Acta Cryst. (1975). B31, 402

The Crystal and Molecular Structure of a Hydrate of 5,6-Dichloro-1,3-diethyl-2-[(5,6-dichloro-1,3-diethyl-2-benzimidazolinylidene)-1-propynyl]benzimidazolium Toluene-*p*-sulfonate, $(C_{25}H_{25}Cl_4N_4^+)(C_7H_7SO_3^-).0\cdot2H_2O$

By Douglas L. Smith and Henry R. Luss

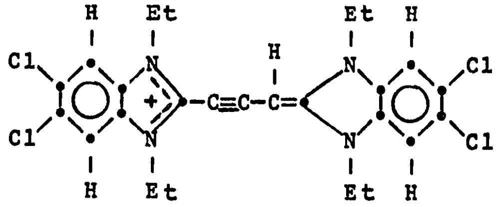
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, *U.S.A.*

(*Received* 1 *May* 1974; *accepted* 18 *July* 1974)

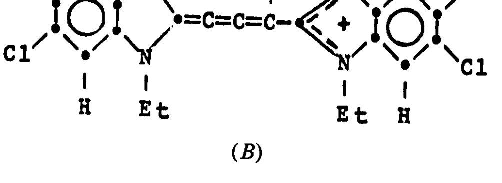
The crystal structure of the title compound has been determined from single-crystal X-ray intensity data collected with a card-controlled diffractometer. The crystals are triclinic, $P\bar{1}$, with $a=12\cdot581$ (8), $b=13\cdot173$ (8), $c=12\cdot168$ (9) Å, $\alpha=106\cdot06$ (5), $\beta=112\cdot96$ (4), $\gamma=102\cdot35$ (4)° and $Z=2$. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to $R_1=0\cdot053$. Most of the hydrogen atoms were located and refined. The bond lengths in the chain linking the benzimidazole groups indicate a somewhat greater contribution from the vinyl acetylene structure than from the butatriene structure. The cations are only approximately planar. They pack plane to plane and end to end on edge in layers parallel to (100) separated by layers containing the anions and water molecules.

Introduction

The title compound is a member of a new class of cationic dyes recently prepared in the Kodak Research Laboratories (Mee, 1974). Formally, these dyes are the oxidation products of the corresponding carbocyanine dyes from which two adjacent chain hydrogen atoms have been removed. The unshared carbon electrons then pair in a π-orbital orthogonal to that of the dye chromophore. However, the two canonical forms, *A* and *B*, are no longer equivalent, being, respectively, a vinyl acetylene and a butatriene. We undertook the crystal structure determination to obtain information on the relative contributions of forms *A* and *B* to the molecular structure.



(*A*)



(*B*)

Experimental

Samples of the dye as the iodide (I^-) and toluene-*p*-sulfonate (PTS^-) salts were furnished by Mr John Mee of the Kodak Research Laboratories. Crystals were grown from solution in a variety of solvents by slow evaporation of solvent. Five crystal forms were eventually characterized with the aid of precession photographs. In Table 1 are listed crystal data for these five forms plus one form of the analogous cyanine dye 5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (DYEA), whose structure we have reported (Smith & Luss, 1972). The close similarity of the unit cells and reflection intensities of DYEA and (I) strongly suggests that they are isostructural.

Generally, the crystals of (I), (II), and (III) were of poor quality or degraded in air. Good stable crystals of (IV) as red plates and (V) as yellow kayaks (often complete with cockpit) grew from the same CH_3CN solution. Since (V) was probably centrosymmetric and appeared to be unsolvated, we chose to determine its structure. The structure analysis confirmed the choice of $P\bar{1}$ for the space group. However, residual electron density led us to postulate the presence of a small amount of water in the structure. For independent confirmation of this, large (~ 1 mm), freshly prepared crystals of (V) were analyzed for water with an automatic microcoulometric Karl Fischer titration apparatus, the Photovolt Aquatest 700® (Meyer & Boyd, 1959), and found to contain 19 mole per cent water. The location of the water close to a center of inversion leads to a maximum possible water content of one-half molecule per dye molecule, or 33·3 mole per cent water.

A crystal ($0\cdot20 \times 0\cdot25 \times 0\cdot50$ mm) was cemented to a thin glass rod and used for intensity data collection on a card-controlled, Picker four-circle goniostat at 24 ± 2°C. 15 reflections at Bragg angles (2θ) between 23·6 and 34·6° (Mo $K\alpha_1$, $\lambda=0{\cdot}70926$ Å) were centered carefully through very narrow vertical and horizontal slits at a take-off angle of 0·5°. Least-squares refinement (Ibers, 1966) of these observations yielded cell (Table 1) and orientation parameters.

Intensity data were collected with Zr-filtered Mo radiation at a take-off angle of 1·5°. A scintillation detector was used and the pulse-height analyzer was set for a 90% window. The θ–2θ scan technique with a 2θ scan rate of 1° min^{-1} was used to measure 5244 unique reflections for $2\theta < 48°$. Scans were from 1·1° below the calculated $K\alpha_1$ peak to 1·0° above the $K\alpha_2$ peak. A fixed 20 s background count was taken at each end of the scan. For count rates above 11000 c.p.s. brass attenuators were automatically inserted in the diffracted beam. To check crystal and electronic stability, the intensity of the $09\bar{2}$ reflection was remeasured every 50th reflection. No systematic variation was observed for these standard intensities.

