has been investigated before by optical methods.[5] The earlier work yielded an axial ratio of 0·8317 : 1 : 0·9887 and β = 63° 1′, which may be compared with the ratio 0·8299 : 1 : 0·9867 and β = 63° 17′ obtained by *X*-rays. The agreement shows that the same substance was being examined in both cases. However, the microanalytical results quoted in the earlier paper indicate unsolvated crystals, whereas the measured values of the volume of the unit cell and of the density (D_m = 1·545) show that the crystals actually contain methyl alcohol.

TABLE 1. *Crystallographic constants for some cyanine dyes.*

Compound	*n*	R	X	Solvent	Formula
(1) 3,3′-Dimethylthiacyanine bromide......	0	Me	Br	Ph·NH$_2$	$C_{17}H_{15}N_2S_2Br,1{\cdot}7C_6H_5{\cdot}NH_2$
(2) 3,3′-Dimethylthiacyanine iodide	0	Me	I	Ph·NH$_2$	$C_{17}H_{15}N_2S_2I,1{\cdot}2C_6H_5{\cdot}NH_2$
(3) 3,3′-Diethylthiacarbocyanine bromide	1	Et	Br	Ac$_2$O	$C_{21}H_{21}N_2S_2Br$
(4) 3,3′-Diethylthiacarbocyanine iodide ...	1	Et	I	MeOH	$C_{21}H_{21}N_2S_2I,CH_3{\cdot}OH$
(5) 3,3′-Diethylthiacarbocyanine bromide	1	Et	Br	EtOH	$C_{21}H_{21}N_2S_2Br,C_2H_5{\cdot}OH$

Space group	*a* (Å)	*b* (Å)	*c* (Å)	α	β	γ	D_m
(1) *P*1 or *P*$\bar{1}$	10·97	14·64	19·57	107·0°	111·2°	82·7°	1·484
(2) *P*2$_1$/*c*	7·26	11·03	31·64	90	99·9	90	1·595
(3) *P*2$_1$/*n*	8·24	16·90	14·50	90	94·3	90	1·475
(4) *I*2/*c*	15·36	18·47	18·26	90	63·3	90	1·545
(5) *P*$\bar{1}$	8·07	11·83	13·11	98·6	77·2	103·3	1·421

The onset of disorder appears to be associated with another curious property of these crystals, that of spontaneous disintegration. Crystals that have been left for some time crumble to a fine powder. The most stable crystals, in this respect, are those of 3,3′-diethylthiacarbocyanine iodide obtained from methyl alcohol. The least stable are those of the bromide of the same dye recrystallized from the same solvent, which fragment as soon as they are removed from the excess of solvent. However, the fragmentation cannot be due solely to loss of solvent from the crystals, since the unsolvated crystals obtained from acetic anhydride show the same property. The disorder manifests itself on Weissenberg photographs as long streaks parallel to the translation direction of the camera. Some of the streaks seem to coincide with Bragg reflexions, but most do not. The crystals used in the present structural investigation, 3,3′-diethylthiacarbocyanine bromide recrystallized unsolvated from acetic anhydride, show a moderate increase of disorder with time. The same crystals used to obtain the *X*-ray intensities were photographed again six months later. The crystals had partially disintegrated, and the later photographs showed no evidence of Bragg reflexions but only disorder streaks.

Structure Determination.—$C_{21}H_{21}N_2S_2Br$, M = 445·4. Monoclinic, $a = 8{\cdot}23_7 \pm 0{\cdot}05$, $b = 16{\cdot}90_1 \pm 0{\cdot}08$, $c = 14{\cdot}50_2 \pm 0{\cdot}08$ Å, β = 94° 17′, U = 2014 Å^3, D_m = 1·475 (by flotation), Z = 4, D_c = 1·469, $F(000)$ = 912. Space group, *P*2$_1$/*n* (C_{2h}^5, No. 14). Cu-K_α radiation (λ = 1·542 Å), single crystal rotation and Weissenberg photographs.

