Lin, G. H-Y., Sundaralingam, M. & Arora, S. K. (1970). *J. Amer. Chem. Soc.* **93**, 1035.

Lipsett, M. N. (1965). *J. Biol. Chem.* **240**, 3975.

Lipsett, M. N. & Doctor, B. P. (1961). *J. Biol. Chem.* **242**, 4072.

McMullan, R. K. & Sundaralingam, M. (1971) *J. Amer. Chem. Soc.* In the press.

Saenger, W. & Scheit, K. H. (1969). *Acta Cryst.* A**25**, 178.

Shefter, E. (1968). *J. Pharm. Sci.* **57**, 1157.

Shefter, E., Barlow, M., Sparks, R. & Trueblood, K. N. (1969). *Acta Cryst.* B**25**, 895.

Shefter, E. & Kalman, T. I. (1968). *Biochem. Biophys. Res. Comm.* **32**, 878.

Shefter, E. & Mautner, H. G. (1967). *J. Amer. Chem. Soc.* **89**, 1249.

Shefter, E. & Trueblood, K. N. (1965). *Acta Cryst.* **18**, 1067.

Spencer, M. (1959). *Acta Cryst.* **12**, 59.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Sundaralingam, M. (1965). *J. Amer. Chem. Soc.* **87**, 599.

Sundaralingam, M. (1968). *Biopolymers*, **6**, 189.

Sundaralingam, M. (1969). *Biopolymers*, **7**, 821.

Sundaralingam, M. & Jensen, L. H. (1965a). *J. Mol. Biol.* **13**, 914.

Sundaralingam, M. & Jensen, L. H. (1965b). *J. Mol. Biol.* **13**, 930.

Sundaralingam, M., Rao, S. T. & Bugg, C. E. (1969). Abstract, Amer. Cryst. Assoc. Meeting, March 1969. Seattle, Washington.

Ueda, T., Iida, Y., Ikeda, K. & Mizuno, Y. (1966). *Chem. Pharm. Bull. Japan*, **14**, 666.

Young, D. W., Tollin, P. & Wilson, H. R. (1969). *Acta Cryst.* B**25**, 1423.

The Crystal Structure of the 1:1 Solvate of 2-Propanol and 1,1',3,3'-Tetraethylimidazo-[4,5-*b*]quinoxalinocyanine Iodide

By Douglas L. Smith and Eileen K. Barrett

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

The crystal structure of the title compound, $C_{27}H_{29}N_8I.C_3H_8O$, has been determined from single-crystal X-ray intensity data collected with an automated diffractometer. The crystals are orthorhombic, *Pcab*, with $a = 18.337$ (12), $b = 21.855$ (14), $c = 15.485$ (11) Å, and $D_x = 1.397$ g.cm^{-3} for $Z = 8$. The structure was solved by the heavy-atom technique and refined by least squares to $R = 0.082$. Because of steric interference between ethyl substituents, the cation is not planar but can be divided into a central and two end planes. The dihedral angles are 55.4° between the end planes and 35.3° and 21.0° between the central and end planes. Several angular distortions of about 5° help to relieve the strain but the crowded methylene carbon atoms are still only 3.28 Å apart. Bond lengths show that despite the distortions the cation is highly conjugated. The cations are packed end to end in chains with their end planes almost parallel and 3.4 Å apart.

Introduction

The influence of molecular overcrowding on the optical properties of cyanine dyes was recognized almost thirty years ago (Sheppard, Lambert & Walker, 1941) and has been investigated extensively since (Brooker, White, Heseltine, Keyes, Dent & Van Lare, 1953; Brooker, 1966; Dewar, 1958). In spite of this interest, few crystal structures have been reported. A partially refined structure of an unsymmetrical 'simple' cyanine with an overcrowded cation has been reported (Effinger, Germain, Meunier, Vanderauwera & Van Meerssche, 1960). The structures of two phospha-cyanines analogous to the simple cyanines have been determined (Allmann, 1966; Kawada & Allmann, 1968). The other structures that have been published are four similar unsymmetric merocyanines (Germain, Piret, Van Meerssche & DeKerf, 1961, 1962; Germain, Patternotte, Piret & Van Meerssche, 1964; Bois

D'Enghien-Peteau, Meunier-Piret & Van Meerssche, 1968) and a symmetric carbocyanine and two of its solvates (Wheatley, 1959*a,b*; Vorontsova, Zvonkova & Zhdanov, 1963). To learn about the conformation of overcrowded cyanines we have determined the structure of the dye 1,1',3,3'-tetraethylimidazo[4,5-*b*]-quinoxalinocyanine iodide,
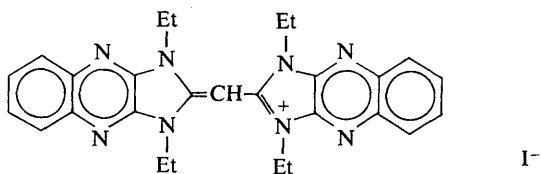
Crystal data

$(C_{27}H_{29}N_8)^+I^-.C_3H_8O$. M.W. 652·59.

1,1',3,3'-Tetraethylimidazo[4,5-*b*]quinoxalinocyanine iodide–2-propanol.

Orange, long prismatic (b) crystals.

Orthorhombic (Cu $K\alpha_1 = 1\cdot5405$ Å)

$a = 18\cdot337 \pm 0\cdot012$ Å

$b = 21\cdot855 \pm 0\cdot014$

$c = 15\cdot485 \pm 0\cdot011$.

Volume of unit cell, 6206 ± 7 Å³.

