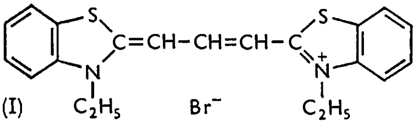
821. *The Crystallography of Some Cyanine Dyes. Part II.*[1] *The Molecular and Crystal Structure of the Ethanol Solvate of* 3,3′-*Diethylthiacarbocyanine Bromide.*

By P. J. Wheatley.

The structure of the 1 : 1 solvate of ethanol and 3,3′-diethylthiacarbocyanine bromide has been determined by *X*-ray single-crystal methods from two projections. The conjugated chain is in the extended form with the sulphur atoms *cis* with respect to this chain. The methyl groups of the ethyl substituents lie on opposite sides of the cationic plane. The cation is not quite planar, the two halves being twisted through an angle of 8°.

In Part I the *X*-ray analysis of unsolvated crystals of 3,3′-diethylthiacarbocyanine bromide (I) was described. The solvated crystals used for the present work exhibited the same increase in internal disorder with time as the unsolvated crystals, and to about the same extent. However, the solvated crystals appear to be indefinitely resistant to spontaneous disintegration.

Structure Determination.—$C_{23}H_{27}N_2OS_2Br$, $M = 491{\cdot}5$, triclinic, $a = 8{\cdot}07_2 \pm 0{\cdot}05$, $b = 11{\cdot}82_8 \pm 0{\cdot}08$, $c = 13{\cdot}10_5 \pm 0{\cdot}08$ Å, $\alpha = 98°\ 45'$, $\beta = 77°\ 14'$, $\gamma = 103°\ 17'$, $U = 1181$ Å^3, $D_m = 1{\cdot}42$ (by flotation), $Z = 2$, $D_c = 1{\cdot}382$, $F(000) = 508$. Space group, $P\bar{1}$ (C^1_i, No. 2). Cu-K_α radiation ($\lambda = 1{\cdot}542$ Å), single-crystal rotation and Weissenberg photographs.



(I)

The crystals, which were needles elongated parallel to the short [*a*] axis, showed a considerable spread in the measured density, and the value of D_m obtained by flotation was not accurate enough to decide whether there were one or two molecules of ethanol in the asymmetric unit. The crystal analysis showed, however, that the crystals were actually a 1 : 1 solvate.

Multiple-film Weissenberg photographs round [*a*] were obtained with an approximately square needle about 0·13 mm. across. The *hk*0 photographs were obtained from a cube of side 0·1 mm. cut from a needles. No correction was made for absorption ($\mu = 44{\cdot}0$ cm.$^{-1}$). Relative intensities were estimated by comparison with standard strips prepared from the same crystals. 212 of the 339 0*kl* reflexions, and 156 of the 328 *hk*0 reflexions obtainable with Cu-K_α radiation were observed to be non-zero.

The 0*kl* projection was solved first. A Patterson synthesis gave the co-ordinates of the bromide 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 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 all the atoms including those of one ethanol molecule. The projection was refined by Fourier and difference syntheses until *R* had fallen to 14%. Unobserved reflexions were omitted from the *R* factors. A single isotropic temperature factor, $B = 4{\cdot}75$ Å^2, was used. At this stage it appeared that the crystal structure was basically very similar to that of the unsolvated crystals, and that the stereochemistry of the cation was practically identical. It was noticed that the model of the cation used for the unsolvated crystals did not fit particularly well over the peaks in this projection