The crystals were needles elongated parallel to the short [*a*] axis. Multiple-film Weissenberg photographs round [*a*] were obtained with a square needle about 0·15 mm. across. The *hk*0 photographs were obtained with a cube of side 0·1 mm. cut from a needle. No correction was made for absorption (μ = 49·3 cm.$^{-1}$). Relative intensities were estimated by comparison

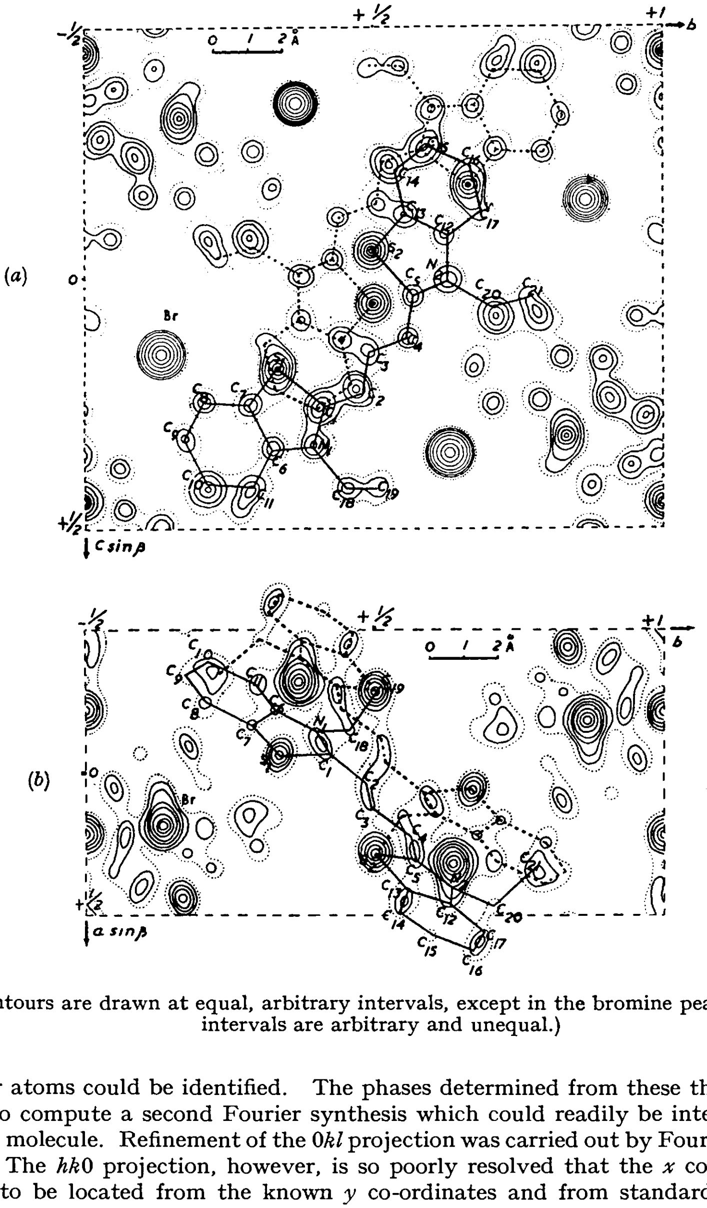
---

[5] Mills, *J.*, 1922, **121**, 455.

with standard strips prepared from the same crystals. 227 of the 321 0*kl* reflexions, and 130 of the 183 *hk*0 reflexions obtainable with Cu-K_{α} radiation were observed to be non-zero.

Each projection was solved in the same manner. A Patterson synthesis gave the co-ordinates of the bromine ion. The phases determined from these co-ordinates were used for a preliminary Fourier synthesis. On the resultant electron-density map the peaks due to the

FIG. 1. (*a*) *Projection of the contents of the unit cell down* [*a*]. (*b*) *Projection of the contents of the unit cell down* [*c*].



(The contours are drawn at equal, arbitrary intervals, except in the bromine peaks, where the intervals are arbitrary and unequal.)

two sulphur atoms could be identified. The phases determined from these three heavy atoms were used to compute a second Fourier synthesis which could readily be interpreted in terms of the whole molecule. Refinement of the 0*kl* projection was carried out by Fourier and difference syntheses. The *hk*0 projection, however, is so poorly resolved that the x co-ordinates of the atoms had to be located from the known y co-ordinates and from standard values of bond lengths and angles. Non-planar models gave significantly worse agreement than planar ones, but little proper refinement could be carried out.

