979. *The Structure of Echitamine: X-Ray Analysis of the Methanol Solvate of Echitamine Bromide.*

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The structure of the quaternary alkaloid echitamine, $C_{22}H_{29}O_4N_2^+$, has been determined by an *X*-ray study of the methanol solvate of echitamine bromide. The crystals are orthorhombic, space group $P2_12_12_1$, with four molecules in the unit cell. Phase determination based on the heavy atom with Fourier and least-squares refinement methods led to the constitution and stereochemistry (apart from absolute configuration) given in formula (VI). In the final results the discrepancy *R* over the 2115 observed reflexions is 13·4%. The bond lengths and angles have average estimated standard deviations of about 0·03Å and 2°.

THE bark of the tree *Alstonia scholaris*, R.Br. (*Echites scholaris*, L.) found in China, India, and the Philippines has been employed as an antimalarial drug since the 17th century.[1] Between 1875 and 1880 Gorup-Besanez,[2] Hesse,[1,3] and Harnack [4] independently isolated from this bark the chief alkaloidal constituent, echitamine, as the chloride; Hesse assigned to it the formula $C_{22}H_{29}ClN_2O_4$. In 1925 Goodson and Henry [5] confirmed this formula, extended the earlier chemical studies, and isolated echitamine from various other *Alstonia* species. In 1957 Birch, Hodson, and Smith [6] suggested the partial structure (I) for echitamine, and more recent work [7-11] led to proposals of the structural formulæ (II),[9] (III),[10] and (IV).[11] Birch and his co-workers have reviewed [12] the chemical and spectroscopic evidence leading to the formulation of structures (II), (III), and (IV) and have concluded that none of these formulæ is entirely satisfactory. What did appear well established, however, was that echitamine is an indole alkaloid containing a methyl ester, an ethylidene and two hydroxyl groups, and one *N*-methyl group in which the nitrogen atom is quarternary.

We began an *X*-ray study of echitamine bromide crystals early in 1960, after some discussion with Professor A. J. Birch, to whom we are grateful for supplies of the alkaloid.

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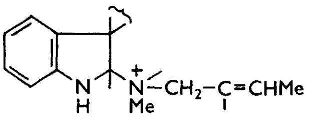
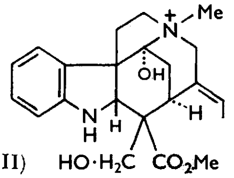
[1] Jobst and Hesse, *Annalen*, 1875, **178**, 49.
[2] Gorup-Besanez, *Annalen*, 1875, **176**, 88.
[3] Hesse, *Annalen*, 1875, **176**, 326; 1880, **203**, 144; *Ber.*, 1878, **11**, 1546; 1880, **13**, 1841.
[4] Harnack, *Ber.*, 1878, **11**, 2004; 1880, **13**, 1648.
[5] Goodson and Henry, *J.*, 1925, **127**, 1640; Goodson, *J.*, 1932, 2626.
[6] Birch, Hodson, and Smith, Résumés des Communications, Tome II, p. 207, XVIth Internat. Congr. Pure Appl. Chem., Paris, 1957.
[7] Govindachari and Rajappa, *Proc. Chem. Soc.*, 1959, 134; *Chem. and Ind.*, 1959, 1154, 1549.
[8] Birch, Hodson, and Smith, *Proc. Chem. Soc.*, 1959, 224.
[9] Conroy, Bernasconi, Brook, Ikan, Kurtz, and K. W. Robinson, *Tetrahedron Letters*, 1960, No. 6, 1.
[10] D. Chakravarti, R. N. Chakravarti, Ghose, and Sir Robert Robinson, *Tetrahedron Letters*, 1960, No. 10, 10; No. 11, 25; No. 12, 33.
[11] Ghosal and Majumdar, *Chem. and Ind.*, 1960, 19; Chatterjee, Ghosal, and Majumdar, *Chem. and Ind.*, 1960, 265; Chatterjee and Ghosal, *Naturwiss.*, 1960, **47**, 234.
[12] Birch, Hodson, Moore, Potts, and Smith, *Tetrahedron Letters*, 1960, No. 19, 36.

In his correspondence with us Professor Birch[13] suggested another formula (V) for echitamine and this is closely related to the true structure (VI) which we deduce from the results of our investigation. Although the available chemical and spectroscopic evidence concerning the alkaloid can be rationalized[14,15] on the basis of structure (VI) for the quaternary salt, the exact nature of echitamine base, $C_{22}H_{28}N_2O_4$, is still not completely certain and two formulæ (VII)[14] and (VIII)[15] have been proposed.



(I)



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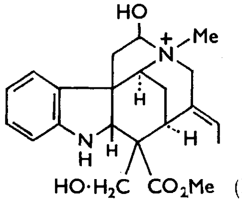

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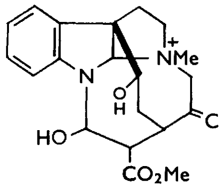

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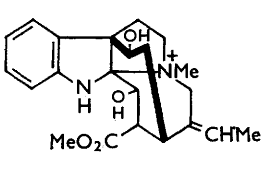
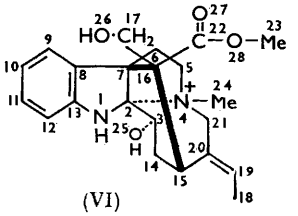
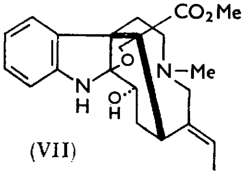


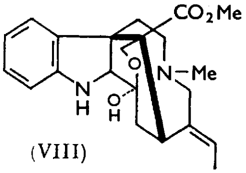
(V)



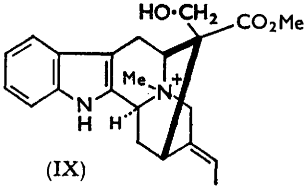
(VI)



(VII)

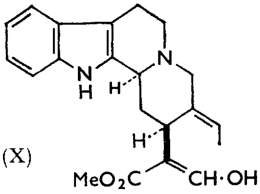


(VIII)



(IX)

Echitamine is closely related biogenetically to such indole alkaloids as macusine-A (IX)[16] and geissoschizine (X), one of the products of the hydrolysis of geissospermine,[17] and a biosynthetic route to echitamine from a precursor of the geissoschizine type has been proposed.[18] The absolute configuration shown in formula (VI) for echitamine is based on the application of Bijvoet's method[19] to echitamine iodide by Manohar and Ramaseshan,[20] and is in accord with the rule[21] of uniform absolute stereochemistry at C-15 in the various indole alkaloids, ψ-akuammicine[22] being the only known exception.



(X)

The first samples which we examined were of the bromide dihydrate, obtained by slow crystallization from water;[23] inspection of the Patterson projections showed that in these crystals the positions of the bromide ions would give rise

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[13] Birch, personal communication, December 1959.

[14] Birch, Hodson, Moore, and Smith, *Proc. Chem. Soc.*, 1961, 62.

[15] Govindachari and Rajappa, *Tetrahedron*, 1961, **15**, 132.

[16] McPhail, Robertson, Sim, Battersby, Hodson, and Yeowell, *Proc. Chem. Soc.*, 1961, 223; McPhail, Robertson, and Sim, unpublished results.

[17] Puisieux, Goutarel, Janot, and Le Hir, *Compt. rend.*, 1959, **249**, 1369; Janot, *Tetrahedron*, 1961, **14**, 113; Rapoport, Windgassen, Hughes, and Onak, *J. Amer. Chem. Soc.*, 1959, **81**, 3166.