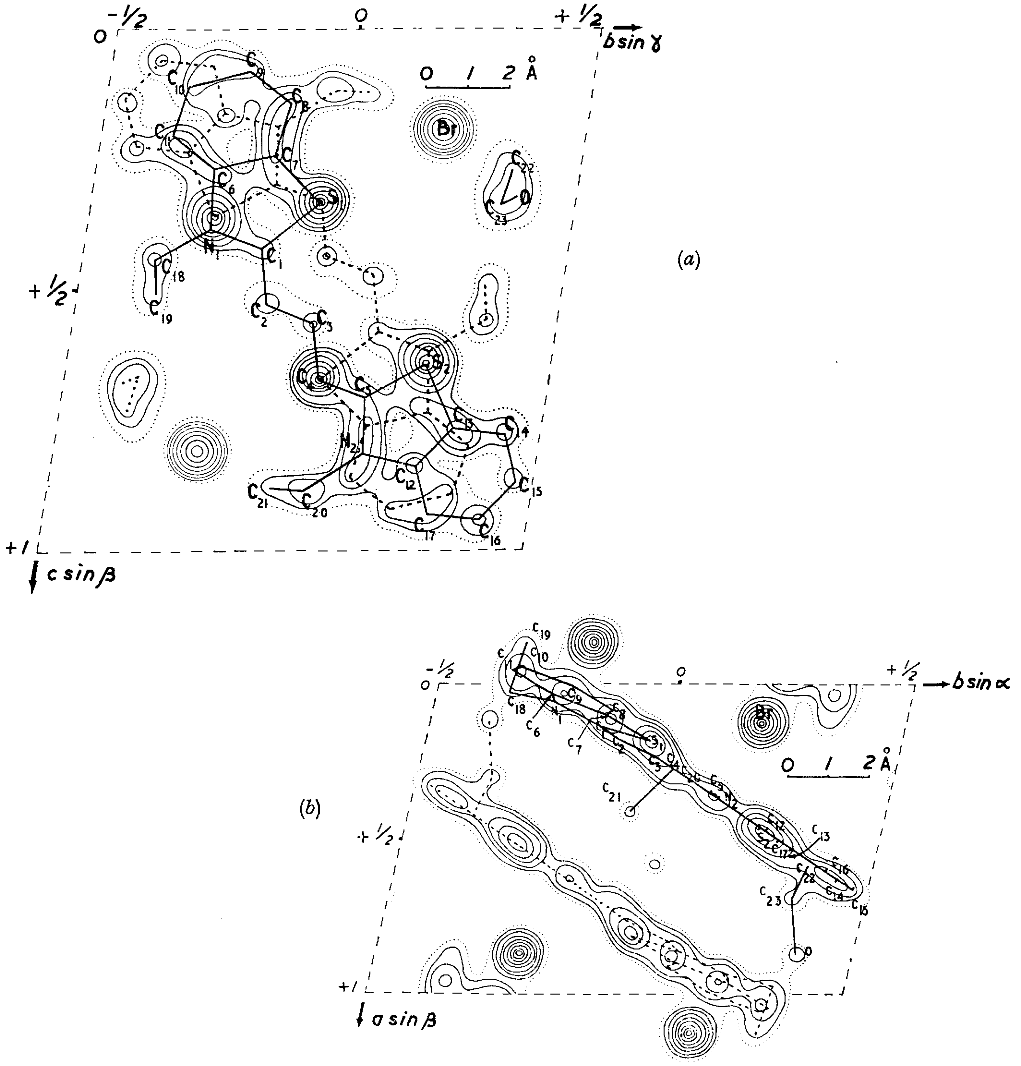
---

[1] The paper, *J.*, 1959, 3245, is considered as Part I, of this series.

of the solvated crystals, but this was attributed to insufficient refinement in the poorly resolved projection.