The measured intensities were reduced to structure amplitudes by correcting for background, attenuator, Lorentz, and polarization effects. An absorption correction was not applied; for an absorption coefficient, μ, of 4·6 cm^{-1} we estimate the maximum error in I caused by absorption to be less than ±4%. Standard deviations, $\sigma(I)$, were calculated according to the formula

$$\sigma^2(I)=\left(\frac{I\sigma(A)}{A}\right)^2+A^2\left[P+\left(\frac{t_p}{2t_b}\right)^2(B_1+B_2)\right],$$

where the net intensity is $I=A[P-(B_1+B_2)t_p/2t_b]$, A is the attenuator factor, P is the integrated scan count obtained in time t_p, and B_1 and B_2 are the background counts, each obtained in time t_b. The 44 largest intensities required attenuation and had relatively large standard deviations because of the uncertainty in A. The 3785 reflections for which $I \geq 2\sigma(I)$ were used to determine and refine the structure.

Determination and refinement of the structure

The observed structure factors were converted to normalized structure factor magnitudes, $|E_H|$ (Hauptman & Karle, 1953); their statistical averages strongly supported the centrosymmetric space group. The 562 E's with $|E| \geq 1{\cdot}6$ were phased by the multiple solution computer program of Long (1965), modified by Tsai (1968), based on the reiterative application of Sayre's (1952) equation. The fourth E map and a subsequent electron-density map yielded all 44 nonhydrogen atoms.

Refinement was carried out with Ahmed's (1970) block-diagonal least-squares program, *NRC*-10. This program employs 4 × 4 blocks for atoms with isotropic temperature factors and 9 × 9 blocks for atoms with anisotropic temperature factors and applies Schomaker's correction (Hodgson & Rollett, 1963) for the interaction between thermal and scale factors. The function minimized was $\sum w(F_o-F_c/K)^2$, where K is the scale factor. The weights w were defined as $w^{-1}=\sigma^2(F_o^2)/4F_o^2+(rF_o)^2$, where r was chosen by inspection to make the averages of $\sum w(F_o-F_c/K)^2$ approximately constant for groups of increasing F_o's (Cruickshank, 1965). Atomic scattering factors were interpolated from those listed in *International Tables for X-ray Crystallography* (1962). The anomalous scattering contributions of sulfur ($\Delta f'=0{\cdot}110$, $\Delta f''=0{\cdot}124$) and chlorine ($\Delta f'=0{\cdot}132$, $\Delta f''=0{\cdot}159$) (Cromer & Liberman, 1970) were included in the calculated structure factors. All computations were performed on an IBM 360/65 computer.

Refinement with individual isotropic temperature factors was followed by refinement with individual anisotropic temperature factors. Difference maps yielded positions for all 32 hydrogen atoms, which were assigned isotropic temperature factors and refined. Some of the hydrogen parameters would not refine nicely, so eventually the methyl hydrogen atoms of the anion were eliminated, and the parameters of the

Table 1. *Crystal data for the various forms of the dye*

	DYEA	I	II	III	IV	V
Anion	I^-	I^-	I^-	I^-	PTS$^-$	PTS$^-$
Solvent	CH_3CN	CH_3CN	CH_2Cl_2	C_2H_5OH	CH_3CN	CH_3CN
Space group	$P1$	$P1$*	$P2_1/a$	$P1$ or $P\bar{1}$	$Pna2_1$*	$P\bar{1}$
Unit cell: a(Å)	10·392 (3)	10·69	14·73	12·63	23·69	12·581 (8)
b	8·242 (2)	8·25	18·32	13·14	13·19	13·173 (8)
c	9·284 (2)	9·24	14·45	10·30	10·96	12·168 (9)
α(°)	93·92 (2)	95·3		103·4		106·06 (5)
β	107·81 (1)	112·8	118·3	94·6		112·96 (4)
γ	77·71 (2)	78·3		67·9		102·35 (4)
V(Å^3)	739·7 (4)	735	3432	1540	3425	1662·3 (22)
Z	1	1	4	2	4	2
D_{obs} (flotation, g cm^{-3})	1·51	†	1·56	1·50	1·41	1·40
D_{calc}	1·556	1·56	1·59	1·50	1·43	1·395
Solvent/dye	1	1	2	1	1	‡

* There is no evidence for disorder.

† The density was not determined. The presence of solvent is presumed because of similarity to DYEA.

‡ Crystal structure and independent analysis showed the presence of approximately 0·2 mole of H_2O per mole of dye.

benzo hydrogens of the anion and the C(21) methyl hydrogens were held constant. The difference maps also contained an extra peak, of height 1·0 e Å^{-3}, 0·8 Å from the center of symmetry at $\frac{1}{2}0\frac{1}{2}$. This was interpreted as a water molecule in a disordered and partially occupied site. The extra atom, labeled O(4), was assigned an occupancy factor of 0·2, which was not allowed to vary, and was refined with an isotropic temperature factor.