[18] Smith, *Chem. and Ind.*, 1961, 1121.

[19] Bijvoet, Peerdeman, and van Bommel, *Nature*, 1951, **168**, 271.

[20] Manohar and Ramaseshan, *Tetrahedron Letters*, 1961, No. 22, 814.

[21] Wenkert and Bringi, *J. Amer. Chem. Soc.*, 1959, **81**, 1474, 6535.

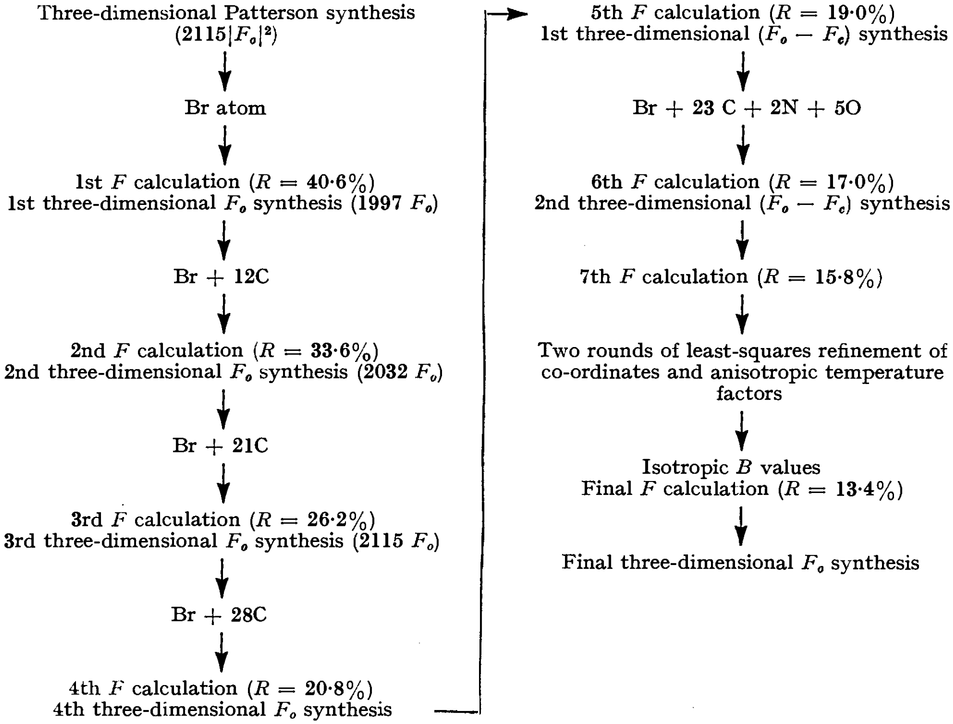
[22] Edwards and Smith, *Proc. Chem. Soc.*, 1960, 215.

[23] Hamilton, Hamor, Robertson, and Sim, *Proc. Chem. Soc.*, 1961, 63.

to false symmetry in the early stages of the analysis. Recrystallization from methanol gave orthorhombic crystals of the methanol solvate,[5] and here the bromide ions were found to occupy general positions in the unit cell. These crystals were then employed for the structure determination, the heavy-atom phase-determining method [24] being used with three-dimensional data. The course of the analysis is described in the Experimental section and summarized in Table 1.

TABLE 1.

Progress of the structure analysis.



The final three-dimensional electron-density distribution is shown in Fig. 1 as superimposed contour sections drawn parallel to (001). The corresponding atomic arrangement is explained in Fig. 2. The stereochemistry of the molecule should also be apparent from Fig. 3 which shows the atomic arrangement in the molecule as seen in projection along the *b*-axis. The echitamine molecule has a compact three-dimensional structure in which the two five-membered rings are fused *cis* and the six-membered ring (carbons 7, 2, 3, 14, 15, 16) is in boat form. There are three other interlocking rings, one eight-membered and two seven-membered, one of which (carbons 2, 3, 14, 15, 20, 21, and N-4) is in boat form.

The molecular dimensions calculated from the final atomic co-ordinates (see Table 2) are listed in Table 3. The standard deviations of the final atomic co-ordinates were estimated in the usual manner from the least-squares residuals (see Experimental section) and are shown in Table 4; from the results the average e.s.d. of a bond between light atoms (C, N, and O) is about 0·03 Å and the average e.s.d. of a valency angle about 2°.

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[24] Robertson and Woodward, *J.*, 1937, 219; 1940, 36; Sim, in " Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 227.

The average length of the aromatic carbon–carbon bonds is 1·42 Å, not significantly different from the value of 1·397 Å attributed [25] to benzene, and none of the individual lengths differs significantly from this value. The average single-bond length between sp^3-hybridized carbon atoms is 1·56 Å and between sp^3- and sp^2-hybridized carbon atoms 1·52 Å, in reasonable agreement with the accepted values of 1·545 Å and 1·525 Å.[25] Again none of the individual lengths differs significantly from these values. The length of the carbon–carbon double bond in the ethylidene group, 1·37 Å, does not differ significantly from the value of 1·334 Å in ethylene.[26]

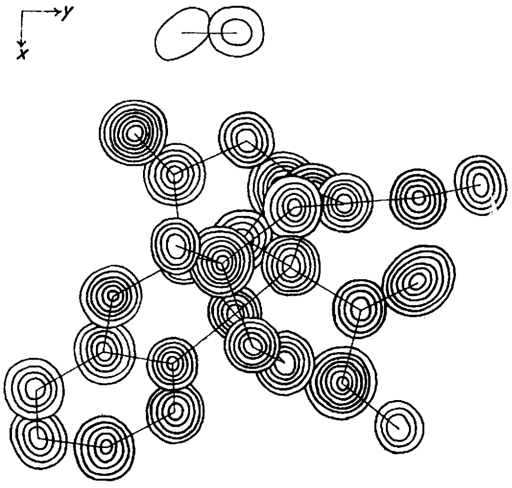

FIG. 1.

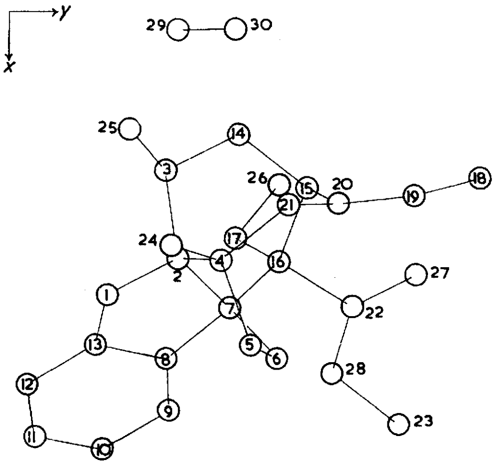

FIG. 2.

FIG. 1. Final three-dimensional electron-density distribution for the methanol solvate of echitamine bromide, shown by means of superimposed contour sections drawn parallel to (001). Contours are at intervals of 1e/Å^3 beginning at the two-electron level. The bromide ion, which lies beyond the field of the diagram, is not included.

FIG. 2. Atomic arrangement corresponding to Fig. 1.

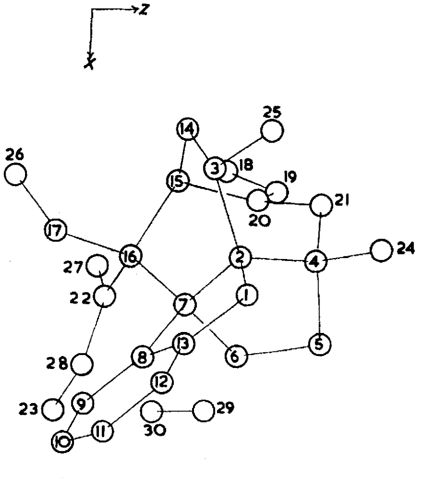

FIG. 3. Atomic arrangement as seen in projection along the *b*-axis.