Density, calculated ($Z = 8$), $1\cdot397$ g.cm⁻³

       measured (flotation), $1\cdot44$ g.cm⁻³.

Linear absorption coefficient, $\mu = 86$ cm⁻¹ (Cu $K\alpha$).

Total number of electrons per unit cell, $F(000) = 2672$.

Absent spectra: $0kl$ for l odd, $h0l$ for h odd, $hk0$ for k odd.

Space group, $Pcab$ (D_{2h}^{15}).

General positions: $\pm(x,y,z; \frac{1}{2}+x, \frac{1}{2}-y, z; x, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}+x, -y, \frac{1}{2}-z)$.

Experimental

A sample of the dye crystallized from 2-propanol was supplied by Dr W. S. Gaugh of the Kodak Research Laboratories. Single crystals suitable for X-ray examination were difficult to produce but eventually a few were obtained by slow evaporation of a 2-propanol solution. Space group extinctions and preliminary lattice dimensions were obtained from precession photographs.

A small needle crystal, $0\cdot05 \times 0\cdot11 \times 0\cdot51$ mm, attached to a thin glass rod with Ambroid® cement, was chosen for intensity data collection on a Picker automatic four-circle goniostat. Narrow source, open-counter ω scans (Furnas, 1957) through several reflections showed the mosaicity to range from $0\cdot15$ to $0\cdot25°$ for various directions in the crystal. Eighteen reflections at moderately high Bragg angles (Cu $K\alpha_1$ radiation) were accurately centered through very narrow vertical and horizontal slits at a take-off angle of $0\cdot5°$. These observations were used as input to the computer program PICK2 (Ibers & Hamilton, 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 Ni-filtered Cu radiation at a take-off angle of $2\cdot0°$. A scintillation detector was used and the pulse-height analyzer was set for an approximately 90 per cent window. All 3202 unique reflections for $2\theta < 100°$ were measured by the θ–2θ scan technique (Furnas, 1957) at a 2θ scan rate of $1\cdot0°$/min. The scan range varied from $1\cdot2°$ at low 2θ to $2\cdot0°$ at high 2θ. Stationary-crystal stationary-counter background counts were taken for 40 sec at each end of the scan. For count rates above 13,000 c.p.s. attenuators made from doublesided cellophane tape ($\sim 35\%$ attenuation) were automatically inserted in the diffracted beam by the Picker system. To check electronic and crystal stability during the period of data collection, the intensity of the 273 reflection was measured every 50th reflection. A small ($\sim 1\cdot5\%$) systematic decrease was observed in the intensity of this standard reflection over the period of data collection. It was

noticed, for some of the more intense reflections, that the scan had not completely traversed the Bragg peak, which resulted in high background counts on one side of the scan. This effect was caused by a shift of the crystal position on the goniometer head and by an increase in the mosaic spread to about $0\cdot5°$. The error in these intensities was not considered serious and was partially compensated for by reducing the higher background to $1\cdot2$ times the lower one.

The reduction of the intensity data to structure amplitudes was accomplished with the computer program DACOR (Smith, 1966). The background for a reflection was approximated by a straight line between the two 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 but absorption was neglected. We estimate the maximum error in $|F_o|$ caused by the absorption to be $\pm 43\%$, but the error is much smaller for most reflections. Absorption errors are known to affect thermal parameters much more than positional parameters (Srivastava & Lingafelter, 1966). Standard deviations $\sigma(I)$ were based on counting statistics and the estimated error of scaling and were corrected to $\sigma(F)$. Of the 3202 measured reflections, 945 were less than $2\sigma(I)$ and were considered unobserved. The intensities of these unobserved reflections were then set equal to $2\sigma(I)$ and corrected to structure amplitudes, F_{lim}.

Determination and refinement of the structure

The iodide ion was easily located from an unsharpened three-dimensional Patterson map. The z parameter of this ion was zero causing the arrangement of iodide ions to be A centered. Consequently a three-dimensional electron density map, phased by the iodide ion, contained two images of the molecule. The known ring structure enabled us to construct about half of the molecule with reasonable certainty. This was sufficient to remove the pseudo-symmetry and a second Fourier synthesis, phased on 18 atoms, revealed most of the remaining atoms. A third Fourier synthesis, phased on 33 atoms, yielded the last three non-hydrogen atoms of the dye plus five relatively weak peaks which suggested a disordered molecule of the 2-propanol solvent. Subsequent difference Fourier syntheses and block-diagonal least-squares refinement with isotropic temperature factors (except for I) led to a satisfactory model for the solvent and explained difficulties encountered in the refinement of other atoms. The 2-propanol molecule is disordered with two unequally probable orientations in which, to a first approximation, oxygen and tertiary hydrogen atoms interchange but the central and methyl carbon atoms retain their positions. The two positions for oxygen straddle the iodide ion along a at relatively close distances ($\sim 3\cdot6$ Å), which accounts for the large B_{11} for I. Also, O(2) is only $3\cdot1$ Å from C(3) and C(10) which could cause less probable

occupancy. The other oxygen position, O(1), is about 3·3 Å from C(27) which probably causes this ethyl group to have slightly different orientations, dependent upon the location of the oxygen atom, and explains the eventual refinement of C(26) and C(27) to unreasonable positions. These perturbations of the structure should affect other parts of the molecule to a lesser degree.