Refinement converged to $R_1=\sum|F_o-F_c/K|/\sum|F_o|=$ 0·053 and $R_2=[\sum w(F_o-F_c/K)^2/\sum F_o^2]^{1/2}=0{\cdot}065$. The coefficient r in the weighting scheme was 0·026, and the standard deviation of an observation of unit weight was 1·75. In the final least-squares cycle, 15 of the 489 variable parameters shifted more than 0·2σ; the maximum shift was 0·43σ. A final difference Fourier map contained residual electron densities between −0·55

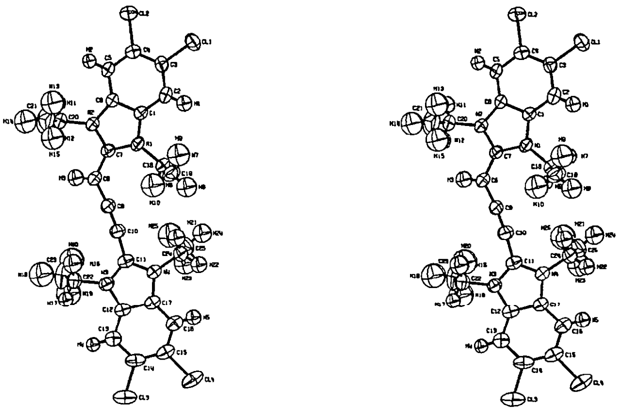


Fig. 1. Stereoscopic view of the cation with 50% probability thermal ellipsoids.