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[25] Sutton *et al.*, " Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.* No. 11, 1958.

[26] Bartell and Bonham, *J. Chem. Phys.*, 1957, **27**, 1414.

TABLE 2.

Atomic co-ordinates and temperature factors.

Atom	*x/a*	*y/b*	*z/c*	*B*	Atom	*x/a*	*y/b*	*z/c*	*B*
$N_{(1)}$	0·5876	0·1239	0·5122	4·4	$C_{(17)}$	$0{\cdot}5158_5$	0·2833	0·2102	4·2
$C_{(2)}$	0·5415	0·2121	0·4991	3·7	$C_{(18)}$	0·4400	0·5835	0·4707	5·9
$C_{(3)}$	$0{\cdot}4379_5$	0·1945	0·4552	3·7	$C_{(19)}$	0·4624	0·5027	$0{\cdot}5544_5$	4·4
$N_{(4)}$	0·5436	0·2654	0·6198	4·1	$C_{(20)}$	0·4725	$0{\cdot}4102_5$	0·5218	3·8
$C_{(5)}$	0·6429	0·3038	0·6294	4·0	$C_{(21)}$	0·4756	0·3480	0·6288	4·1
$C_{(6)}$	0·6591	0·3385	0·4973	3·7	$C_{(22)}$	0·5943	0·4293	0·2892	4·5
$C_{(7)}$	0·6010	0·2752	0·4138	3·3	$C_{(23)}$	0·7364	0·4877	0·2118	5·5
$C_{(8)}$	0·6631	$0{\cdot}1999_5$	0·3520	4·2	$C_{(24)}$	0·5279	$0{\cdot}2037_5$	0·7322	4·9
$C_{(9)}$	0·7243	0·2050	0·2567	4·6	$O_{(25)}$	0·3880	0·1507	0·5446	4·7
$C_{(10)}$	0·7719	0·1212	0·2259	4·9	$O_{(26)}$	0·4519	0·3344	0·1411	4·8
$C_{(11)}$	0·7576	0·0388	0·2869	4·6	$O_{(27)}$	0·5579	0·5053	0·2729	5·6
$C_{(12)}$	$0{\cdot}6951_5$	$0{\cdot}0275_5$	0·3829	4·4	$O_{(28)}$	0·6778	0·4071	0·2568	4·7
$C_{(13)}$	0·6462	0·1137	0·4161	4·1	$C_{(29)}$ *	0·2691	0·2068	0·0492	10·8
$C_{(14)}$	$0{\cdot}3918_5$	0·2857	0·4113	4·2	$O_{(30)}$ *	0·2667	0·2787	0·1324	11·6
$C_{(15)}$	0·4533	0·3694	0·3972	3·8	Br	0·5520	0·4354	−0·0769	†
$C_{(16)}$	0·5437	$0{\cdot}3387_5$	0·3286	3·8					

* Denotes the atoms of the methanol molecule.

† For the bromide ion an anisotropic temperature factor was employed. This was of the form

$$T = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{13}hl + b_{12}hk)}$$

with parameters:

$b_{11} = 0{\cdot}00930$ $b_{22} = 0{\cdot}00850$ $b_{33} = 0{\cdot}01373$

$b_{23} = -0{\cdot}00130$ $b_{13} = 0{\cdot}00137$ $b_{12} = 0{\cdot}00160$

The dimensions of the ester group are very similar to those reported for dimethyl oxalate [27] and for the ester and lactone groups in bromogeigerin acetate [28] and epilimonol iodoacetate.[29] As in dimethyl oxalate the terminal methyl group $C_{(23)}$ of the ester group is *trans* to the $C_{(16)}$–$C_{(22)}$ bond. The five atoms $C_{(16)}$, $C_{(22)}$, $C_{(23)}$, $O_{(27)}$, and $O_{(28)}$ are coplanar to within 0·06 Å.

The carbon–oxygen single bonds in the echitamine and methanol molecules, $C_{(3)}$–$O_{(25)}$ = 1·38, $C_{(17)}$–$O_{(26)}$ = 1·41, $C_{(29)}$–$O_{(30)}$ = 1·38 Å, appear to be rather short, but within the limits of the experimental error cannot be said to differ significantly from the accepted value [25] of 1·43 Å.

The carbon–nitrogen bond lengths show a considerable spread, varying from 1·38 to 1·56 Å. Three different types are involved, however, $C(sp^2)$–N, $C(sp^3)$–N, and $C(sp^3)$–N^+. The length of the $C(sp^2)$–N bond, *i.e.*, $C_{(13)}$–$N_{(1)}$, is 1·38 Å and this compares favourably with the values reported for such bonds in *p*-nitroaniline (1·371 Å),[30] 2-chloro-4-nitroaniline (1·38 Å),[31] acetanilide (1·426 Å),[32] ibogaine hydrobromide (1·39 and 1·40 Å),[33] and calycanthine dihydrobromide dihydrate (1·38 and 1·42 Å).[34] The $C(sp^3)$–N bond, *i.e.*, $C_{(2)}$–$N_{(1)}$, at 1·43 Å is rather shorter than the usual carbon–nitrogen single bond length of 1·47 Å,[25] but not really significantly so. Of the four $C(sp^3)$–$N_{(4)}^+$ bonds three are 1·54 Å and the fourth 1·56 Å in length. The occurrence in amino-acids of C–NH_3^+ bonds longer than 1·47 Å has been discussed by Hahn,[35] who has listed the results of a number of crystal-structure analyses and has concluded that the mean C–NH_3^+ bond length in amino-acids is 15·03 Å. However, some recent accurate determinations from three-dimensional data have yielded rather lower values, 1·474 Å in glycine,[36] 1·480, 1·484 Å in L-lysine

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[27] Dougill and Jeffrey, *Acta Cryst.*, 1953, **6**, 831.

[28] Hamilton, McPhail, and Sim, *J.*, 1962, 708.

[29] Arnott, Davie, Robertson, Sim, and Watson, *J.*, 1961, 4183.

[30] Trueblood, Goldish, and Donohue, *Acta Cryst.*, 1961, **14**, 1009.

[31] McPhail and Sim, unpublished results.

[32] Brown and Corbridge, *Acta Cryst.*, 1954, **7**, 711.

[33] Arai, Coppola, and Jeffrey, *Acta Cryst.*, 1960, **13**, 553.

[34] Hamor, Robertson, Shrivastava, and Silverton, *Proc. Chem. Soc.*, 1960, 78; Hamor and Robertson, *J.*, 1962, 194.

[35] Hahn, *Z. Krist.*, 1957, **109**, 438.

[36] Marsh, *Acta Cryst.*, 1958, **11**, 654.

TABLE 3.

Molecular dimensions.