The data were of too low resolution and accuracy to refine an elaborate partial atom model so only the oxygen was given two positions. Refinement was resumed with weights defined as $w=[\sigma^2(F_o)+(0.04F_o)^2]^{-1}$ and unobserved reflections included if $|F_c| > F_{lim}$. The five solvate atoms and C(26) and C(27) were assigned anisotropic temperature factors and the scale factor and the parameters for these seven atoms, including the O(1) occupancy factor [the O(2) occupancy being constrained as $1.0-O(1)$], were refined by full-matrix least squares. The O(1) occupancy converged to 0·63. All atoms were then assigned aniso-

tropic temperature factors and refined by several cycles of block-diagonal least squares. One additional cycle, in which only the scale factor and the O(1) occupancy factor were varied, concluded the refinement. The final agreement indices, for the 2257 observed reflections plus the 112 unobserved reflections with $|F_c| > F_{lim}$, were $R=\sum||F_o|-|F_c||/\sum|F_o|=0.082$ and $R_2=[\sum w(F_o-|F_c|)^2/\sum wF_o^2]^{1/2}=0.11$. The standard deviation of an observation of unit weight was 2·00. The averages of $\sum w(F_o-|F_c|)^2$ for eight groups of increasing F_o's were reasonably constant, ranging from 3·13 to 3·90. Of the 112 unobserved reflections with $|F_c| > F_{lim}$, none had $|F_c| > 1.7F_{lim}$. For the last cycle of atomic parameter refinement four of the 123 positional parameter shifts were greater than 0.2σ with a maximum shift of 0.28σ. Of the 246 thermal parameters, 47 shifted more than 0.2σ and the maximum shift was 0.62σ. A final difference Fourier synthesis contained values between -1.06 and $+0.93$ e.Å^{-3} with considerable detail near the iodide ion. If one ex-

Table 1. *Final atomic parameters with their estimated standard deviations (in parentheses).*
Thermal parameters are defined by the expression:

$$T_i = \exp\left[-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)\right]$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
I	0·17134 (6)	0·19369 (4)	0·00378 (5)	11·41 (7)	5·98 (4)	5·23 (4)	−0·38 (4)	−0·72 (4)	0·57 (3)
N(1)	0·3272 (5)	0·2988 (4)	0·2135 (6)	7·3 (5)	4·5 (4)	4·6 (4)	1·0 (4)	−0·8 (4)	−0·2 (4)
N(2)	0·2824 (5)	0·3976 (4)	0·2662 (5)	6·2 (4)	4·7 (4)	4·0 (4)	0·5 (4)	−0·0 (4)	0·2 (3)
N(3)	0·3416 (5)	0·4382 (4)	0·1020 (5)	6·6 (5)	4·3 (4)	4·1 (4)	0·8 (4)	−0·3 (4)	0·2 (3)
N(4)	0·3700 (5)	0·3322 (4)	0·0883 (5)	7·2 (5)	4·7 (4)	4·4 (4)	1·1 (4)	−0·3 (4)	0·2 (3)
N(5)	0·4340 (5)	0·1712 (4)	0·2375 (6)	7·5 (5)	4·0 (4)	6·4 (5)	0·3 (4)	−2·6 (4)	−1·0 (4)
N(6)	0·4911 (5)	0·0940 (4)	0·3236 (6)	6·8 (5)	3·9 (4)	6·9 (5)	1·4 (4)	−1·7 (4)	−0·9 (4)
N(7)	0·4406 (4)	0·0172 (4)	0·1826 (5)	5·0 (4)	4·4 (4)	5·0 (4)	0·5 (4)	−0·3 (4)	0·0 (4)
N(8)	0·3963 (4)	0·1145 (4)	0·1303 (5)	5·4 (4)	4·8 (4)	4·4 (4)	−0·1 (4)	−0·1 (4)	−0·4 (3)
C(1)	0·3763 (6)	0·2226 (4)	0·1084 (7)	6·7 (6)	3·2 (4)	6·2 (6)	0·5 (5)	−0·8 (5)	−0·1 (4)
C(2)	0·3602 (7)	0·2808 (5)	0·1394 (7)	7·4 (6)	4·8 (5)	4·4 (5)	0·1 (5)	−0·8 (5)	1·1 (4)
C(3)	0·3145 (6)	0·3623 (4)	0·2088 (7)	6·4 (6)	3·9 (4)	4·4 (5)	1·1 (4)	−0·3 (5)	0·1 (4)
C(4)	0·2790 (6)	0·4566 (5)	0·2393 (6)	6·2 (6)	3·8 (5)	4·5 (5)	0·4 (4)	−1·0 (5)	0·2 (4)
C(5)	0·2421 (7)	0·4982 (5)	0·2937 (8)	7·1 (6)	5·6 (6)	6·9 (6)	1·6 (5)	−0·6 (6)	−1·4 (5)
C(6)	0·2363 (7)	0·5604 (5)	0·2697 (8)	6·9 (7)	4·9 (6)	8·7 (7)	0·5 (5)	−1·7 (6)	−1·2 (5)
C(7)	0·2661 (7)	0·5806 (5)	0·1917 (8)	7·0 (7)	5·3 (5)	6·4 (6)	0·7 (5)	−0·4 (6)	−0·1 (5)
C(8)	0·3016 (7)	0·5404 (5)	0·1364 (8)	6·4 (6)	4·3 (5)	8·0 (7)	0·0 (5)	−0·5 (6)	−0·2 (5)
C(9)	0·3074 (6)	0·4768 (5)	0·1582 (7)	6·1 (6)	4·6 (5)	5·5 (6)	0·2 (5)	−1·0 (5)	0·1 (5)
C(10)	0·3420 (6)	0·3830 (4)	0·1314 (7)	6·0 (6)	4·2 (5)	4·4 (5)	0·6 (5)	−0·4 (5)	−0·2 (4)
C(11)	0·2904 (7)	0·2606 (5)	0·2795 (7)	8·3 (6)	4·6 (5)	4·6 (5)	−0·1 (5)	1·4 (5)	1·9 (4)
C(12)	0·2133 (7)	0·2453 (7)	0·2486 (8)	7·4 (6)	8·3 (7)	7·2 (7)	−2·2 (6)	−0·0 (7)	0·6 (6)
C(13)	0·4087 (7)	0·3327 (7)	0·0035 (7)	7·2 (7)	7·9 (7)	4·6 (6)	0·6 (6)	1·0 (5)	0·1 (5)
C(14)	0·3511 (9)	0·3358 (7)	−0·0706 (9)	10·5 (9)	12·9 (10)	4·7 (6)	−2·4 (8)	−1·1 (7)	−0·0 (7)
C(15)	0·4002 (6)	0·1732 (5)	0·1582 (7)	5·8 (6)	4·5 (5)	4·7 (5)	0·7 (4)	−0·9 (5)	−1·8 (4)
C(16)	0·4544 (6)	0·1125 (4)	0·2566 (7)	5·7 (6)	3·6 (4)	6·2 (5)	1·5 (4)	−1·1 (5)	−0·3 (4)
C(17)	0·5030 (6)	0·0309 (5)	0·3210 (7)	5·3 (6)	4·5 (5)	5·7 (6)	0·9 (5)	0·5 (5)	−0·4 (5)
C(18)	0·5418 (7)	0·0047 (5)	0·3904 (8)	6·7 (6)	5·6 (6)	7·2 (7)	1·5 (5)	−0·8 (6)	0·6 (5)
C(19)	0·5562 (7)	−0·0575 (5)	0·3906 (8)	7·4 (7)	6·2 (6)	6·8 (6)	0·8 (6)	0·9 (6)	0·9 (6)
C(20)	0·5326 (7)	−0·0941 (6)	0·3206 (8)	6·7 (6)	6·5 (6)	7·7 (7)	−1·1 (6)	0·5 (6)	1·4 (6)
C(21)	0·4932 (7)	−0·0707 (4)	0·2535 (8)	7·0 (6)	3·3 (4)	7·5 (7)	0·9 (5)	0·4 (6)	0·6 (5)
C(22)	0·4780 (5)	−0·0067 (4)	0·2525 (8)	4·9 (6)	4·9 (5)	5·2 (5)	−0·3 (5)	−0·1 (5)	−0·1 (4)
C(23)	0·4287 (6)	0·0754 (4)	0·1889 (6)	6·4 (6)	3·3 (4)	4·5 (5)	0·2 (4)	−0·6 (5)	−0·5 (4)
C(24)	0·3562 (7)	0·0932 (5)	0·0500 (7)	6·8 (6)	6·1 (6)	5·1 (5)	−1·0 (5)	−1·1 (5)	−0·8 (5)
C(25)	0·4081 (8)	0·0960 (7)	−0·0292 (8)	9·8 (9)	9·3 (8)	5·5 (6)	−0·5 (8)	1·5 (7)	−1·4 (6)
C(26)	0·4644 (9)	0·2284 (7)	0·2989 (12)	8·5 (9)	12·1 (10)	15·7 (12)	1·2 (8)	−0·3 (10)	6·3 (9)
C(27)	0·5253 (10)	0·2398 (7)	0·2528 (10)	13·3 (12)	9·3 (10)	10·4 (10)	0·9 (9)	2·1 (10)	0·6 (9)
C(28)	0·1176 (10)	0·4262 (7)	0·1204 (12)	11·9 (12)	10·1 (10)	13·5 (12)	0·8 (9)	−0·2 (11)	−3·8 (9)
C(29)	0·1309 (10)	0·3768 (7)	0·0611 (12)	13·5 (12)	9·0 (9)	11·3 (11)	1·0 (9)	1·1 (11)	1·2 (9)
C(30)	0·1402 (12)	0·3932 (9)	−0·0307 (11)	18·4 (13)	15·8 (13)	7·9 (8)	8·1 (11)	4·9 (9)	3·6 (9)
O(1)	0·0748 (11)	0·3318 (8)	0·0749 (13)	14·1 (12)	10·8 (11)	15·3 (13)	−0·6 (10)	6·6 (11)	1·6 (11)
O(2)	0·1889 (14)	0·3391 (9)	0·0853 (16)	11·5 (15)	4·7 (10)	10·4 (14)	1·8 (10)	−4·9 (12)	2·4 (10)

Table 2. *Observed and calculated structure amplitudes*

The column headings are $h, k, |F_o|/K$, and $|F_c|$. An asterisk designates 'less than.'

Table 2 (cont.)

cludes that region, the range was from −0·39 to +0·68 e.Å^{-3} and verified the structure. Many of the hydrogen atoms could be recognized on this map but we did not try to include them in the calculations because of the inaccuracies in the model caused by the disorder.

The final positional and thermal parameters, with standard deviations estimated from the least-squares process, are given in Table 1. The average standard deviations of the positional parameters expressed in Å are 0·0009 for I, 0·0084 for N, 0·011 for ring carbon atoms, 0·014 for the ethyl carbon atoms, and 0·019 for solvate atoms. The standard deviations are certainly underestimated more than the usual amount owing to the complication caused by the disorder. Two other parameters that were refined are the scale factor (applied to F_c), $K = 0·452 \pm 0·001$, and the O(1) occupancy factor $0·632 \pm 0·016$. The final values of the observed and calculated structure amplitudes are compared in Table 2.