The solution of the *hk*0 projection was attempted in the same way, but offered some difficulties until it was realized that, in an unsharpened Patterson synthesis, no Br–Br or Br–S peaks could be seen. Only in a sharpened Patterson synthesis did these peaks involving the three heavy atoms appear. Moreover, the two strongest reflexions ($\bar{2}20$ and $\bar{4}40$ with unitary structure factors of 0·57 and 0·56 respectively) had phases opposite to that of the bromine atom. Once these difficulties had been overcome, refinement proceeded by Fourier methods until *R* had dropped to 24%. At this stage it had already been decided that the methyl groups of the ethyl substituents must lie on opposite sides of the cationic plane, whereas in the unsolvated crystals the methyl groups lie on the same

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 50, 100, 200 . . . arbitrary units, except in the bromine peaks where some contours have been omitted.

side. However, despite many trials, no positions were found for the atoms of a planar cation that would reduce *R* below 24%. Reluctantly, the notion of a planar cation had to be abandoned, and, as soon as the two halves of the cation were assumed to be twisted out of co-planarity, *R* began to drop again. The model that gave the best agreement with the observed intensities was one in which one half of the cation was viewed exactly sideways on, and the twist occurred about the bond of C(2)–C(3) of the conjugated chain. However, although this projection is suitable for deciding whether or not the cation is planar, the lack of resolution makes it difficult to decide exactly how the departure from planarity is achieved. A three-dimensional analysis is really needed to establish whether all the twisting occurs about the C(2)–C(3) bond, or whether small twists about other bonds are also playing a part.

TABLE 1. *Fractional co-ordinates* (*x*/*a*, *y*/*b*, *z*/*c*) *and orthogonal co-ordinates* (*X*, *Y*, *and Z in* Å).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*X*	*Y*	*Z*
Br	0·129	0·202	0·190	1·489	1·771	2·415
$S_{(1)}$	0·193	−0·030	0·330	2·343	−1·371	4·194
$S_{(2)}$	0·470	0·211	0·639	5·293	0·705	8·120
O	0·875	0·376	0·320	7·676	2·186	4·067
$N_{(1)}$	0·062	−0·247	0·372	1·418	−3·779	4·727
$N_{(2)}$	0·373	0·138	0·812	4·964	−0·679	10·319
$C_{(1)}$	0·140	−0·137	0·421	2·154	−2·719	5·350
$C_{(2)}$	0·178	−0·123	0·523	2·709	−2·828	6·646
$C_{(3)}$	0·242	−0·005	0·562	3·309	−1·628	7·142
$C_{(4)}$	0·260	0·008	0·668	3·716	−1·719	8·489
$C_{(5)}$	0·363	0·117	0·707	4·623	−0·699	8·984
$C_{(6)}$	0·030	−0·250	0·270	0·912	−3·551	3·431
$C_{(7)}$	0·100	−0·136	0·241	1·389	−2·275	3·062
$C_{(8)}$	0·090	−0·122	0·139	1·055	−1·887	1·767
$C_{(9)}$	0·010	−0·217	0·078	0·274	−2·741	0·991
$C_{(10)}$	−0·058	−0·329	0·111	−0·177	−4·006	1·411
$C_{(11)}$	−0·050	−0·348	0·213	0·140	−4·448	2·706
$C_{(12)}$	0·482	0·244	0·842	5·896	0·313	10·700
$C_{(13)}$	0·543	0·311	0·755	6·157	1·167	9·594
$C_{(14)}$	0·643	0·422	0·769	6·977	2·265	9·773
$C_{(15)}$	0·680	0·472	0·867	7·514	2·593	11·018
$C_{(16)}$	0·618	0·405	0·953	7·242	1·744	12·111
$C_{(17)}$	0·510	0·293	0·938	6·356	0·650	11·920
$C_{(18)}$	0·033	−0·352	0·428	1·331	−5·077	5·439
$C_{(19)}$	−0·133	−0·342	0·507	0·225	−4·809	6·443
$C_{(20)}$	0·273	0·045	0·880	4·349	−1·729	11·183
$C_{(21)}$	0·420	−0·020	0·875	5·491	−2·760	11·120
$C_{(22)}$	0·588	0·358	0·265	5·283	2·615	3·368
$C_{(23)}$	0·695	0·342	0·342	6·317	2·074	4·346

The final *R* factor for the *hk*0 projection was 17%. It was not necessary to introduce anisotropic temperature factors as in the unsolvated crystal, an overall temperature factor of 5·12 Å^2 being sufficient to obtain satisfactory agreement between the calculated and observed intensities.