Intramolecular bonded distances (Å)

$N_{(1)}-C_{(2)}$	1·43	$N_{(4)}-C_{(24)}$	1·54	$C_{(11)}-C_{(12)}$	1·42	$C_{(18)}-C_{(19)}$	1·51
$N_{(1)}-C_{(13)}$	1·38	$C_{(5)}-C_{(6)}$	1·56	$C_{(12)}-C_{(13)}$	1·47	$C_{(19)}-C_{(20)}$	1·37
$C_{(2)}-C_{(3)}$	1·62	$C_{(6)}-C_{(7)}$	1·55	$C_{(14)}-C_{(15)}$	1·50	$C_{(20)}-C_{(21)}$	1·48
$C_{(2)}-C_{(7)}$	1·57	$C_{(7)}-C_{(8)}$	1·56	$C_{(15)}-C_{(16)}$	1·59	$C_{(22)}-O_{(27)}$	1·22
$C_{(2)}-N_{(4)}$	1·54	$C_{(7)}-C_{(16)}$	1·55	$C_{(15)}-C_{(20)}$	1·52	$C_{(22)}-O_{(28)}$	1·32
$C_{(3)}-C_{(14)}$	1·54	$C_{(8)}-C_{(13)}$	1·44	$C_{(16)}-C_{(17)}$	1·59	$C_{(23)}-O_{(28)}$	1·52
$C_{(3)}-O_{(25)}$	1·38	$C_{(8)}-C_{(9)}$	1·39	$C_{(16)}-C_{(22)}$	1·55	$C_{(29)}-O_{(30)}$	1·38
$N_{(4)}-C_{(5)}$	1·56	$C_{(9)}-C_{(10)}$	1·42	$C_{(17)}-O_{(26)}$	1·41	(methanol)	
$N_{(4)}-C_{(21)}$	1·54	$C_{(10)}-C_{(11)}$	1·37				

Intramolecular non-bonded distances (Å)

$C_{(2)}...C_{(15)}$	2·82	$C_{(6)}...C_{(22)}$	2·81	$C_{(9)}...C_{(22)}$	3·73	$C_{(16)}...C_{(13)}$	3·66
$C_{(2)}...C_{(12)}$	3·69	$C_{(6)}...C_{(23)}$	3·97	$C_{(9)}...N_{(1)}$	3·66	$C_{(16)}...C_{(21)}$	3·48
$C_{(2)}...C_{(20)}$	3·00	$C_{(6)}...N_{(1)}$	3·22	$C_{(9)}...O_{(28)}$	2·94	$C_{(16)}...C_{(19)}$	3·62
$C_{(2)}...C_{(17)}$	3·38	$C_{(6)}...O_{(27)}$	3·74	$C_{(11)}...N_{(1)}$	3·74	$C_{(16)}...C_{(23)}$	3·77
$C_{(2)}...C_{(22)}$	3·94	$C_{(6)}...O_{(28)}$	2·85	$C_{(13)}...C_{(17)}$	3·83	$C_{(16)}...N_{(1)}$	3·72
$C_{(3)}...C_{(16)}$	2·93	$C_{(7)}...C_{(10)}$	3·93	$C_{(13)}...N_{(4)}$	3·46	$C_{(16)}...N_{(4)}$	3·39
$C_{(3)}...C_{(6)}$	3·87	$C_{(7)}...C_{(12)}$	3·79	$C_{(14)}...C_{(7)}$	3·08	$C_{(21)}...C_{(18)}$	3·81
$C_{(3)}...C_{(5)}$	3·90	$C_{(7)}...C_{(21)}$	3·19	$C_{(14)}...C_{(21)}$	2·85	$C_{(21)}...N_{(1)}$	3·81
$C_{(3)}...C_{(8)}$	3·51	$C_{(7)}...C_{(20)}$	2·95	$C_{(14)}...C_{(19)}$	3·61	$C_{(21)}...O_{(25)}$	3·22
$C_{(3)}...C_{(13)}$	3·30	$C_{(7)}...C_{(24)}$	3·83	$C_{(14)}...N_{(1)}$	3·85	$C_{(20)}...C_{(24)}$	3·83
$C_{(3)}...C_{(21)}$	2·96	$C_{(7)}...C_{(17)}$	2·59	$C_{(14)}...O_{(25)}$	3·23	$C_{(20)}...C_{(17)}$	3·95
$C_{(3)}...C_{(20)}$	3·19	$C_{(7)}...O_{(25)}$	3·88	$C_{(14)}...O_{(26)}$	3·20	$C_{(20)}...C_{(22)}$	3·15
$C_{(3)}...C_{(24)}$	3·35	$C_{(7)}...O_{(26)}$	3·83	$C_{(14)}...C_{(17)}$	2·88	$C_{(20)}...O_{(25)}$	3·89
$C_{(3)}...C_{(17)}$	3·21	$C_{(7)}...O_{(27)}$	3·67	$C_{(15)}...C_{(6)}$	3·26	$C_{(20)}...O_{(27)}$	3·32
$C_{(5)}...C_{(8)}$	3·42	$C_{(7)}...O_{(28)}$	2·79	$C_{(15)}...C_{(5)}$	3·91	$C_{(19)}...C_{(22)}$	3·68
$C_{(5)}...C_{(13)}$	3·58	$C_{(8)}...C_{(17)}$	2·93	$C_{(15)}...C_{(8)}$	3·94	$C_{(19)}...N_{(4)}$	3·64
$C_{(5)}...C_{(20)}$	3·16	$C_{(8)}...C_{(22)}$	3·48	$C_{(15)}...C_{(18)}$	3·15	$C_{(19)}...O_{(27)}$	3·42
$C_{(5)}...C_{(19)}$	3·96	$C_{(8)}...O_{(28)}$	3·13	$C_{(15)}...C_{(17)}$	2·58	$N_{(4)}...O_{(25)}$	2·93
$C_{(6)}...C_{(9)}$	3·41	$N_{(1)}...O_{(25)}$	2·99	$C_{(15)}...O_{(26)}$	2·88	$C_{(23)}...O_{(27)}$	2·73
$C_{(6)}...C_{(13)}$	3·32	$C_{(17)}...O_{(27)}$	3·28	$C_{(15)}...N_{(4)}$	3·17	$C_{(24)}...N_{(1)}$	2·83
$C_{(6)}...C_{(21)}$	3·07	$C_{(17)}...O_{(28)}$	3·00	$C_{(15)}...O_{(25)}$	3·63	$C_{(24)}...O_{(25)}$	3·02
$C_{(6)}...C_{(20)}$	2·94	$C_{(18)}...C_{(22)}$	3·74	$C_{(15)}...O_{(27)}$	2·82	$O_{(26)}...O_{(27)}$	3·22
$C_{(6)}...C_{(19)}$	3·77	$C_{(18)}...O_{(27)}$	3·01	$C_{(15)}...O_{(28)}$	3·69	$O_{(26)}...O_{(28)}$	3·71
$C_{(6)}...C_{(24)}$	3·76	$C_{(22)}...O_{(26)}$	2·98	$C_{(16)}...C_{(5)}$	3·67		
$C_{(6)}...C_{(17)}$	3·90	$C_{(9)}...C_{(17)}$	3·30	$C_{(16)}...C_{(9)}$	3·36		