The Fourier and block-diagonal least-squares computer programs were local modifications of programs obtained from Trotter (1965). The least-squares program was block-diagonal in coordinates and diagonal in thermal parameters. The full-matrix least-squares program was a modification of the Busing, Martin & Levy (1962) program, ORFLS. The atomic scattering factors were obtained from Cromer & Waber (1965) for the iodide ion and from International Tables for X-ray Crystallography (1962). All computations were performed on an IBM 360 computer.

Description of the structure

Figs. 1 and 2 show the atomic labeling and the intramolecular distances and angles, uncorrected for thermal motion. The values shown in Fig. 1(c) are averages of similarly situated bonds or angles, but exclude the unreliable C(26)–C(27) ethyl group. The cell parameter errors and the coordinate standard deviations obtained from the least-squares refinement were used to calculate estimated standard deviations for the distances and angles. These e.s.d.'s average 0·014 Å for C–N, 0·017 Å for C–C, and 0·026 Å for the C(26)–C(27) ethyl group and the solvate. The e.s.d.'s for the angles are 0·9° for C–N–C, 1·0° for N–C–N and C–C–N, 1·1° for C–C–C, and 1·6° for the solvate.

The cationic conformation is shown stereoscopically (Johnson, 1965) in Fig. 3. Steric interference between two of the ethyl groups results in a significant departure from planarity. With the exception of the four ethyl groups the cation can be divided into three planar parts (planes A, B and C, Table 3). Plane A includes atoms N(1)···N(4) and C(3)···C(10) of the upper fused ring system of Fig. 3 and plane B includes atoms N(5)···N(8) and C(16)···C(23) of the lower rings.

The third plane, plane C, is formed by the central atoms C(1), C(2) and C(15). The dihedral angles between the planes are 55·4° for A and B, 35·3° for A and C, 21·0° for B and C. These angles are a composite of bends and twists; plane A is bent 7·8° from and rotated 34·6° about the C(1)–C(2) bond and plane B is bent 6·9° from and rotated 19·9° about the C(1)–C(15) bond. The bends cause C(1) to lie 0·25 Å away from

both planes A and B; C(2) and C(15) deviate from planes A and B, respectively, by smaller amounts. In addition, the angles at N(1), C(2), C(1), C(15) and N(5) are distorted by approximately 5° to further separate the crowded ethyl groups. Despite these bends and twists, the crowded methylene carbon atoms, C(11) and C(26), are only 3·28 Å apart, much closer than the 4·0 Å expected from van der Waals radii (Pauling,
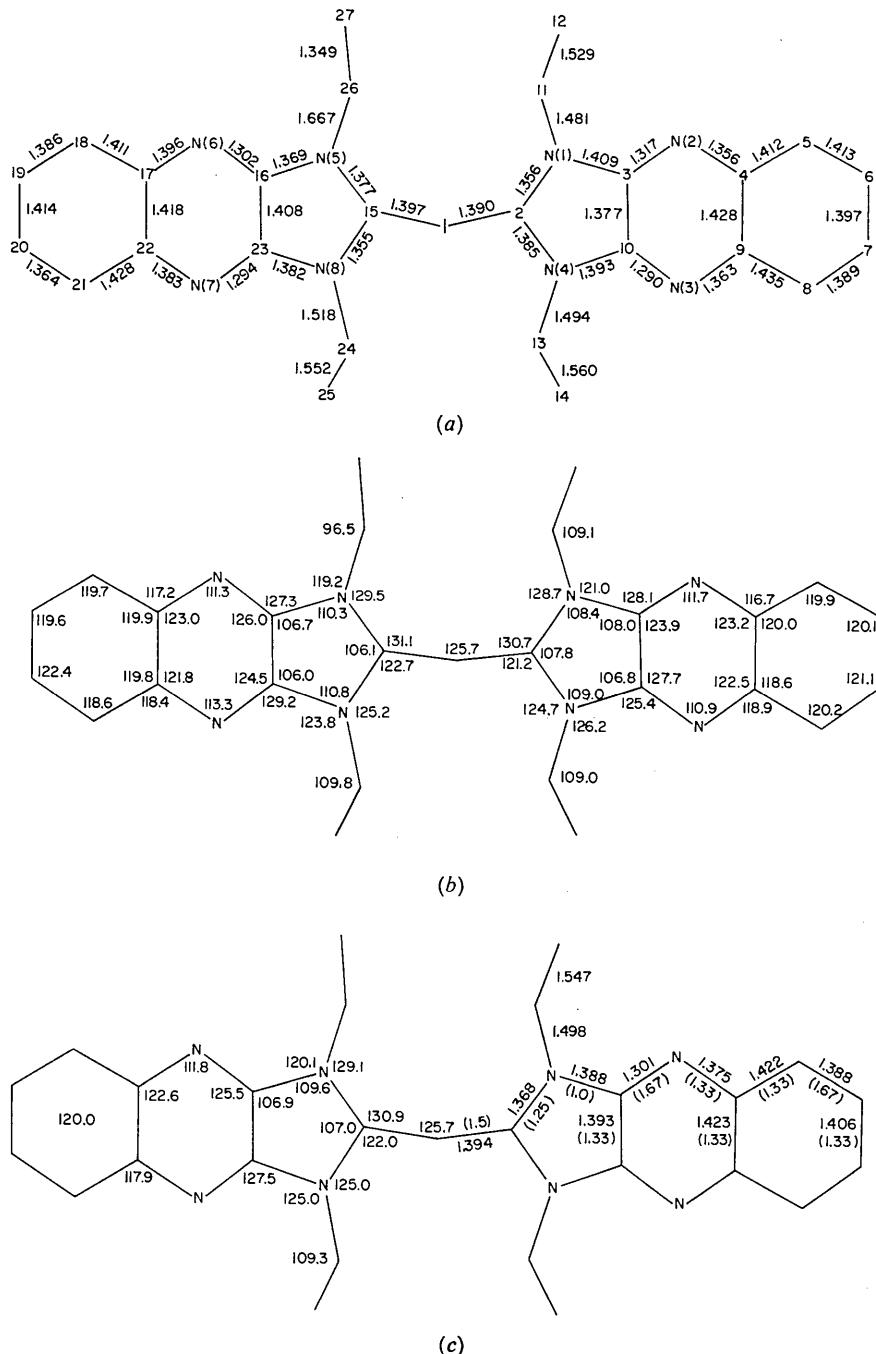
Fig. 1. Atomic labeling and bond lengths and angles for the dye cation. (c) shows averages for equivalent bonds and, in parentheses, the bond numbers expected on the basis of the unexcited valence-bond structures.