The scattering factors used in this analysis were those of Berghuis *et al.*[2] for the carbon, nitrogen, and oxygen atoms; that of Tomiie and Stam [3] for the sulphur atom; and that of Thomas and Umeda [4] for the bromide ion. Thomas and Umeda's figures were modified at low values of θ for the additional electron, and corrected for the real part of the dispersion.[5] The deficiency of one electron spread out over many atoms of the cation was ignored.

Electron-density maps projected down [*a*] and [*c*] are shown in Figs. 1 (*a*) and (*b*), respectively. The molecule drawn in full lines corresponds to the co-ordinates listed in Table 1. Apart from the fractional co-ordinates with respect to the original triclinic axes,

[2] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[3] Tomiie and Stam, *ibid.*, 1958, **11**, 126.

[4] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[5] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

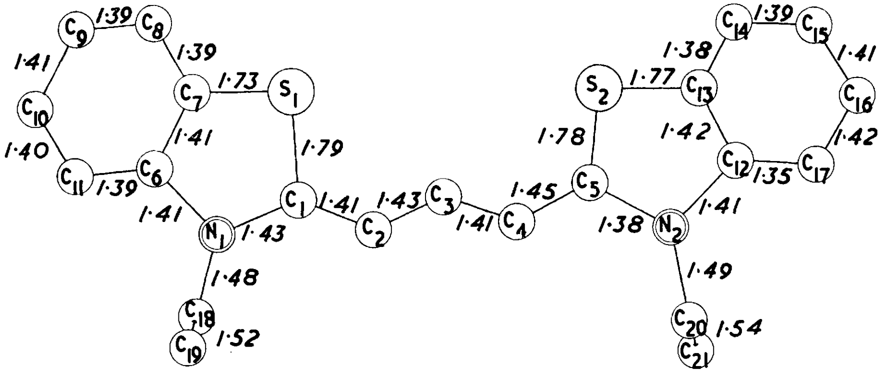
TABLE 2. *Observed and calculated structure factors for one asymmetric unit.*