Interbond angles

$C_{(2)}C_{(3)}C_{(14)}$	112°	$C_{(16)}C_{(7)}C_{(2)}$	113°	$C_{(6)}C_{(5)}N_{(4)}$	101°	$C_{(21)}C_{(20)}C_{(19)}$	111°
$C_{(2)}C_{(3)}O_{(25)}$	111	$C_{(16)}C_{(7)}C_{(6)}$	109	$C_{(5)}N_{(4)}C_{(21)}$	110	$C_{(21)}C_{(20)}C_{(15)}$	120
$C_{(2)}N_{(4)}C_{(5)}$	104	$C_{(16)}C_{(7)}C_{(8)}$	117	$C_{(8)}C_{(7)}C_{(2)}$	102	$C_{(20)}C_{(19)}C_{(18)}$	126
$C_{(2)}N_{(4)}C_{(24)}$	115	$C_{(16)}C_{(17)}O_{(26)}$	112	$C_{(8)}C_{(9)}C_{(10)}$	117	$C_{(24)}N_{(4)}C_{(21)}$	106
$C_{(3)}C_{(2)}N_{(4)}$	111	$C_{(16)}C_{(22)}O_{(27)}$	124	$C_{(8)}C_{(13)}N_{(1)}$	114	$C_{(17)}C_{(16)}C_{(22)}$	108
$C_{(3)}C_{(14)}C_{(15)}$	116	$C_{(16)}C_{(22)}O_{(28)}$	109	$C_{(9)}C_{(8)}C_{(13)}$	122	$C_{(17)}C_{(16)}C_{(15)}$	108
$C_{(14)}C_{(3)}O_{(25)}$	112	$C_{(7)}C_{(2)}C_{(3)}$	116	$C_{(9)}C_{(8)}C_{(7)}$	133	$C_{(22)}C_{(16)}C_{(7)}$	113
$C_{(14)}C_{(15)}C_{(16)}$	110	$C_{(7)}C_{(2)}N_{(4)}$	104	$C_{(9)}C_{(10)}C_{(11)}$	121	$C_{(22)}O_{(28)}C_{(23)}$	116
$C_{(14)}C_{(15)}C_{(20)}$	109	$C_{(7)}C_{(2)}N_{(1)}$	107	$C_{(10)}C_{(11)}C_{(12)}$	125	$N_{(4)}C_{(21)}C_{(20)}$	115
$C_{(15)}C_{(16)}C_{(7)}$	109	$C_{(7)}C_{(16)}C_{(17)}$	111	$C_{(11)}C_{(12)}C_{(13)}$	115	$O_{(28)}C_{(22)}O_{(27)}$	126
$C_{(15)}C_{(16)}C_{(22)}$	108	$C_{(7)}C_{(6)}C_{(5)}$	107	$C_{(12)}C_{(13)}C_{(8)}$	120	$N_{(1)}C_{(2)}C_{(3)}$	110
$C_{(15)}C_{(20)}C_{(19)}$	126	$C_{(7)}C_{(8)}C_{(13)}$	105	$C_{(12)}C_{(13)}N_{(1)}$	126	$N_{(1)}C_{(2)}N_{(4)}$	109
$C_{(16)}C_{(15)}C_{(20)}$	112	$C_{(6)}C_{(7)}C_{(2)}$	106	$C_{(13)}N_{(1)}C_{(2)}$	108		

monohydrochloride dihydrate,[37] 1·468 Å in serine phosphate,[38] and it is clear that Hahn's estimate is a little too high. Table 5 shows the results of a number of *X*-ray measurements of $C(sp^3)-N^+$ bonds in alkaloids; the average of the more accurate values (e.s.d $\leqslant$0·05 Å) is 1·52 Å, and the echitamine results do not differ significantly from this.

In a model of the echitamine molecule constructed with standard bond lengths and valency angles the distance between the carboxyl-carbon atom $C_{(22)}$ of the ester group and the terminal carbon atom $C_{(18)}$ of the ethylidene group is about 2·5 Å. In the actual molecule, however, our results show that these atoms are 3·74 Å apart, and this increased

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[37] Wright and Marsh, *Acta Cryst.*, 1962, **15**, 54.
[38] McCallum, Robertson, and Sim, *Nature*, 1959, **184**, 1863.

separation is brought about because the ethylidene group is bent out of its ideal position with some distortions of valency angles. Thus the angle $N_{(4)}C_{(21)}C_{(20)}$, 115°, exceeds the tetrahedral value and the angles $C_{(15)}C_{(20)}C_{(19)}$ and $C_{(20)}C_{(19)}C_{(18)}$, both 126°, are appreciably greater than the angle $C_{(21)}C_{(20)}C_{(19)}$, 111°, although the last three might have been expected to be equal.

TABLE 4.

Standard deviations of the final atomic co-ordinates (Å).

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
$N_{(1)}$	0·016	0·015	0·016	$C_{(17)}$	0·018	0·018	0·018
$C_{(2)}$	0·020	0·016	0·017	$C_{(18)}$	0·023	0·020	0·020
$C_{(3)}$	0·019	0·016	0·016	$C_{(19)}$	0·020	0·018	0·018
$N_{(4)}$	0·016	0·014	0·014	$C_{(20)}$	0·017	0·017	0·018
$C_{(5)}$	0·019	0·018	0·018	$C_{(21)}$	0·018	0·018	0·018
$C_{(6)}$	0·019	0·018	0·019	$C_{(22)}$	0·020	0·021	0·020
$C_{(7)}$	0·017	0·016	0·018	$C_{(23)}$	0·023	0·021	0·020
$C_{(8)}$	0·019	0·019	0·020	$C_{(24)}$	0·019	0·019	0·021
$C_{(9)}$	0·020	0·019	0·020	$O_{(25)}$	0·013	0·012	0·012
$C_{(10)}$	0·020	0·019	0·020	$O_{(26)}$	0·014	0·012	0·013
$C_{(11)}$	0·020	0·018	0·019	$O_{(27)}$	0·015	0·013	0·013
$C_{(12)}$	0·019	0·018	0·019	$O_{(28)}$	0·013	0·012	0·014
$C_{(13)}$	0·018	0·017	0·020	$C_{(29)}$	0·033	0·031	0·033
$C_{(14)}$	0·018	0·017	0·019	$O_{(30)}$	0·022	0·021	0·022
$C_{(15)}$	0·019	0·015	0·016	Br	0·002	0·002	0·002
$C_{(16)}$	0·020	0·017	0·017				

TABLE 5.

$C(sp^3)$–N^+ bond lengths in alkaloids.

Compound	Bond length (Å)	Estimated standard deviation (Å)
Ibogaine hydrobromide [33]	1·49, 1·54, 1·57	0·03
Calycanthine dihydrobromide dihydrate [34]	1·43, 1·49, 1·56, 1·50, 1·49, 1·53	0·03
(±)-Alphaprodine hydrochloride [39]	1·50, 1·50, 1·53	0·01
(+)-Methadone hydrobromide [40]	1·55, 1·49, 1·48	0·03
(+)-Demethanolaconinone hydriodide trihydrate [41]	1·54, 1·57, 1·52	0·04
Hunterburnine methiodide [42]	1·51, 1·54, 1·57, 1·64	0·05
Macusine-A iodide [16]	1·36, 1·46, 1·50, 1·66	0·06
Codeine hydrobromide dihydrate [43]	1·51, 1·52, 1·56	0·06
(+)-De(oxymethylene)lycoctonine hydriodide monohydrate [44]	1·51, 1·51, 1·49	—
Strychnine hydrobromide dihydrate [45]	1·55, 1·44, 1·59	—

The mean of the valency angles of the five-membered ring (carbons 2, 7, 6, 5, and N-4) is 106°, perhaps significantly smaller than tetrahedral and in good agreement with the average values for the angles of the five-membered rings in hydroxy-L-proline (106°),[46] copper proline dihydrate (104°),[47] isoclovene hydrochloride (105°),[48] clerodin bromolactone (106°),[49] and bromodihydroisophotosantonic lactone acetate (105°).[50] The angles of the benzene ring vary from 115° to 125°, the average value being 120°.

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[39] Kartha, Ahmed, and Barnes, *Acta Cryst.*, 1960, **13**, 525.

[40] Hanson and Ahmed, *Acta Cryst.*, 1958, **11**, 724.

[41] Przybylska, *Acta Cryst.*, 1961, **14**, 429.