For the 0*kl* projection an isotropic temperature factor B = 3·5 Å^2 proved adequate to reduce the R factor to 14%. Unobserved reflexions were omitted from the R factors. Refinement of the *hk*0 projection would not proceed satisfactorily until an anisotropic temperature factor was employed. This was of the form $A + B\cos^2\phi$, where ϕ is the angle between any crystallographic plane and the [*a*] axis.[6] The direction of greatest thermal motion is thus taken to be along [*a*]. The values of *A* and *B* were chosen as 3 and 1·5 Å^2 respectively. The final *R* factor for the *hk*0 projection was 19%. The scattering factors used were those of Berghuis *et al.*[7] for the carbon and nitrogen atoms, that of Tomiie and Stam [8] for the sulphur atom, and that of Thomas and Umeda [9] for the bromide ion. Thomas and Umeda's figures were modified at low values of θ to allow for the additional electron, and corrected for the real part of the dispersion.[10] Since the cation bears a single positive charge, there is a deficiency of one electron spread out over many atoms. This deficiency was ignored.

TABLE 2. *Fractional co-ordinates.*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
Br	0·190	0·133	$0{\cdot}150_5$	$N_{(1)}$	0·862	0·396	0·336
				$N_{(2)}$	0·403	0·629	0·006
$S_{(1)}$	0·940	0·333	0·179				
$S_{(2)}$	0·284	0·501	0·947				
$C_{(1)}$	0·937	0·417	0·256	$C_{(11)}$	0·688	0·292	0·418
$C_{(2)}$	0·042	0·481	0·230	$C_{(12)}$	0·458	0·627	0·916
$C_{(3)}$	0·124	0·492	0·146	$C_{(13)}$	0·412	0·553	0·873
$C_{(4)}$	0·225	0·558	0·120	$C_{(14)}$	0·483	0·537	0·787
$C_{(5)}$	0·310	0·570	0·036	$C_{(15)}$	0·576	0·594	0·738
$C_{(6)}$	0·780	0·325	0·342	$C_{(16)}$	0·628	0·667	0·779
$C_{(7)}$	0·817	0·285	0·253	$C_{(17)}$	0·558	0·685	0·867
$C_{(8)}$	0·755	0·205	0·247	$C_{(18)}$	0·852	0·453	0·419
$C_{(9)}$	0·652	0·172	0·321	$C_{(19)}$	0·700	0·506	0·420
$C_{(10)}$	0·627	0·212	0·412	$C_{(20)}$	0·470	0·702	0·057
				$C_{(21)}$	0·344	0·768	0·037

Electron-density maps projected down [*a*] and [*c*] are shown in Fig. 1 (*a*) and (*b*) respectively. The molecule drawn in full lines corresponds to the co-ordinates listed in Table 2. The molecule drawn in dotted lines is centrosymmetrically related to the first. For clarity the molecules related to these two by screw axes and glide planes are not drawn in. A list of observed and calculated structure factors is given in Table 3. The molecular dimensions and the numbering of the atoms are shown in Fig. 2.

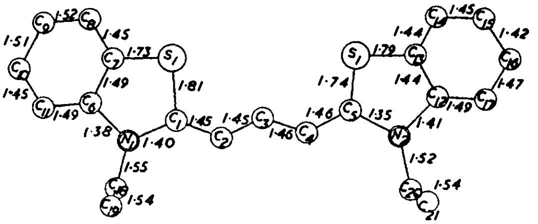


FIG. 2. *The numbering of the atoms and the molecular dimensions.*

DISCUSSION

Within the limits of the experimental results the cation is planar except for the methyl groups of the ethyl substituents. The conjugated chain is in the extended form with the sulphur atoms *cis* with respect to this chain. There appears to be no obvious reason why the *cis*-form should be preferred. In simpler molecules *trans*-configurations are normally found, but it is evident that other factors come into play when steric requirements are no longer dominant. Since the energy barrier resisting conversion from the *cis*- into the *trans*-form must be considerable, it is probable that the cation exists in the *cis*-configuration in solution as well as in the solid.

The internal consistency of chemically similar bonds shows that the C–C and C–N bond

---

[6] Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.
[7] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.
[8] Tomiie and Stam, *ibid.*, 1958, **11**, 126.
[9] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.
[10] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

lengths are not accurate to more than 0·1 Å. The accuracy of the lengths of bonds involving sulphur atoms is a little higher. The mean length of the C–S bonds is 1·77 Å, of the C–C bonds in the conjugated chain 1·46 Å, and of the C–C bonds in the benzene rings 1·47 Å. These last two figures are higher than expected, but there is no significant difference from the standard values. The intermolecular contacts are normal. The four atoms nearest to the bromide ion are $C_{(4)}$, $C_{(11)}$, $C_{(2)}$, and $C_{(19)}$ at 3·58, 3·60, 3·73, and 3·94 Å respectively.