1960), and are bent away from each other so they deviate by 0·30 and 0·23 Å from planes *A* and *B*, respectively. On the other hand, the uncrowded methylene carbon atoms, C(13) and C(24), are 5·37 Å apart and depart from their respective planes by only 0·005 and 0·074 Å.

Three Kekulé structures for each of the naphthalene-like quinoxalino segments combine with four equivalent bonding structures for the central portion of the cation to produce 36 possible conventional unexcited valence-bond representations of the bonding. The bond numbers *n* (Pauling, 1960) expected on the basis of these structures are given in parentheses in Fig. 1(*c*). The averaged bond lengths agree quite well with the valence-bond picture and with the ability of the un-

shared electron pair of sp^2 nitrogen to enter into further conjugation. Specifically, the average of the two central C–C bonds (1·394 Å, $n=1·5$) agrees very well with the 1·394 Å typical of aromatic C–C bonds (Sutton, 1965). The four C(5)–C(6)-type bonds ($n=1·67$) average 1·388 Å compared with 1·37 Å expected on the basis of a bond-length bond-number correlation curve (Pauling, 1960). For C–C bonds with $n=1·33$ the correlation curve predicts a bond length of 1·42 Å. The average of ten such bonds in the cation is 1·413 Å. The distribution of the individual bond lengths about this average indicates a standard deviation, σ, of 0·017 Å, in good agreement with the value obtained from the e.s.d.'s of the coordinates. The remaining C–C bond in the cation, the unconjugated sp^3–sp^3 bond of the ethyl groups, averages a typical 1·547 Å.

Standard distances are less well established for sp^2C–sp^2N bonds than for similar C–C bonds. From covalent radii, the double bond ($n=2$) is 1·29 Å (Pauling, 1960). In conjugated heterocyclic molecules the C–N distance ($n=1·5$) is well known at 1·34 Å (Sutton, 1965). The pure single bond, a state rarely achieved because nitrogen's extra electron pair interacts with the carbon p_z orbital, can be taken as 1·45 Å (Lide, 1962). In actual experience, conjugation usually reduces this bond to the range 1·36–1·41 Å (Karle & Karle, 1967; Smith, 1969). The four C(3)–N(2)-type bonds ($n=1·67$) average 1·301 Å, a value between the double bond and aromatic bond values. Bond types C(2)–N(1) (1·368 Å), C(3)–N(1) (1·388 Å), and C(4)–N(2) (1·375 Å) are all longer than the aromatic distance but shorter than the single bond distance, as expected. The remaining type of C–N bond is the unconjugated bond to a methylene carbon and averages 1·498 Å compared to the 1·47 Å expected (Toman & Ocenaskova, 1966; Smith & Luss, 1969).

Apart from the distorted angles caused by the crowded ethyls, the cation angles are reasonably normal. The angles at the quinoxalino nitrogen atoms (average 111·8°) are slightly smaller than the 115·7° average for such angles tabulated by Singh (1965).

The interatomic distances and angles shown in Fig. 2 for the solvate are quite unreliable because of the disorder. The two oxygen positions relative to the iodide ion suggest the possibility of hydrogen bonding, but the distances are close to the sum of the van der Waals radii.

Shorter intermolecular contacts are given in Table 4. The molecular packing is shown stereoscopically in Fig. 4. The molecules are arranged in layers perpendicular to **c**. Within these layers, cations related by the *b* glide pack plane to plane to form chains parallel to **b**. The planar ends of each cation are almost parallel, the dihedral angle being 2·9°, and are separated by approximately 3·4 Å. Neighboring chains in the layers are related by the *a* glide so that sharp zigzag rows of cations are formed along **a**. The iodide ions and solvate molecules fit into the gaps between the neighboring chains.


(*a*)

(*b*)
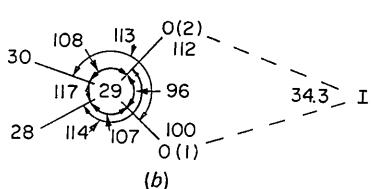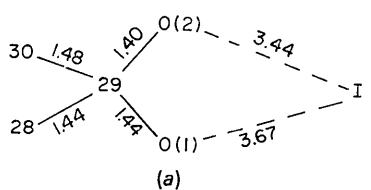
Fig. 2. Interatomic distances and angles for the solvate and anion.
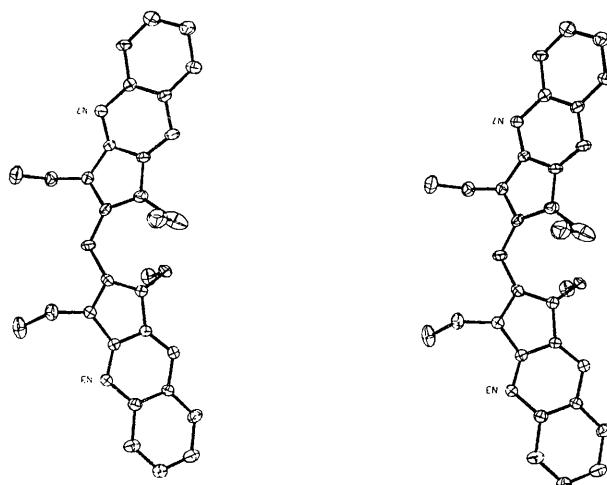
Fig. 3. Stereoscopic view of the molecule showing the 50% probability thermal ellipsoids.