hkl	F_o	F_c
0.0.1	3·8	−3·7
2	54·2	−53·8
3	14·7	−14·6
4	15·9	−18·1
5	4·8	+6·8
6	19·5	+18·9
7	16·7	−15·7
8	12·5	−10·0
9	5·9	+4·6
11	4·4	+3·1
13	8·2	−7·9
0.1.0	32·2	+31·1
1	20·1	+17·4
2	22·0	−22·0
3	24·5	+21·7
4	8·9	+7·4
5	3·3	+4·3
6	11·0	+11·3
7	18·7	−18·7
8	9·4	−6·8
9	18·6	+18·1
10	6·8	+5·1
11	4·9	−4·8
13	7·3	− 6·6
15	4·7	+4·2
0.2.0	39·9	−39·3
2	11·4	−10·3
3	10·5	+12·5
4	20·3	+20·9
5	40·2	−36·9
6	12·5	−15·5
7	8·6	+12·8
8	5·5	+5·1
9	15·1	+16·2
11	14·8	−16·8
0.3.0	9·5	+11·3
1	6·0	−6·0
2	34·1	+34·8
3	13·6	+17·1
4	17·2	−22·3
5	23·7	−22·9
6	2·8	−1·6
7	9·8	+12·1
8	6·9	+7·2
11	4·9	−5·0
0.4.0	10·9	+11·0
1	22·8	+25·2
2	5·8	+7·6
3	6·4	+0·9
4	32·3	−33·8
5	6·2	−2·6
6	13·6	+15·3
7	7·3	+4·3
8	4·9	−2·9
9	6·6	−9·1
11	5·6	+7·7
12	4·2	+3·2
0.5.0	23·7	+26·8
1	16·4	+18·1
2	25·7	−32·4
4	13·1	+13·4
6	13·9	+12·9
7	2·9	−4·9
8	15·8	−17·7
9	3·7	+9·6
0.6.0	4·4	+9·2
1	18·8	−21·1
2	23·8	−19·9
4	21·3	+19·7
6	5·0	−3·5
8	9·1	−9·7
9	9·2	+11·3
10	4·4	+6·0
11	3·4	−4·8
0.7.0	9·1	−8·9
1	9·4	−11·0
3	6·7	+7·6
4	9·3	+10·7
5	3·0	−3·8
6	11·5	−13·5
0.8.2	6·0	+2·6
3	4·8	+4·0
5	5·2	−6·1
7	7·2	+10·6
0.9.0	9·5	+13·2
1	13·7	+13·7
3	5·9	−5·5
4	4·7	−8·3
5	4·0	−7·2
6	3·1	+7·3
7	3·6	+3·1
0.10.1	10·6	+14·5
3	5·3	−7·3
4	4·2	+7·6
8	4·5	−7·1
0.11.0	4·4	−4·3
1	4·2	−6·2
4	6·4	+9·1
0.12.0	3·0	−3·7
1	3·7	−6·3
$0.\bar{1}.1$	32·0	−37·2
2	4·6	+2·5
3	33·8	−31·3
4	48·2	−37·3
5	9·6	−6·3
6	15·7	+14·6
7	21·1	+22·7
8	8·2	−9·3
9	7·9	−9·0
11	7·7	+8·4
12	6·0	+5·0
14	6·1	−6·1
$0.\bar{2}.1$	12·7	−13·4
2	49·8	+46·9
3	16·2	+18·3
4	24·1	−26·7
5	18·0	−15·4
6	6·1	+11·2
7	19·9	+20·3
8	3·3	+0·9
9	12·5	+10·0
10	7·9	−7·3
11	11·4	−9·4
12	4·9	+4·5
14	3·5	−2·6
$0.\bar{3}.1$	32·7	−29·7
2	11·5	−16·3
3	47·7	+48·4
4	16·3	+17·2
5	30·5	−29·9
6	7·5	−7·1
7	9·3	−9·2
8	5·7	+5·3
9	28·0	+24·1
10	14·6	−14·8
11	12·2	−12·0
15	4·3	+2·4
$0.\bar{4}.1$	17·7	−20·4
2	19·6	−18·2
3	22·3	+20·1
4	13·1	−11·7
5	10·2	+10·8
6	4·7	+2·9
7	21·4	−19·9
8	3·2	+4·0
9	14·8	+13·1
10	4·8	−3·1
11	4·9	+3·2
12	4·4	−5·7
13	5·5	−3·7
14	2·7	+3·8
15	5·0	+4·0
$0.\bar{5}.1$	13·5	−12·8
2	6·0	+3·2
3	7·6	−7·8
4	28·7	−26·4
5	32·2	+29·0
6	10·3	+11·7
7	13·7	−13·0
8	7·5	−8·9
9	5·6	−6·5
10	7·1	+7·2
11	10·2	+7·6
13	6·6	−5·0
$0.\bar{6}.1$	17·8	+20·1
2	17·1	+16·7
3	25·2	−24·3
4	18·3	−15·2
6	6·4	+7·4
7	8·2	+7·7
12	6·6	+6·8
14	4·7	−4·0
$0.\bar{7}.1$	6·7	+6·0
2	9·8	+9·6
3	8·0	+7·2
4	6·5	−6·6
5	10·6	−10·1
7	6·8	+6·6
8	9·2	+8·2
10	13·7	−13·9
11	3·9	−4·2
12	6·3	+5·4
$0.\bar{8}.1$	18·4	−22·6
3	16·3	+19·0