Table 2. *Final atomic parameters for the nonhydrogen atoms*

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters, in Å^2, are in the form $\exp[-0{\cdot}25(h^2a^{*2}B_{11}+\cdots 2klb^*c^*B_{23})]$. For O(4), B_{11} is the isotropic Debye–Waller factor. The site occupancy for O(4) is 0·2.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	0·2598 (1)	0·3022 (1)	1·0177 (1)	3·69 (5)	5·42 (6)	5·76 (6)	2·25 (4)	1·71 (4)	2·23 (5)
Cl(2)	0·0017 (1)	0·1389 (1)	0·9547 (1)	5·11 (5)	3·87 (4)	4·54 (5)	1·82 (4)	2·34 (4)	2·36 (4)
Cl(3)	−0·0935 (1)	1·2773 (1)	0·5319 (1)	9·39 (8)	4·08 (5)	5·04 (5)	3·29 (5)	3·69 (6)	2·70 (4)
Cl(4)	0·1894 (1)	1·3107 (1)	0·6523 (1)	8·27 (7)	3·32 (4)	7·00 (7)	1·09 (5)	5·27 (6)	2·06 (5)
S	0·4931 (1)	0·8743 (1)	0·1826 (2)	4·92 (6)	8·68 (8)	8·30 (8)	2·51 (6)	3·83 (6)	4·99 (7)
N(1)	0·0115 (2)	0·5357 (2)	0·8259 (3)	2·7 (1)	2·7 (1)	3·3 (1)	0·3 (1)	1·3 (1)	1·1 (1)
N(2)	−0·1690 (3)	0·4236 (2)	0·7851 (3)	2·8 (1)	3·1 (1)	3·9 (1)	0·7 (1)	1·5 (1)	1·8 (1)
N(3)	−0·1464 (3)	0·9121 (2)	0·6249 (3)	3·5 (1)	3·0 (1)	3·5 (1)	0·8 (1)	1·4 (1)	1·4 (1)
N(4)	0·0528 (3)	0·9367 (2)	0·7114 (3)	3·5 (1)	3·1 (1)	3·8 (1)	0·9 (1)	1·8 (1)	1·5 (1)
C(1)	0·0312 (3)	0·4478 (3)	0·8642 (3)	3·1 (2)	2·8 (2)	2·8 (2)	0·8 (1)	1·4 (1)	1·0 (1)
C(2)	0·1372 (3)	0·4254 (3)	0·9180 (4)	2·9 (2)	3·6 (2)	3·6 (2)	0·5 (1)	1·6 (1)	1·0 (1)
C(3)	0·1268 (3)	0·3300 (3)	0·9473 (3)	3·1 (2)	3·6 (2)	3·3 (2)	1·3 (1)	1·5 (1)	1·0 (1)
C(4)	0·0121 (3)	0·2591 (3)	0·9207 (3)	4·0 (2)	2·9 (2)	3·0 (2)	1·2 (1)	1·8 (1)	1·2 (1)
C(5)	−0·0950 (3)	0·2818 (3)	0·8666 (3)	2·7 (1)	3·1 (2)	3·1 (2)	0·4 (1)	1·3 (1)	1·0 (1)
C(6)	−0·0831 (3)	0·3775 (3)	0·8391 (3)	2·7 (1)	2·8 (1)	2·8 (2)	0·8 (1)	1·4 (1)	1·0 (1)
C(7)	−0·1120 (3)	0·5189 (3)	0·7750 (3)	3·1 (2)	2·7 (2)	3·2 (2)	0·8 (1)	1·4 (1)	1·1 (1)
C(8)	−0·1732 (3)	0·5835 (3)	0·7226 (4)	3·0 (2)	3·6 (2)	4·6 (2)	0·6 (1)	1·6 (1)	2·0 (2)
C(9)	−0·1237 (3)	0·6818 (3)	0·7119 (3)	3·3 (2)	3·5 (2)	3·4 (2)	1·1 (1)	1·4 (1)	1·5 (1)
C(10)	−0·0895 (4)	0·7686 (3)	0·6984 (4)	4·0 (2)	3·4 (2)	4·2 (2)	1·2 (1)	1·7 (2)	1·7 (1)
C(11)	−0·0612 (3)	0·8688 (3)	0·6800 (3)	4·2 (2)	2·9 (2)	3·1 (2)	0·9 (1)	1·8 (1)	1·2 (1)
C(12)	−0·0851 (3)	1·0115 (3)	0·6220 (3)	4·5 (2)	2·8 (2)	2·9 (2)	1·2 (1)	2·0 (1)	1·1 (1)
C(13)	−0·1302 (4)	1·0866 (3)	0·5747 (4)	4·6 (2)	3·3 (2)	3·3 (2)	1·5 (1)	2·0 (2)	1·1 (1)
C(14)	−0·0423 (4)	1·1797 (3)	0·5866 (4)	6·9 (2)	2·9 (2)	3·6 (2)	2·3 (2)	3·0 (2)	1·7 (1)
C(15)	0·0832 (4)	1·1937 (3)	0·6405 (4)	5·9 (2)	2·8 (2)	4·2 (2)	1·2 (2)	3·3 (2)	1·3 (1)
C(16)	0·1272 (4)	1·1189 (3)	0·6854 (4)	4·7 (2)	3·1 (2)	4·0 (2)	1·1 (1)	2·6 (2)	1·1 (1)
C(17)	0·0397 (3)	1·0267 (3)	0·6753 (3)	4·0 (2)	3·0 (2)	3·1 (2)	1·0 (1)	2·0 (1)	1·1 (1)
C(18)	0·1086 (3)	0·6247 (3)	0·8310 (4)	3·3 (2)	3·0 (2)	5·2 (2)	0·6 (1)	1·8 (2)	2·0 (2)
C(19)	0·1114 (4)	0·5943 (4)	0·7031 (5)	5·9 (2)	4·7 (2)	8·0 (3)	2·2 (2)	4·9 (2)	3·8 (2)
C(20)	−0·3006 (3)	0·3772 (3)	0·7467 (4)	2·8 (2)	4·7 (2)	6·5 (2)	0·9 (1)	1·8 (2)	3·2 (2)
C(21)	−0·3773 (5)	0·3031 (5)	0·6061 (6)	4·6 (3)	8·1 (4)	8·3 (4)	−0·6 (2)	0·9 (2)	2·1 (3)
C(22)	−0·2785 (4)	0·8636 (3)	0·5836 (4)	3·6 (2)	4·0 (2)	4·1 (2)	0·8 (2)	1·1 (2)	1·4 (2)
C(23)	−0·3056 (4)	0·9028 (5)	0·6949 (5)	4·5 (2)	9·1 (4)	7·0 (3)	0·6 (2)	3·1 (2)	0·7 (3)
C(24)	0·1700 (4)	0·9219 (3)	0·7814 (4)	3·8 (2)	4·0 (2)	5·6 (2)	1·8 (2)	2·5 (2)	2·2 (2)
C(25)	0·2231 (4)	0·9768 (4)	0·9262 (4)	4·7 (2)	6·7 (3)	4·8 (2)	2·4 (2)	1·8 (2)	2·7 (2)
C(26)	0·4707 (4)	0·7786 (4)	0·0339 (5)	2·7 (2)	6·5 (3)	8·3 (3)	1·1 (2)	2·3 (2)	4·7 (2)
C(27)	0·4565 (4)	0·6670 (4)	0·0130 (5)	3·7 (2)	7·8 (3)	7·6 (3)	1·8 (2)	2·6 (2)	4·4 (3)
C(28)	0·4378 (4)	0·5922 (4)	−0·1023 (6)	3·9 (2)	6·5 (3)	10·1 (4)	1·6 (2)	2·6 (2)	4·8 (3)
C(29)	0·4342 (4)	0·6245 (5)	−0·2047 (5)	4·0 (2)	8·3 (3)	7·8 (3)	0·9 (2)	2·3 (2)	3·8 (3)
C(30)	0·4490 (5)	0·7371 (5)	−0·1818 (5)	5·3 (3)	9·4 (4)	7·6 (3)	1·7 (2)	2·5 (2)	5·6 (3)
C(31)	0·4661 (4)	0·8131 (4)	−0·0651 (5)	4·4 (2)	7·4 (3)	7·8 (3)	1·2 (2)	2·5 (2)	4·8 (3)
C(32)	0·4190 (6)	0·5429 (6)	−0·3303 (6)	8·3 (4)	10·1 (4)	8·1 (4)	2·0 (3)	3·8 (3)	2·4 (3)
O(1)	0·3748 (4)	0·8424 (3)	0·1763 (5)	7·3 (2)	8·6 (2)	15·9 (4)	2·9 (2)	8·6 (2)	6·3 (2)
O(2)	0·5330 (4)	0·9864 (3)	0·1835 (5)	12·6 (3)	6·8 (2)	11·7 (3)	−0.9 (2)	7·4 (3)	3·5 (2)
O(3)	0·5829 (5)	0·8546 (6)	0·2777 (5)	14·1 (4)	23·6 (6)	8·5 (3)	14·0 (4)	5·6 (3)	7·5 (3)
O(4)	0·434 (2)	0·965 (2)	0·485 (2)	8·4 (5)					

and $+0·58$ e Å^{-3} with all detail beyond $\pm 0·25$ e Å^{-3} located near the anion methyl group, the sulfonate group, and the water of hydration. The detail was not sufficient to resolve reasonable positions for the hydrogen atoms of the methyl group, which is probably freely oscillating in a large hole in the packing (see Fig. 5). The water packs in a large gap between two sulfonate groups and the detail in this region probably arises from incomplete treatment of the disorder.