TABLE 3. *Observed and calculated structure factors for one asymmetric unit*

$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$0kl$	F_o	F_c	$hk0$	F_o	F_c	$hk0$	F_o	F_c
0.2.0	5·6	+6·0	1	26·1	−31·3	15	4·5	+5·0	3	7·1	−5·8	5	11·0	−11·3	11	5·4	+5·0
4	11·7	−13·8	2	3·3	+0·3	16	6·3	+5·0	4	9·7	−9·4	6	24·1	−20·4	12	3·8	+0·2
6	28·3	+32·5	3	1·4	−1·1	19	2·4	−3·1	5	4·2	+4·4	7	7·0	+7·2	14	2 7	+2·9
8	11·9	+13·1	4	19·9	+19·0	20	2·2	−2·6	6	1·9	+1·5	8	5·6	+8·4	15	1·6	−1·5
10	6·1	+3·2	5	5·9	+4·5				7	3·5	+2·7	9	4·8	+6·7	16	3·4	+3·0
14	10·6	+10·5	6	10·1	−11·5	0.1.8	10·5	+9·3	8	2·1	+1·9	10	7·3	+10·8			
16	7·9	+7·9	7	12·4	−9·4	3	2·8	+5·3	9	7·8	−8·9	11	11·2	−10·3	5.1.0	13·2	+14·4
18	5·8	+3·0	8	5·1	−6·8	4	8·6	−8·6	11	3·5	−3·0	12	11·3	−11·7	2	4·1	+2·4
20	1·3	−1·4	9	10·4	−8·5	5	12·0	−11·3	12	2·0	−3·0	13	6·8	−7·5	3	5·0	−2·3
			10	9·4	+9·1	6	14·3	−12·3	13	5·6	+5·3	14	12·6	−13·4	4	4·4	−5·5
0.1.1	15·2	−20·5	11	4·6	+1·2	7	4·8	−4·0	16	2·3	−1·6	15	13·5	+12·8	5	1·4	+2·3
2	11·7	−13·0	12	7·1	+8·1	9	8·3	+6·9				16	2·9	+4·5	6	2·3	+3·3
3	10·4	−12·1	13	6·8	+7·8	12	10·9	−9·0	0.1.13	10·5	+10·9	18	2·8	+3·9	7	12·0	+12·7
4	6·2	−5·9	15	2·5	−1·0	13	9·4	−9·3	2	6·1	−5·0	19	3·6	−4·3	8	3·5	+4·2
5	17·8	−18·8	16	6·7	−6·9	18	3·8	−4·7	3	7·3	−6·4	20	1·6	−3·5	9	9·0	+8·7
6	19·8	−20·7							5	2·9	−2·7	21	3·7	+4·3	10	7·3	−6·4
7	1·4	+1·4	0.1.5	7·1	−8·7	0.1.9	5·7	−4·7	6	3·5	+3·8				13	3·1	+2·9
9	4·8	+3·9	2	20·3	−18·3	2	13·5	+12·9	7	3·0	+3·8	2.0.0	27·5	−24·6	14	3·3	+4·5
10	14·7	+14·7	3	2·7	+3·8	3	10·1	+8·6	14	1·2	−0·7	1	13·3	+11·7	15	6·6	+8·9
11	13·3	−13·0	4	7·5	−6·6	4	1·8	−3·6	15	2·1	+3·3	3	2·1	+1·8	16	4·1	−4·0
12	9·0	−10·9	5	6·3	−8·5	5	12·5	+11·8				4	7·1	−3·7			
13	7·1	−4·4	6	18·9	+19·2	6	10·5	−13·4	0.0.14	2·5	+3·1	5	6·2	−5·0	6.0.0	1·7	+3·3
14	13·2	−13·6	7	10·1	−9·5	8	7·3	+7·0	2	3·0	+3·2	6	3·3	−6·2	1	2·1	+1·9
15	3·6	−1·5	9	8·4	+8·0	9	2·3	+0·3	3	1·9	+1·6	7	5·3	−9·2	2	3·4	−1·6
16	8·3	+8·9	10	18·8	−17·8	10	6·9	+4·8	4	2·9	−3·3	8	15·5	−17·2	3	6·2	+6·3
17	4·9	−4·1	11	2·3	−2·0	11	13·2	+12·9	5	4·3	−4·0	9	16·2	+17·9	4	1·6	−1·9
18	1·9	+2·9	12	9·1	+9·4	12	4·9	−6·1	8	7·0	+6·9	10	5·4	−2·8	6	1·9	−0·8
19	3·6	−4·4	14	5·4	+4·6	13	6·4	+6·3	9	6·1	+5·0	11	9·2	+8·4	7	5·7	−4·9
20	3·2	−3·5	15	4·2	+3·8	14	7·3	−6·7	12	5·6	−5·6	12	5·3	+5·2	8	3·7	+5·1
			16	4·7	−5·5	15	1·5	−1·3	13	2·2	−2·4	13	14·7	−17·3	9	4·6	+6·6
0.2.0	17·8	−21·4	18	1·2	−2·7	17	2·3	+1·1				14	14·6	−15·0	10	2·6	−2·1