Table 3. *Equations of least-squares planes and distances* (Å) *of atoms from these planes*

X, Y and Z are expressed in Å relative to the Cartesian axial system defined by the a, b and c axes. The planes were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) as modified by Blow (1960).

$$\text{Plane } A: \ 0.8770X + 0.1837Y + 0.4439Z = 7.9370$$
$$B: \ 0.8604X + 0.1582Y - 0.4845Z = 5.6417$$
$$C: \ 0.9489X + 0.2771Y - 0.1509Z = 7.6422$$

Plane A				Plane B				Plane C	
N(1)	0·008	C(9)	−0·009	N(5)	−0·015	C(22)	0·018	C(1)	0·000
N(2)	−0·031	C(10)	−0·005	N(6)	−0·004	C(23)	0·035	C(2)	0·000
N(3)	−0·016	*C(1)	0·247	N(7)	0·001	*C(1)	−0·251	C(15)	0·000
N(4)	0·046	*C(2)	0·059	N(8)	−0·030	*C(2)	0·034	*N(1)	0·639
C(3)	−0·010	*C(11)	0·298	C(16)	0·009	*C(15)	−0·084	*N(4)	−0·601
C(4)	−0·029	*C(12)	1·812	C(17)	0·008	*C(24)	0·074	*N(5)	−0·391
C(5)	0·025	*C(13)	0·005	C(18)	0·006	*C(25)	−1·347	*N(8)	0·357
C(6)	0·033	*C(14)	1·427	C(19)	−0·004	*C(26)	−0·232		
C(7)	0·008	*C(15)	−0·281	C(20)	−0·030	*C(27)	−1·578		
C(8)	−0·021			C(21)	0·007				

* Not included in the calculation of the plane.

Table 4. *Short interatomic contacts*

C(3)····O(2)	3·04 Å
C(10)···O(2)	3·05
C(11)···C(26)	3·28
C(12)···O(2)	3·29
C(27)···O(1)^i = O(1)····C(27)^{ii}	3·29
N(4)····O(2)	3·33
N(1)····O(2)	3·34
I·······O(2)	3·44
C(9)····C(22)^{iii} = C(22)···C(9)^{iv}	3·44
C(10)···C(21)^{iii} = C(21)···C(10)^{iv}	3·45
N(2)····C(30)^v = C(30)···N(2)^{vi}	3·45
C(15)···O(1)^i = O(1)····C(15)^{ii}	3·45
C(4)····N(7)^{iii} = N(7)····C(4)^{iv}	3·46
C(27)···C(12)^i = C(12)···C(27)^{ii}	3·46

i	$\frac{1}{2}+x, \frac{1}{2}-y, z$	iv	$x, -\frac{1}{2}+y, \frac{1}{2}-z$
ii	$-\frac{1}{2}+x, \frac{1}{2}-y, z$	v	$\frac{1}{2}-x, y, \frac{1}{2}+z$
iii	$x, \frac{1}{2}+y, \frac{1}{2}-z$	vi	$\frac{1}{2}-x, y, -\frac{1}{2}+z$

The cationic conformation determined here is close to what one would predict from a consideration of molecular models. In spite of the twists and bends,

considerable conjugation remains along the chromophore, as evidenced by the C(1)–C(2) and C(1)–C(15) bond lengths. This conjugation is strong enough to force angular distortions of about 5° at several atoms and to resist further twisting even though the crowded methylenes are still much closer together than the sum of the van der Waals radii.

References

ALLMANN, R. (1966). *Chem. Ber.* **99**, 1332.

BLOW, D. M. (1960). *Acta Cryst.* **13**, 168.

BOIS D'ENGHIEN-PETEAU, M., MEUNIER-PIRET, J. & VAN MEERSSCHE, M. (1968). *J. Chim. Phys.* **65**, 1221.

BROOKER, L. G. S. (1966). *Theory of the Photographic Process*, Chap. 11. 3rd Ed. Edited by C. E. K. MEES & T. H. JAMES. New York: Macmillan.

BROOKER, L. G. S., WHITE, F. L., HESELTINE, D. W., KEYES, G. H., DENT, S. G. & VAN LARE, E. J. (1953). *J. Phot. Sci.* **1**, 173.
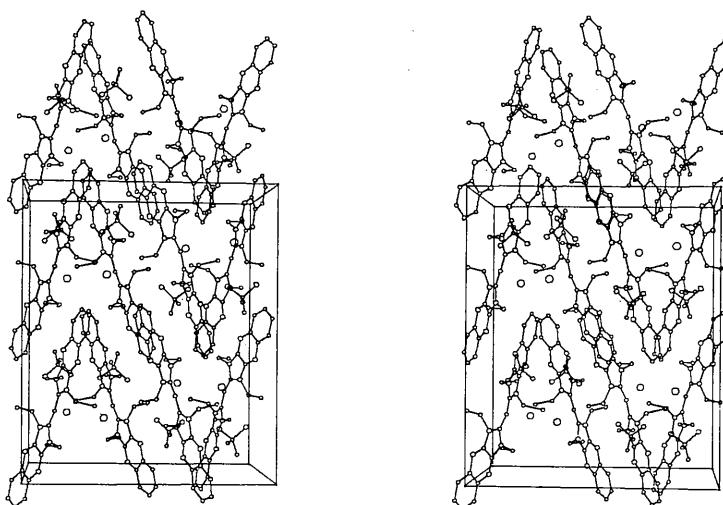
Fig. 4. Stereoscopic view of the molecular packing down the c axis. The a axis is horizontal and the b axis is vertical.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS: A FORTRAN Crystallographic Least-Squares Program.* Publication ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104.