Table 3. *Atomic parameters for the hydrogen atoms*

r is the C–H bond length. Parameters without estimated standard deviations were held constant during the refinement.

	x	*y*	*z*	*B*	*r*
H(1)	0·212 (3)	0·472 (3)	0·936 (3)	3·9 (7)	0·91
H(2)	−0·169 (3)	0·235 (2)	0·850 (3)	3·0 (7)	0·91
H(3)	−0·251 (3)	0·557 (3)	0·693 (3)	4·1 (8)	0·85
H(4)	−0·214 (3)	1·077 (2)	0·537 (3)	2·9 (7)	0·93
H(5)	0·206 (3)	1·127 (3)	0·724 (3)	3·3 (7)	0·89
H(6)	0·090 (3)	0·689 (3)	0·850 (3)	3·4 (7)	0·92
H(7)	0·190 (3)	0·632 (3)	0·903 (3)	3·9 (8)	1·01
H(8)	0·170 (4)	0·652 (3)	0·710 (4)	5·9 (10)	0·90
H(9)	0·133 (4)	0·522 (4)	0·681 (4)	7·6 (12)	1·04
H(10)	0·028 (4)	0·590 (4)	0·629 (4)	8·2 (12)	1·06
H(11)	−0·303 (3)	0·338 (3)	0·802 (3)	4·3 (8)	0·96
H(12)	−0·333 (3)	0·440 (3)	0·765 (4)	5·7 (9)	1·01
H(13)	−0·354	0·240	0·584	8·0	0·95
H(14)	−0·457	0·290	0·591	8·0	0·91
H(15)	−0·358	0·346	0·558	8·0	0·97
H(16)	−0·289 (4)	0·779 (3)	0·544 (4)	5·8 (10)	1·04
H(17)	−0·321 (3)	0·889 (3)	0·518 (3)	3·4 (7)	0·96
H(18)	−0·393 (5)	0·875 (4)	0·667 (5)	9·8 (15)	0·96
H(19)	−0·277 (5)	0·987 (4)	0·728 (5)	10·0 (15)	1·00
H(20)	−0·257 (5)	0·898 (5)	0·777 (5)	10·8 (16)	0·98
H(21)	0·144 (3)	0·842 (3)	0·745 (3)	4·5 (8)	0·95
H(22)	0·230 (3)	0·950 (3)	0·749 (3)	4·1 (8)	1·02
H(23)	0·233 (5)	1·059 (4)	0·959 (5)	9·3 (14)	1·00
H(24)	0·296 (4)	0·957 (3)	0·964 (4)	6·1 (10)	0·98
H(25)	0·169 (5)	0·943 (4)	0·949 (5)	10·3 (15)	0·91
H(26)	0·465	0·642	0·085	8·0	0·99
H(27)	0·430	0·522	−0·121	8·0	0·87
H(28)	0·434	0·757	−0·246	8·0	0·86
H(29)	0·483	0·895	−0·050	8·0	1·00

Table 4. *Average estimated standard deviations for atomic positions and for interatomic distances and angles*

Atomic positions	
Cl	0·0013 Å
S	0·0017
N	0·0032
C (cation, except methyl)	0·0042
C (cation methyl, anion ring)	0·0058
C (anion methyl)	0·0077
O (anion)	0·0055
O (H_2O)	0·023
H (cation, except methyl)	0·037
H (methyl)	0·055

Distances		Angles	
C–Cl	0·005 Å	C–C–C (anion)	0·6°
C–N	0·005	C–C–S	0·5
S–C	0·006	C–C–H	2·7
S–O	0·006	N–C–H	2·2
C–C (anion)	0·009	H–C–H	4·1
C–C (cation methyl)	0·007	All others	0·4
C–C (rest)	0·006		
C–H	0·05		

The final atomic parameters with standard deviations estimated from the least-squares process are given in Tables 2 and 3. The final scale factor was 0·4610 (5). The average standard deviations for the positional parameters expressed in Å are shown in Table 4. Also in Table 4 are listed the estimated standard deviations for the interatomic distances and angles, calculated from the coordinate standard deviations and the cell parameter errors.*

Description and discussion of the structure

The cation geometry

A stereoscopic view (Johnson, 1971) of the cation is shown in Fig. 1. The cation is approximately planar; the atoms Cl(1)···Cl(4), N(1)···N(4), and C(1)···C(17) show maximum and root-mean-square deviations of 0·047 and 0·023 Å, respectively, from a least-squares plane. The deviations from planarity are systematic as the cation twists and bends at C(8) to divide itself into two reasonably good planes inclined 2·0° to each other. Atoms N(1), N(2), and C(1)···C(7) form one plane (maximum deviation 0·016 Å, r.m.s. deviation 0·008 Å) and atoms N(3), N(4) and C(9)···C(17) form the other (maximum deviation 0·009 Å, r.m.s. deviation 0·005 Å). Atom C(8) lies 0·046 and 0·020 Å from these planes.