1	9·7	+14·1	20	4·3	+4·8				0.1.15	2·3	−2·2	16	10·3	−10·2	11	4·0	+4·0
2	11·2	+11·5				0.0.10	23·2	−24·0	2	6·5	+5·9	17	10·8	+11·3	12	3·5	−5·4
3	21·2	+20·3	0.0.6	5·7	+7·4	2	5·0	−2·7	4	3·3	−2·2	18	1·6	−0·8	13	3·7	−5·6
4	22·3	+22·8	1	11·7	−13·3	4	5·8	+4·6	6	6·5	−6·8	20	1·9	−1·9	17	1·8	+3 5
5	28·2	−32·7	2	8·4	−8·8	5	6·5	+3·8	10	1·6	+2·7	21	2·0	−3·0			
6	5·5	−5·5	3	7·7	−5·0	6	6·0	−4·9	12	1·7	−2·6				7.1.0	6·9	−5·8
8	7·9	+8·9	4	35·4	−34·2	7	2·2	+4·2				3.1.0	16·0	−13·6	2	7·4	+7·4
9	24·9	+24·2	5	4·7	+4·7	8	13·2	−11·5	0.0.16	1·3	−1·8	2	2·6	−1·3	3	4·4	−2·0
10	4·2	+4·8	6	14·2	+11·4	9	2·7	−1·3	3	2·2	+3·1	3	8·4	+5·7	4	4·1	−3·7
13	4·0	−5·0	7	11·0	+9·7	10	5·5	−4·5	4	4·4	+4·0	4	1·3	+1·6	5	2·4	−2·8
14	7·7	+6·8	8	8·4	+9·3	11	6·2	+4·9	7	3·8	−2·9	5	4·3	+7·0	9	7·7	−6·9
16	7·7	+6·6	9	3·6	−3·0	14	6·8	−4·6	8	2·6	−4·0	6	2·0	+1·0	11	2·1	+0·9
17	4·7	+7·5	10	14·0	−14·0	15	3·0	−1·0	10	2·0	+2·2	7	25·8	−24·6	15	5·1	−4·4
20	2·4	+2·9	11	3·5	−2·6	16	4·5	−4·6				8	2·6	+0·7			
21	2·5	−3·6	13	6·7	+8·4				0.1.17	5·4	−5·4	9	3·9	−4·0	8.0.0	7·0	−6·8
			14	4·2	−3·7	0.1.11	2·3	+2·3	3	2·6	+3·7	10	3·5	−4·8	2	2·1	+0·6
0.1.3	13·7	−14·7	16	2·3	+3·9	2	3·3	−3·9	7	4·6	−5·3	13	4·8	−6·4	4	2·3	+4·4
2	17·0	+18·6	17	4·6	−5·3	3	18·0	+19·6	$hk0$			14	1·7	+1·4	6	1·8	−2·2
3	13·4	+13·9	20	3·0	−4·3	4	4·8	+4·8	0.3.18	2·2	−3·0	15	9·2	−11·9	9	1·6	−0·7
4	5·6	+5·0				5	9·1	+9·2				16	3·2	−4·3	13	1·5	+0·9
5	25·6	+28·5	0.1.7	12·3	+13·4	6	5·7	+6·1	0.2.0	5·8	+6·1	18	3·8	−3·2			
6	3·7	−2·8	2	8·4	+7·2	7	3·6	−3·7	4	13·3	−14·1	19	1·2	+3·9	9.1.0	2·0	+1·4
7	18·3	−17·8	3	13·0	−15·4	8	4·4	−4·3	6	32·5	+33·7	20	1·2	+2·0	2	1·4	−3·2
9	22·1	−20·7	4	9·2	+7·9	10	5·9	−6·9	8	12·7	+14·0				4	1·6	+1·8
11	12·2	+11·6	5	4·7	−3·3	11	5·7	+6·4	10	6·2	+3·6	4.0.0	2·3	−0·9	5	1·9	+1·8
13	3·9	+2·4	6	3·8	−4·2	12	2·0	+3·0	14	13·0	+12·9	1	20·1	−18·6	6	2·2	+1·2
14	4·0	+3·2	7	17·9	+18·0	13	1·9	+0·7	16	9·7	+10·3	2	9·5	+4·6	7	1·4	+1·0
15	14·5	−15·1	8	1·3	−2·2	14	4·4	+4·1	18	7·2	+4·2	3	7·2	−7·2			
16	2·7	+3·4	9	8·6	+6·6	15	3·2	+2·1	20	2·4	−2·2	4	9·3	+5·9	10.2.10	1·4	+1·0
17	2·1	+2·1	10	6·8	+4·5	16	2·9	−2·5				5	18·3	+18·4	4	1·3	−0·4
19	4·0	+4·7	11	5·1	−6·5				1.1.0	7·6	+10·7	6	5·7	+5·7			
21	3·3	−2·6	12	3·1	−1·8	0.0.12	10·8	+9·2	2	44·8	+48·8	7	3·4	+4·0			
			13	1·5	+0·1	1	4·6	−5·5	3	9·2	−6·6	9	3·1	−4·5			
0.0.4	19·1	−18·0	14	4·1	−4·8	2	7·3	−6·7	4	9·8	+9·7	10	3·8	+2·7			