[42] Asher, Robertson, Sim, Bartlett, Sklar, and Taylor, *Proc. Chem. Soc.*, 1962, 72; Asher, Robertson, and Sim, further unpublished work.

[43] Lindsey and Barnes, *Acta Cryst.*, 1955, **8**, 227.

[44] Przybylska, *Acta Cryst.*, 1961, **14**, 424.

[45] Robertson and Beevers, *Acta Cryst.*, 1951, **4**, 270.

[46] Donohue and Trueblood, *Acta Cryst.*, 1952, **5**, 419.

[47] Mathieson and Welsh, *Acta Cryst.*, 1952, **5**, 599.

[48] Clunie and Robertson, *J.*, 1961, 4382.

[49] Sim, Hamor, Paul, and Robertson, *Proc. Chem. Soc.*, 1961, 75; and unpublished work.

[50] Asher and Sim, *Proc. Chem. Soc.*, 1962, 111; and unpublished work.

TABLE 6.

The shorter intermolecular contacts and some associated angles.

Distances (Å)

$O_{(26)} \ldots O_{(30)}$	2·84	$C_{(11)} \ldots C_{(19)}{}^{II}$	3·54	$C_{(6)} \ldots C_{(21)}{}^{IV}$	3·75	$C_{(18)} \ldots C_{(9)}{}^{I}$	3·90
$O_{(26)} \ldots Br$	3·17	$C_{(5)} \ldots C_{(23)}{}^{IV}$	3·57	$C_{(17)} \ldots O_{(30)}$	3·77	$C_{(5)} \ldots C_{(14)}{}^{II}$	3·90
$Br \ldots O_{(25)}{}^{I}$	3·20	$O_{(30)} \ldots C_{(12)}{}^{I}$	3·58	$C_{(29)} \ldots Br^{VIII}$	3·79	$C_{(10)} \ldots C_{(29)}{}^{VI}$	3·91
$O_{(26)} \ldots C_{(29)}$	3·40	$C_{(14)} \ldots O_{(30)}$	3·60	$O_{(30)} \ldots C_{(11)}{}^{I}$	3·81	$Br \ldots C_{(24)}{}^{V}$	3·92
$C_{(6)} \ldots O_{(25)}{}^{II}$	3·40	$Br \ldots C_{(21)}{}^{V}$	3·67	$C_{(24)} \ldots O_{(30)}{}^{II}$	3·83	$Br \ldots C_{(3)}{}^{I}$	3·92
$C_{(5)} \ldots O_{(30)}{}^{II}$	3·42	$C_{(9)} \ldots C_{(29)}{}^{VI}$	3·68	$C_{(18)} \ldots C_{(10)}{}^{I}$	3·84	$O_{(27)} \ldots C_{(13)}{}^{I}$	3·97
$C_{(10)} \ldots C_{(21)}{}^{II}$	3·43	$C_{(3)} \ldots O_{(27)}{}^{III}$	3·69	$C_{(9)} \ldots O_{(25)}{}^{II}$	3·85	$C_{(6)} \ldots C_{(14)}{}^{II}$	3·98
$Br \ldots N_{(1)}{}^{I}$	3·45	$C_{(19)} \ldots C_{(24)}{}^{VII}$	3·71	$C_{(11)} \ldots C_{(20)}{}^{II}$	3·88	$C_{(9)} \ldots C_{(21)}{}^{II}$	3·98
$C_{(12)} \ldots O_{(26)}{}^{III}$	3·50	$C_{(11)} \ldots C_{(21)}{}^{II}$	3·71	$C_{(17)} \ldots Br$	3·88	$O_{(28)} \ldots C_{(29)}{}^{VI}$	3·99
$C_{(18)} \ldots C_{(17)}{}^{I}$	3·53	$C_{(18)} \ldots C_{(24)}{}^{VII}$	3·74	$O_{(28)} \ldots O_{(25)}{}^{II}$	3·89	$Br \ldots C_{(5)}{}^{V}$	3·99

The superscripts refer to the positions:

I	$1 - x,$	$\frac{1}{2} + y,$	$\frac{1}{2} - z$	V	$x,$	$y,$	$z - 1$
II	$\frac{1}{2} + x,$	$\frac{1}{2} - y,$	$1 - z$	VI	$\frac{1}{2} + x,$	$\frac{1}{2} - y,$	$-z$
III	$1 - x,$	$-\frac{1}{2} + y,$	$\frac{1}{2} - z$	VII	$1 - x,$	$\frac{1}{2} + y,$	$1\frac{1}{2} - z$
IV	$1\frac{1}{2} - x,$	$1 - y,$	$\frac{1}{2} + z$	VIII	$-\frac{1}{2} + x,$	$\frac{1}{2} - y,$	$-z$

Angles

$O_{(30)}O_{(26)}C_{(17)}$	121°	$C_{(3)}O_{(25)}Br^{III}$	111°	$O_{(30)}O_{(26)}Br$	123°
$C_{(29)}O_{(30)}O_{(26)}$	102	$C_{(13)}N_{(1)}Br^{III}$	117	$N_{(1)}Br^{III}O_{(25)}$	53
$N_{(1)}Br^{III}O_{(26)}{}^{III}$	85	$C_{(17)}O_{(26)}Br$	110	$C_{(2)}N_{(1)}Br^{III}$	115
$O_{(25)}Br^{III}O_{(26)}{}^{III}$	118				

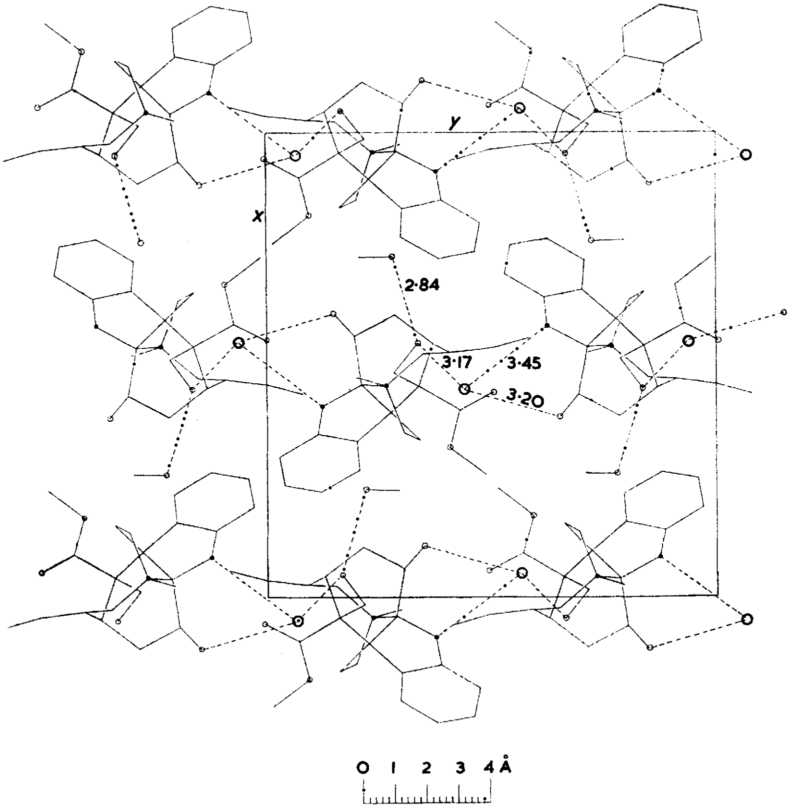

FIG. 4. Projection of the crystal structure on (001).