Table 5. *Comparison of average bond distances* (Å) *and angles* (°)

	This work	DYEM[d]	DYEA[d]	Reported
C–Cl	1·734	1·737	1·735	1·737[a]
C–C (benzo)	1·389	1·386	1·390	1·394[b]
(ethyl)	1·499	1·495	1·511	1·526[c]
N–C (ethyl)	1·467	1·458	1·478	1·472[b]
(benzo)	1·390	1·388	1·378	1·383[b](pyrrole)
(chain)	1·363	1·371	1·372	

	This work	DYEM	DYEA
C–C–Cl (outer)	118·1	117·7	118·0
(inner)	120·3	120·3	120·0
C–C–C (benzo, small)	116·7	116·2	115·9
(benzo, large)	121·6	121·9	122·0
N–C–C (ethyl)	112·0	112·9	111·3
(benzo)	107·1	107·1	107·2
C–N–C [ring, N(1), N(2)]	109·4		
[ring, N(3), N(4)]	108·0	109·4	109·4
N–C–N [ring, C(7)]	107·4		
[ring, C(11)]	109·4	107·1	106·8

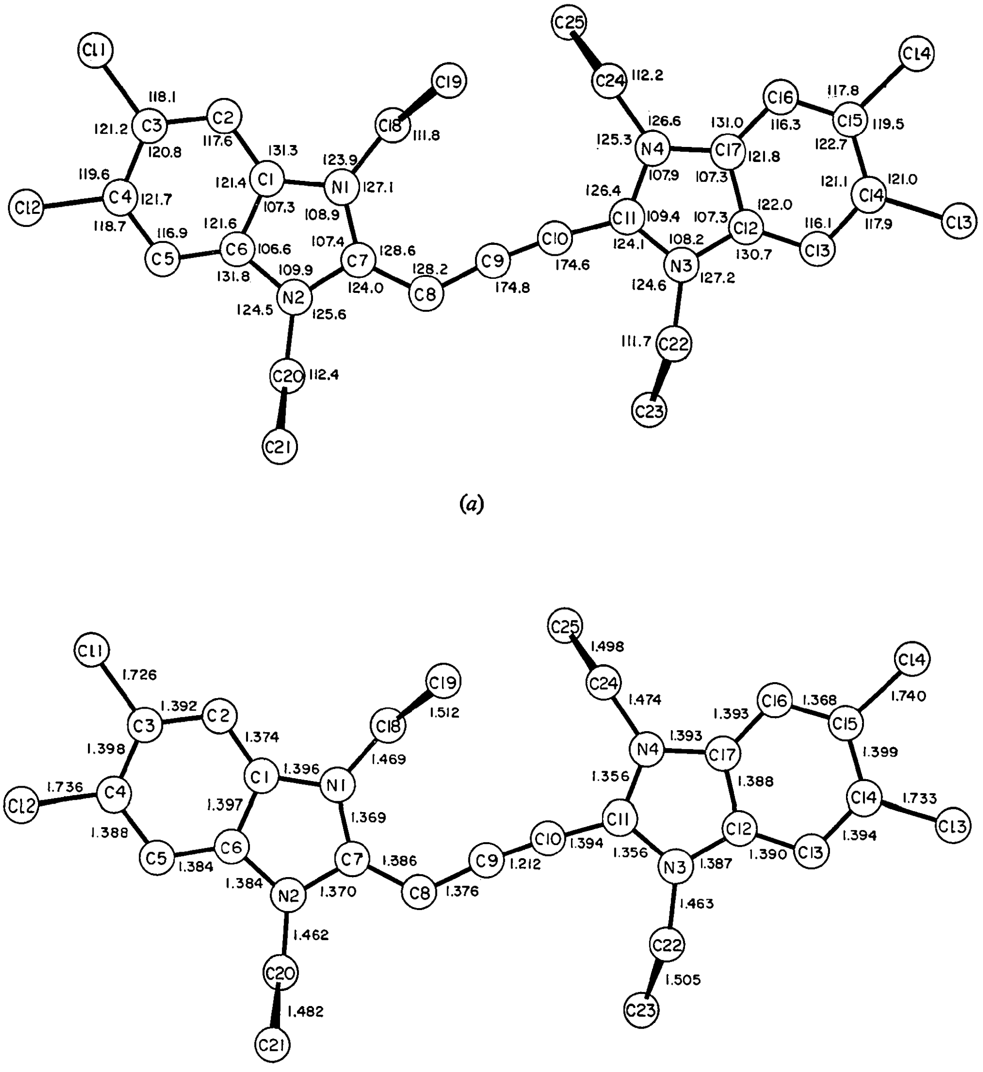
(*a*) Palenik, Donohue & Trueblood (1968). (*b*) Sutton (1965). (*c*) Lide (1962). (*d*) Smith & Luss (1972).

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30643 (23pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The bond lengths and angles, uncorrected for thermal motion, are shown in Fig. 2. With the expected exception of the C(7)···C(11) chain, they compare very well (see Table 5) with commonly accepted values and with those of the two solvates of 5,5′,6,6′-tetrachloro-1,1′,3,3′-tetraethylbenzimidazolocarbocyanine iodide (DYEM and DYEA), whose structures we have reported (Smith & Luss, 1972). Repulsion arising from the close contact of the N(1) and N(4) ethyl groups [C(19)···C(24) = 3·99 Å, C(18)···C(24) = 4·08 Å] causes the enlargement of the C–C–C angle at C(8) to 128·2°, bends the C(8)···C(11) chain from the expected linearity to angles of 174·8° at C(9) and 174·6° at C(10), and contributes to the departure from planarity.