5	4·4	−5·1
6	5·1	−5·4
7	6·5	−6·4
8	8·3	+7·7
9	5·3	+4·5
10	5·7	−5·3
13	3·2	−2·0
14	6·7	+5·3
$0.\bar{9}.1$	18·5	−19·1
2	4·7	−2·4
4	8·2	+7·3
5	14·5	+13·8
6	5·4	−4·5
7	11·0	−9·4
9	3·6	±4·2
12	5·8	−4·5
$0.\overline{10}.3$	4·4	−5·8
5	6·7	+6·8
8	4·3	−5·8
9	3·2	−1·3
11	3·4	+2·9
$0.\overline{11}.1$	4·9	+5·3
2	3·7	+3·2
3	4·2	−2·7
4	5·0	−7·5
6	4·3	+5·3
10	5·1	−1·8
$0.\overline{12}.2$	3·7	+6·2
0.1.0	32·2	+31·0
2	39·9	−39·2
3	9·5	+11·2
4	10·9	+10·9
5	23·7	+26·3
6	4·4	+9·0
7	9·2	−8·6
9	9·5	+12·5
11	4·4	−3·9
12	3·0	−3·3
13	3·3	−3·0
1.0.0	21·8	+23·2
1	5·3	+7·4
2	35·2	−33·8
3	12·5	+15·7
4	4·7	+4·7
5	20·9	+13·9
6	2·3	+2·3
7	15·7	−13·8
8	4·1	+4·6
9	12·7	+12·5
10	5·3	+4·3
12	3·6	−3·7
14	1·9	+2·4
2.0.0	19·2	+19·0
1	26·9	−32·0
2	22·9	−22·2
3	11·3	+11·7
4	23·8	+18·8
5	4·7	−4·7
6	22·3	−24·7
7	17·0	−18·2
8	14·3	+13·2
9	17·0	+15·3
11	4·4	−3·2
13	1·5	+1·9
3.0.0	21·7	−22·9
1	25·2	−26·5
2	8·0	+6·7
3	18·7	+16·9
4	1·8	−4·3
5	9·6	−11·4
6	6·7	−7·7
8	7·4	+6·9
9	2·8	+1·6
10	2·5	−3·8
4.0.0	14·5	−15·2
1	2·5	+5·7
2	2·0	+4·2
3	6·7	+6·6
5	7·6	−4·1
6	6·9	−5·8
7	5·5	−3·5
10	6·4	−5·2
12	1·8	+1·6
5.0.0	6·9	−8·4
1	5·0	+10·4
2	19·0	+19·7
3	1·7	+0·9
4	7·6	−6·1
5	3·8	−2·8
6	2·4	+3·3
7	3·1	+6·2
9	3·9	−4·1
10	1·9	−0·9
6.0.0	8·7	+4·3
1	8·6	+9·2
3	7·0	−10·5
4	2·4	−3·9
5	9·2	+7·9
6	7·9	+6·6
7.1.0	1·8	+2·3
5	2·9	+4·0
6	2·2	+3·3
8.2.0	1·6	−4·1
3	5·5	−5·5
5	3·0	+3·4
9.1.0	2·5	−3·4
2	2·9	−3·1
$\bar{1}.1.0$	15·7	+17·7
3	41·1	−42·0
4	33·8	−24·7
5	11·5	−12·0
6	23·5	+20·8
7	11·7	−9·9
8	15·9	−15·0
9	5·8	−7·0
10	1·8	+1·5
11	3·3	+2·4
12	2·2	−4·0
13	5·2	−5·7
$\bar{2}.1.0$	10·6	−12·3
2	91·0	−83·3
3	20·4	−14·6
4	13·7	−14·2
5	6·6	−7·5
6	2·4	+6·7
7	11·4	+9·8
8	5·5	−8·0
9	16·7	−14·9
10	8·8	−6·6
12	5·9	+5·5
14	2·5	−3·0
$\bar{3}.1.0$	14·9	−11·4
2	28·3	+27·8
3	13·7	−10·0
4	23·7	−23·8
5	11·4	−11·7
6	7·6	+7·4
7	10·4	+12·2
8	5·0	−6·6
9	2·3	−5·5
10	3·0	−1·9
11	1·8	+2·9
12	5·0	+5·4
$\bar{4}.1.0$	14·3	−6·8
3	42·6	+36·5
4	41·7	+33·9
5	9·2	−14·0
7	13·9	+15·2
8	13·9	+13·4
10	2·4	−4·0
11	3·6	+4·0
12	6·7	+7·7
13	2·6	+3·3
$\bar{5}.1.0$	4·4	−3·3
2	4·2	+8·0
3	17·6	+17·6
5	4·2	+4·2
7	2·7	+1·9
9	4·7	+4·1
11	3·8	−4·4
$\bar{6}.1.0$	9·3	−12·8
2	7·1	−10·2
3	10·2	+5·6
4	11·1	+11·5
5	17·5	−12·5
6	17·2	−17·6
7	3·0	−3·5
12	2·4	−2·9
13	2·2	−1·1
$\bar{7}.1.0$	2·1	−2·2
2	3·3	−7·2
3	2·4	−3·1
5	2·3	+2·3
6	2·3	+1·0
7	9·2	−12·3
8	3·9	−3·1
11	1·8	−1·6
12	1·8	−3·3
$\bar{8}.2.0$	4·5	−4·3
3	1·4	−2·7
5	1·7	+3·6
7	4·8	+1·9
$\bar{9}.2.0$	1·4	+2·1
3	2·0	−3·4