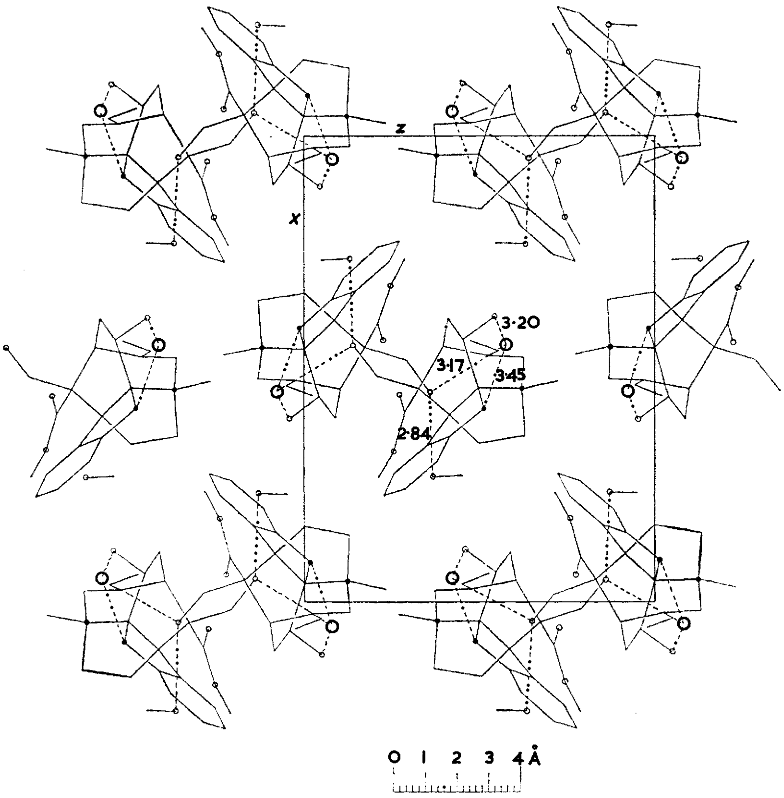

FIG. 5. Projection of the crystal structure on (010).

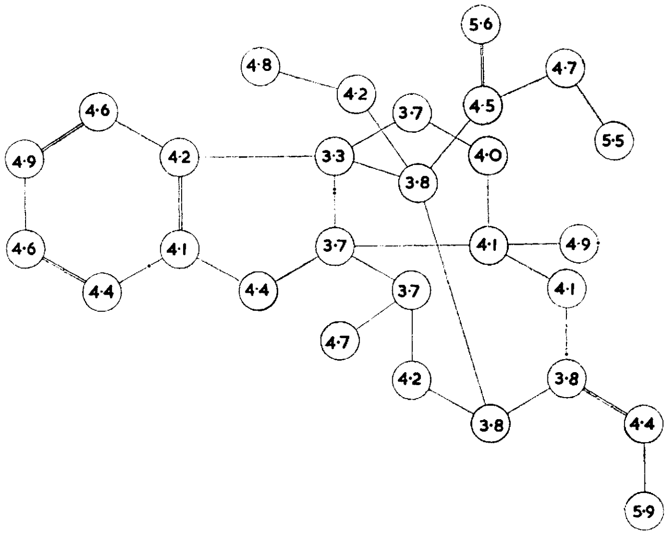

FIG. 6. Final isotropic temperature factors for the atoms of the echitamine molecule.

In the crystal the positively charged echitamine molecules and the bromide ions form a three-dimensional network held together by the normal ionic forces and by a system of hydrogen bonds involving the two hydroxyl-oxygen atoms $O_{(25)}$ and $O_{(26)}$, the indole-nitrogen atom $N_{(1)}$, and the bromide ion. It is clear from a consideration of distances and angles that the hydrogen atoms attached to $O_{(25)}$, $O_{(26)}$, and $N_{(1)}$ are directed towards the bromide ion; this is illustrated in Figs. 4 and 5 which show the contents of the unit cell as seen in projection on (001) and (010), respectively. The angles $C_{(3)}O_{(25)}Br$, $C_{(17)}O_{(26)}Br$, and $C_{(2)}N_{(1)}Br$ are all within 6° of tetrahedral, while the distances $OH \cdots Br^-$ (3·17 and 3·20 Å) and $NH \cdots Br^-$ (3·45 Å) are similar to the hydrogen-bonded distances found in cystine dihydrobromide,[51] calycanthine dihydrobromide dihydrate,[34] and 11-amino-undecanoic acid hydrobromide hemihydrate.[52] The methanol molecule of solvation is hydrogen-bonded to the hydroxyl-oxygen $O_{(26)}$ of the echitamine molecule, the distance $O_{(26)} \cdots HO_{(30)}$ being 2·84 Å and the angle $O_{(26)}O_{(30)}C_{(29)}$ 102°. There is no particularly close contact between the positively charged nitrogen atoms and the negatively charged bromide ions in the unit cell, the four values of $d(N_{(4)} \cdots Br)$ being 4·14, 4·91, 7·63, and 8·10 Å.

The shortest separation between a carbon atom and a bromide ion is 3·67 Å, rather similar to the minimum $C \cdots Br^-$ distances in the crystal structures of (+)-methadone hydrobromide (3·62 Å),[40] calycanthine dihydrobromide dihydrate (3·60 Å),[34] and ibogaine hydrobromide (3·95 Å).[33] The closest approach between two echitamine molecules, 3·40 Å, involves $C_{(6)}$ of the reference molecule and $O_{(25)}$ of the molecule related to it by the two-fold screw axis parallel to *a*. There are two short van der Waals contacts between the methanol and echitamine molecules, $O_{(26)} \cdots C_{(29)}$ of 3·40 Å, and $C_{(5)} \cdots O_{(30)}^{II}$ of 3·42 Å (the superscript II referring to the position $\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 - z$). Table 6 gives a full list of the intermolecular contacts of less than 4 Å and some of the associated angles.

The final isotropic temperature factors for the atoms of the echitamine molecule are shown in Fig. 6. The atoms of the peripheral groups have, on the whole, rather higher temperature factors than the atoms of the ring systems. Moreover, the groups which participate in hydrogen bonding, $HO_{(25)}$ and $HO_{(26)}C_{(20)}$, have smaller temperature factors than the methyl ester, ethylidene, and methyl groups which are much less tightly bound by the crystal forces. A detailed treatment of the thermal vibrations, such as carried out for naphthalene[53] and anthracene,[54] is not practicable for a molecule of the complexity of echitamine; nevertheless the observed variations in the atomic temperature factors are clearly physically acceptable.

The temperature factors derived for the carbon ($B = 10{\cdot}8$ Å^2) and oxygen ($B = 11{\cdot}2$ Å^2) atoms of the methanol molecule are exceptionally high, suggesting that there is only partial occupancy of the methanol sites in the crystal. If it is assumed that the difference between the measured (1·416 g./c.c.) and the calculated (1·430 g./c.c.) crystal density is due to this defect, then only 85% of the methanol sites are occupied. Electron counts on the final Fourier synthesis (Fig. 1) support this, indicating an occupancy of 79% of the sites.

EXPERIMENTAL

Crystal Data.—Echitamine bromide, methanol solvate, $C_{22}H_{29}BrN_2O_4,CH_3{\cdot}OH$; $M = 497{\cdot}43$. Orthorhombic, $a = 14{\cdot}72 \pm 0{\cdot}04$, $b = 14{\cdot}17 \pm 0{\cdot}02$, $c = 11{\cdot}09 \pm 0{\cdot}02$ Å, $U = 2312$ Å^3, $D_m = 1{\cdot}416$ g./c.c. (by flotation), $Z = 4$, $D_c = 1{\cdot}430$ g./c.c., $F(000) = 1040$, space group $P2_12_12_1\text{–}D_2^4$. Absorption coefficient for *X*-rays ($\lambda = 1{\cdot}542$ Å) $\mu = 29$ cm.$^{-1}$.