The basic difference between the cations of the present dye and those of DYEM and DYEA lies in the C(7)···C(11) chain. In DYEM and DYEA this chain, along with atoms N(1)···N(4), can be represented by four equally probable canonical structures, so it is not surprising that the C–C bonds average a fully aromatic 1·395 Å. In the present dye there are also four possible canonical structures but they are not necessarily equally probable since two involve a vinyl acetylene linkage and two a butatriene linkage. These canonical structures are represented in Fig. 3(*a*) and (*d*) with appropriate bond lengths obtained from a tabulation (Dewar & Schmeising, 1960) of characteristic distances for classical (one canonical structure) molecules. Of course, the actual molecular state is some mixture of (*a*) and (*d*); in Fig. 3(*c*) is shown a representation of the fully conjugated or aromatic structure for contributions of equal weight from (*a*) and (*d*). Aromatic distances for bonds to *sp*-hybridized atoms are unknown so we postulated the values by adding 40% of the difference between bonds in (*a*) and (*d*) to the bond of higher order. The value 40% was obtained from the



(*a*)

(*b*)

Fig. 2. Bond lengths and angles with atom numbering for the cation.

known lengths of C(sp^2)–C(sp^2) bonds shown for the C(7)–C(8) bond [(1·394–1·338)/(1·479–1·338) = 0·40]. This assumption is probably reasonable for the single–double bond resonance of C(8)–C(9) and C(10)–C(11), but is of questionable validity for C(9)–C(10), where the resonance is between double and triple bonds. The bond lengths determined for the present structure are shown in Fig. 3(*b*); for all four C–C bonds they lie between the values for the vinyl acetylene (*a*) and the aromatic (*c*) forms. In addition, the C(11)–N bonds are 0·014 Å shorter than the C(7)–N bonds. The differences between (*b*) and (*c*) and between C–N bonds are only a few standard deviations but they are systematic, which supports the conclusion that the vinyl acetylene form makes a somewhat greater contribution to the cation structure than does the butatriene form. This dictated the choice of name for the cation given in the title.

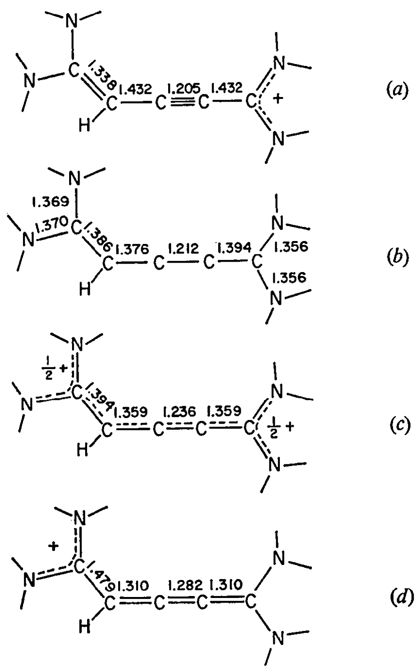


Fig. 3. Bonding representations for the chromophore. (*a*) and (*d*) Table 6, Dewar & Schmeising (1960). (*b*) This work. (*c*) Postulated for aromatic behavior.

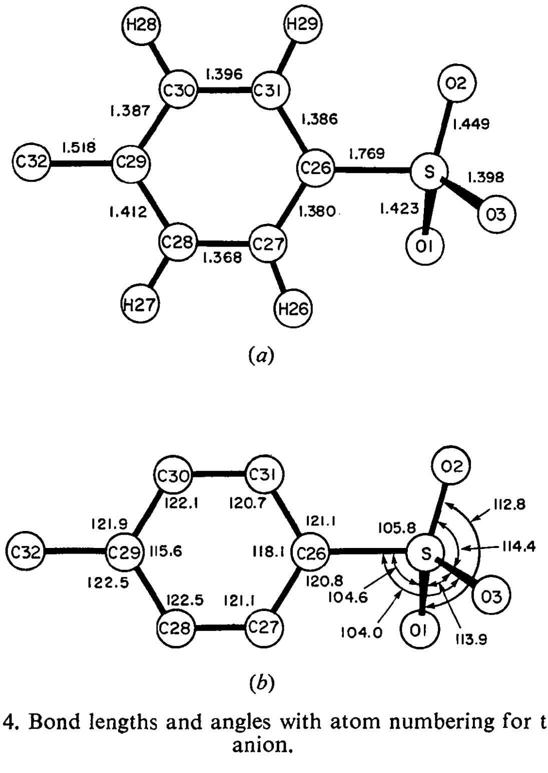


Fig. 4. Bond lengths and angles with atom numbering for the anion.

A similar resonance situation occurs in polymeric 2,4-hexadiynylenebis(phenylurethane) (Hädicke, Mez, Krauch, Wegner & Kaiser, 1971). Their bond distancces fall between the values in (*a*) and (*b*) and indicate an even greater dominance of the resonance by the vinyl acetylene form.

The anion geometry

Bond lengths and angles for the toluene-*p*-sulfonate ion are shown in Fig. 4. The C–C aromatic distances average 1·387 Å and the S–O distances average 1·423 Å. The angles O–S–O and C–S–O average 113·7° and 104·8°, respectively. These values agree well with those tabulated for toluene-*p*-sulfonic acid monohydrate and related compounds (Arora & Sundaralingam, 1971) except that the S–O distance is somewhat short, perhaps because of thermal motion and the disorder of the water molecule. The ion is reasonably planar; atoms C(26)···C(32) and S show maximum and r.m.s. deviations of 0·026 and 0·013 Å, respectively, from a least-squares plane.