there are also given in Table 1 the co-ordinates in Å with respect to orthogonal axes. These orthogonal axes are oriented as follows: $[b_0]$ coincides with the original triclinic axis $[b]$; $[a_0]$ is the projection of the triclinic axis $[a]$ on to the plane perpendicular to $[b_0]$; $[c_0]$ is perpendicular to $[a_0]$ and $[b_0]$. The following relations then hold: $X = x \sin\gamma + z(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma$; $Y = y + x\cos\gamma + z\cos\alpha$; $Z = z[\sin^2\alpha - \{(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma\}^2]^{\frac{1}{2}}$. The lengths of the orthogonal axes are $a_0 = 7{\cdot}85_6$, $b_0 = 11{\cdot}82_8, c_0 = 12{\cdot}70_8$ Å. The molecular dimensions and the numbering of the atoms are shown in Fig. 2.

Results.—The analysis shows that, apart from the methyl groups of the ethyl substituents, the remaining atoms of the cation no longer lie in one plane as they do in the same cation in the unsolvated crystals, but that the atoms lie in two planes making an angle of about 8° with each other. The methyl groups lie on opposite sides of the cation. Apart from these differences the crystal structures of the solvated and unsolvated crystals are very similar. Columns of cations, each pair being centrosymmetrically related, are stacked parallel to the [*a*] axis. The bromide ions and ethanol molecules lie between these columns.

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



The molecular dimensions shown in Fig. 2 are close to the expected values and to the values obtained in Part I. The distances C(22)–C(23) and C(23)–O in the ethanol molecule are 1·52 and 1·39 Å respectively. The intermolecular contacts are normal, with the exception of the Br...O distance which is only 3·27 Å, indicating, perhaps, the presence of a weak hydrogen bond between the bromine ion and the oxygen atom. The only other bromine contacts of less than 3·8 Å are S(1) at 3·71 Å and C(8) at 3·74 Å. There appear to be no short contacts between the ethanol molecule and the atoms of the cation that might account, in terms of packing forces, for the departure of the cation from planarity.

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

MONSANTO RESEARCH S.A., BINZSTRASSE 39,
ZURICH 3/45, SWITZERLAND.

[*Received, May* 26*th*, 1959.]