Both methyl groups lie on the same side of the plane of the cation. The planes containing the atoms $N_{(1)}$, $C_{(18)}$, $C_{(19)}$ and $N_{(2)}$, $C_{(20)}$, $C_{(21)}$ are approximately perpendicular to the cationic plane. The cations are stacked in columns up the [*a*] axis, and are best considered in pairs. The pair shown in Figs. 1 (*a*) and (*b*) forms a sort of box with the methyl groups as flaps enclosing the space between the cationic planes. The next pair of cations is obtained by a unit translation along [*a*]. The space between each pair is not enclosed by methyl groups. However, the perpendicular distance between each successive cationic plane is constant at 3·3 Å, so that the methyl groups cannot be playing any substantial part in determining the distance apart of the cations. The bromide ions lie between the columns.

When dye cations are adsorbed on a photographic emulsion it is generally assumed that they are held with their long axes parallel to the surface and with the nitrogen atoms pointing towards rather than away from the surface.[11] These conclusions were reached from a consideration of the adsorption isotherms, and from the areas of the cation viewed flat, edge on, and end on. The results of the structure analysis show that other arrangements of the adsorbed dye need to be considered. At high concentrations in solution it is probable that columns of cations similar to the columns found in the crystal are formed. Thus a J-aggregate may well consist of dye cations arranged alternately head-to-tail. Similarly, when the dye is adsorbed it seems more probable that this head-to-tail arrangement should be favoured. Further, since the crystal structure shows that the cations have a tendency to associate in pairs across a centre of symmetry, it is possible that the surface, instead of being covered with a " unimolecular " layer of cations edge on, is covered with a double layer of head-to-tail cations with the cationic planes parallel to the surface. Each of these explanations appears to be equally compatible with the evidence so far available, and further experiments will be required to decide between them.

I thank Drs. L. G. S. Brooker and D. W. Heseltine, of Eastman Kodak Company, for many of the crystals and all of the dyes used in this work.

MONSANTO RESEARCH SA.,
BINZSTRASSE 39, ZÜRICH 3/45,
SWITZERLAND.

[*Received, April* 15*th*, 1959.]

---

[11] Ref. 4, p. 165.