Molecular packing

The molecular packing is shown stereoscopically (Johnson, 1971) in Fig. 5. The cations pack plane to plane and end to end (along [03$\bar{1}$]) on edge in layers parallel to (100). The plane separations for the two greater overlaps, both at inversion centers, average 3·41 Å, and for the lesser, translational overlap is 3·47 Å. The mean cation planes make angles of 81·6° with (100) and 6·8° with ($\bar{1}$13), the plane corresponding to the most intense reflection. The (100) projections of a single sheet of the present compound and of DYEM are very similar. The principal differences are in the tilt of the cation planes to (100) (87·6° in DYEM) and in the end-to-end packing. Although the over-all lengths of the cations are very similar [Cl(1)···Cl(4) = 17·39 Å in DYEM, Cl(2)···Cl(3) = 17·27 Å here], each cation in the present structure occupies 22·2 Å along its row compared to 20·8 Å in DYEM. This results in an angle of stacking of 20·0° compared to the 24·2° in DYEM.

The anions and water molecules lie in layers between the cation sheets. The anion planes are inclined 8·1° to

(100) and 87·3° to the mean cation planes. Within the layers, the anions lie in ribbons along [010]. Between these ribbons, the disordered water molecules occur in holes between opposing sulfonate groups. With six sulfonate oxygen atoms available, one might expect hydrogen bonding to occur and to be the cause of the disorder. However, the minimum intermolecular O(4)···O distance is 3·31 Å, much too long for hydrogen bonding. It is possible that O(4) represents an average of several unresolved positions that are close enough to the sulfonate groups for hydrogen bonding. The source of the partial occupancy for water is also not clear, but it is presumably caused by a deficiency of water in the crystallization solvent.

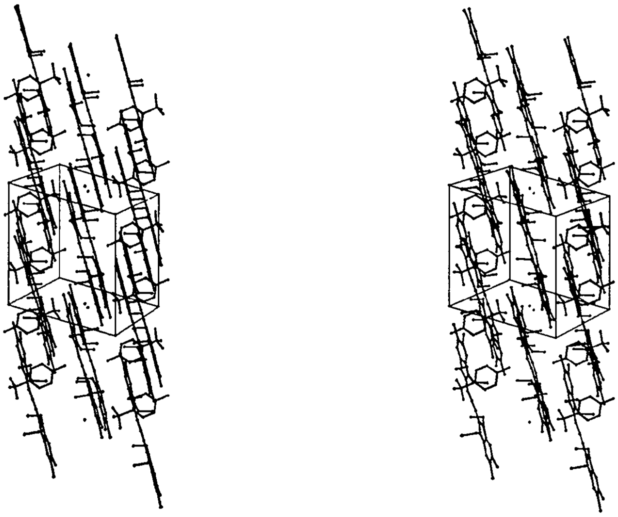


Fig. 5. Stereoscopic view of the molecular packing. The *a* axis points into the picture, *b* is vertical, top to bottom, and *c* runs from right to left.

We are indebted to Mr John Mee for the dye samples and to Mrs Denise Secord for the Karl Fischer coulometric titration.

References

AHMED, F. R. (1970). Private communication.

ARORA, S. K. & SUNDARALINGAM, M. (1971). *Acta Cryst.* B**27**, 1293–1298.

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

CRUICKSHANK, D. W. J. (1965). In *Computing Methods in Crystallography*, edited by J. S. ROLLETT, chap. 14. Oxford: Pergamon Press.

DEWAR, M. J. S. & SCHMEISING, H. N. (1960). *Tetrahedron*, **11**, 96–120.

HÄDICKE, E., MEZ, E. C., KRAUCH, C. H., WEGNER, G. & KAISER, J. (1971). *Angew. Chem. Int. Ed.* **10**, 266–267.

HAUPTMAN, H. & KARLE, J. (1953). *Solution of the Phase Problem. I. The Centrosymmetric Crystal.* Monograph No. 3, American Crystallographic Association.

HODGSON, L. I. & ROLLETT, J. S. (1963). *Acta Cryst.* **16**, 328–335.

IBERS, J. A. (1966). Program *PICK*2. Private communication.

International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.

JOHNSON, C. K. (1971). *ORTEP*-II. Oak Ridge National Laboratory Report ORNL-3794 (2nd rev.).

LIDE, D. R. (1962). *Tetrahedron*, **17**, 125–134.

LONG, R. E. (1965). *A Program for Phase Determination by Reiterative Application of Sayre's Equation.* Doctoral Dissertation (Part III). Univ. of California, Los Angeles.

MEE, J. D. (1974). *J. Amer. Chem. Soc.* **96**, 4712–4714.

MEYER, A. S. JR & BOYD, C. M. (1959). *Anal. Chem.* **31**, 215–219.

PALENIK, G. J., DONOHUE, J. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 1139–1146.

SAYRE, D. (1952). *Acta Cryst.* **5**, 60–65.

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

SUTTON, L. E. (1965). *Interatomic Distances and Configuration in Molecules and Ions, Supplement.* Spec. Publ. No. 18. London: The Chemical Society.

TSAI, C. (1968). Private communication.