DEWAR, M. J. S. (1958). *Steric Effects in Conjugated Systems,* pp. 46–51. Edited by G. W. GRAY. London: Butterworths.

EFFINGER, J., GERMAIN, G., MEUNIER, J., VANDERAUWERA, J. & VAN MEERSSCHE, M. (1960). *Bull. Soc. Chim. Belges,* 69, 387.

FURNAS, T. C. (1957). *Single Crystal Orienter Instruction Manual.* Milwaukee, Wisconsin: General Electric Co.

GERMAIN, G., PATTERNOTTE, C., PIRET, P. & VAN MEERSSCHE, M. (1964). *J. Chim. Phys.* 61, 1059.

GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DeKERF, J. (1961). *Bull. Soc. chim. Fr.* p. 1407.

GERMAIN, G., PIRET, P., VAN MEERSSCHE, M. & DeKERF, J. (1962). *Acta Cryst.* 15, 373.

IBERS, J. A. & HAMILTON, W. C. (1966). Private communication.

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

JOHNSON, C. K. (1965). *ORTEP: A FORTRAN Thermal Ellipsoid Program for Crystal Structure Illustrations.* Publication ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

KARLE, J. & KARLE, I. L. (1967). *J. Amer. Chem. Soc.* 89, 804.

KAWADA, I. & ALLMANN, R. (1968). *Angew. Chem.* Internat. Edit. 7, 69.

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

PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd Ed. Ithaca: Cornell Univ. Press.

SCHOMAKER, V., WASER, J., MARSH, R. E. & BERGMAN, G. (1959). *Acta Cryst.* 12, 600.

SHEPPARD, S. E., LAMBERT, R. H. & WALKER, R. D. (1941). *J. Chem. Phys.* 9, 96.

SINGH, C. (1965). *Acta Cryst.* 19, 861.

SMITH, D. L. (1966). Unpublished program.

SMITH, D. L. (1969). *Acta Cryst.* B25, 625.

SMITH, D. L. & LUSS, H. R. (1969). Unpublished results.

SRIVASTAVA, R. C. & LINGAFELTER, E. C. (1966). *Acta Cryst.* 20, 918.

SUTTON, L. E. (1965). *Interatomic Distances, Supplement.* Special Publication No. 18, London: The Chemical Society.

TOMAN, K. & OCENASKOVA, D. (1966). *Acta Cryst.* 20, 514.

TROTTER, J. (1965). Private communication.

VORONTSOVA, L. G., ZVONKOVA, Z. V. & ZHDANOV, G. S. (1963). *Kristallografiya* 8, 374.

WHEATLEY, P. J. (1959a). *J. Chem. Soc.* p. 3245.

WHEATLEY, P. J. (1959b). *J. Chem. Soc.* p. 4096.

The Crystal Structure of the 1,3-Diglyceride of 11-Bromoundecanoic Acid

By ALBERT HYBL AND DOUGLAS DORSET

The Department of Biophysics, University of Maryland School of Medicine, Baltimore, Maryland 21201, *U.S.A.*

The symmetric diglyceride of 11-bromoundecanoic acid, $C_{25}H_{46}Br_2O_5$ (DBU), was crystallized from chloroform showing a tabular monoclinic aspect and having space group $C2/c$, with unit-cell dimensions $a = 9.36$, $b = 5.58$, $c = 54.53$ Å, $\beta = 90.40°$ and with $Z = 4$. The structure was determined by a three-dimensional X-ray diffraction analysis. Data were collected with a General Electric XRD-6 manual diffractometer and nickel-filtered Cu $K\alpha$ radiation. The structure was solved by the heavy atom method. Block-diagonal least-squares refinement led to an R of 0.09. A pseudo twofold axis of molecular symmetry is utilized as a statistical axis of symmetry by the space group. The two hydrocarbon chain tails in the molecule point in opposite directions and are packed in layers with the chain axis parallel. The direction of the chain tilt, however, alternates in successive layers.

Introduction

Several rather detailed models (O'Brien, 1965; Vandenheuvel, 1963) for the unit membrane (Robertson, 1959; Korn, 1966) have been postulated. Most of these models incorporate the Finean (1967) conformations for the phospholipids in which the two fatty acid chains are folded in a parallel orientation. Because very few relevant single-crystal structure results have been reported for diacyl compounds, we have undertaken a series of crystallographic studies with the purpose of establishing experimentally the stable crystal conformation of these molecules.

We chose to begin our studies using the simple synthetic diacyl derivatives of 11-bromoundecanoic acid in order to have a heavy atom present in the structure. From the similarities in long spacing and polymorphism (Finean, 1967) between the diglycerides and the phospholipids it is clear that the hydrocarbon chain packing has a dominating influence. We may expect conformational similarities in the chain structure between the diglycerides and the diacyl phospholipids.