Well-formed prisms elongated along *a* were obtained by slow crystallization from methanol.

Experimental Measurements.—Rotation, oscillation, and moving-film photographs were

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[51] Peterson, Steinrauf, and Jensen, *Acta Cryst.*, 1960, **13**, 104.
[52] Sim, *Acta Cryst.*, 1955, **8**, 833.
[53] Cruickshank, *Acta Cryst.*, 1957, **10**, 504.
[54] Cruickshank, *Acta Cryst.*, 1957, **10**, 470.

obtained from crystals rotated about the three crystallographic axes. Copper-K_α (λ = 1·542 Å) radiation was employed.

The space group was determined uniquely from the systematic halvings in the reflexions. The intensity data, consisting of the layer lines 0*kl*—12 *kl*, *h*0*l*, and *hk*0, were collected by means of equi-inclination multiple-film[55] Weissenberg exposures and estimated visually. The crystals were cut so that the cross-section perpendicular to the rotation axis was approximately 0·2 × 0·2 mm. and absorption corrections were not applied. The intensities were corrected for Lorentz, polarization, and the rotation factors appropriate to upper layers.[56] The various layers were placed on the same relative scale by comparison of common reflexions on different photographs. The absolute scale was obtained at a later stage by correlation with the final calculated structure amplitudes, $|F_c|$. In all 2115 independent structure amplitudes were measured (Table 7). The crystal density was determined by flotation in carbon tetrachloride–light petroleum.

Structure Analysis.—The co-ordinates of the bromide ion were obtained from the Harker sections of the three-dimensional Patterson synthesis. Phase angles calculated from these co-ordinates were then associated with the observed structure amplitudes and a three-dimensional electron-density distribution was calculated. When the function was displayed as contoured sections drawn on sheets of glass and stacked in a frame significant peaks which could be attributed to twelve of the thirty carbon, nitrogen, and oxygen atoms in the asymmetric crystal unit were located. Co-ordinates were assigned to these atoms and they were included (all as carbon atoms) in the calculation of a second set of structure amplitudes and phase angles, an overall isotropic temperature factor B of 4·0 Å^2 being assumed. The value of R, the average discrepancy between the calculated and the measured structure amplitudes, was 33·6%.

The improved phase constants were employed in the computation of a second three-dimensional Fourier synthesis in which we were able to recognize a further nine atoms. When the structure amplitudes and phase angles were recalculated with the inclusion of these atoms the value of R fell to 26·2%. A third three-dimensional electron-density distribution based on the revised phase angles was then calculated and all the atoms (other than hydrogen) could be seen. A fourth Fourier synthesis gave better definition to the peaks; the fifth structure-factor calculation, with the twenty-eight atoms (hydrogen omitted) of the echitamine molecule weighted as carbon and the methanol molecule excluded, reduced R to 19·0%.

The nitrogen and oxygen atoms were next distinguished from the carbon atoms, first, by consideration of the peak heights in the electron-density distributions, secondly, by consideration of the intermolecular hydrogen-bonded contacts, and thirdly, by taking into account the available chemical information concerning the functional groups of the molecule. Confirmation of our assignment was obtained by evaluating a three-dimensional difference Fourier synthesis; the atoms designated as nitrogen and oxygen in (VI) fell on regions of positive electron density while the carbon atoms did not. The methanol molecule also showed up clearly. On calculation of a further set of structure factors, with each atom of the echitamine and methanol molecules assigned its correct chemical type, the value of R fell to 17·0%.

A second difference Fourier synthesis was then calculated and examination of this showed that the temperature factors of many of the atoms of the echitamine molecule required small adjustments and that in the case of the methanol molecule a considerably larger value of B was necessary. It was also obvious that the thermal vibration of the bromide ion was distinctly anisotropic. With these adjustments the value of R was 15·8%.

The analysis was completed by means of two rounds of least-squares refinement of positional and anisotropic thermal parameters. The programme employed was that devised by Rollett.[57] and the weighting scheme was as follows:

$$\sqrt{w} = |F_o|/8|F_{\text{min.}}| \text{ if } |F_o| < 8|F_{\text{min.}}|;$$
$$\sqrt{w} = 8|F_{\text{min.}}|/|F_o| \text{ if } |F_o| > 8|F_{\text{min.}}|.$$

As some doubt was felt about the significance of the anisotropic temperature factors derived

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[55] Robertson, *J. Sci. Inst.*, 1943, **20**, 175.

[56] Tunell, *Amer. Min.*, 1939, **24**, 448.

[57] Rollett, in " Computing Methods and the Phase Problem in X-ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961, p. 87.

TABLE 7.

Measured and calculated values of the structure factors.

h	*k*	*l*	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α°
0	0	2	62	71	0
		4	20	12	0
		6	66	89	180
		8	6	6	0
		10	6	6	0
		12	14	10	0
		14	12	12	0
0	1	1	97	136	270
		2	46	47	90
		3	8	19	270
		4	72	74	90
		5	8	14	270
		6	41	45	90
		7	31	29	270
		8	36	33	270
		9	28	20	270
		10	30	25	270
		12	8	5	270
		14	8	9	90
0	2	0	35	38	180
		1	15	12	180
		2	12	12	180
		3	83	97	180
		4	36	43	0
		5	32	36	180
		6	50	55	180
		7	13	10	0
		8	37	38	180
		9	17	17	0
		10	6	5	0
		11	9	10	0
		12	8	3	0
		14	3	4	0
0	3	1	69	85	90
		2	27	37	90
		3	7	14	90
		4	12	10	270
		5	70	73	270
		6	36	38	270
		7	42	39	270
		8	6	0	270
		9	17	15	270
		11	9	9	90
		12	11	9	270
		13	15	13	90
0	4	0	12	10	0
		1	49	63	180
		2	56	57	180
		3	88	117	180
		4	23	20	180
		5	48	45	180
		6	23	20	180
		9	40	39	0
		11	16	12	0
		12	5	6	180
		13	6	5	180
0	5	1	92	110	90
		2	76	91	270
		3	33	45	90
		4	11	6	270
0	5	5	27	28	270
		6	9	5	270
		7	37	29	270
		8	6	1	90
		9	16	18	270
		10	7	8	270
		11	16	13	90
		12	9	8	90
		13	11	8	90
0	6	0	22	23	180
		1	30	32	180
		2	40	35	180
		3	55	65	180
		5	18	20	180
		6	53	50	0
		8	18	17	0
		10	7	10	180
		11	9	6	0
		12	12	12	180
0	7	1	22	19	90
		2	45	46	270
		3	8	10	90
		4	63	62	270
		5	30	27	270
		6	11	7	270
		7	11	11	270
		8	28	30	90
		10	27	26	90
		11	10	9	90
		12	11	7	90
0	8	0	53	54	180
		1	9	10	180
		2	28	25	180
		3	31	33	0
		4	18	16	0
		6	28	21	0
		7	25	25	0
		8	19	18	0
		9	14	11	0
		10	5	5	0
		11	7	3	180
		12	9	8	180
0	9	1	34	34	270
		2	36	39	270
		3	11	10	270
		4	36	34	270
		5	33	27	90
		6	20	15	270
		7	11	8	90
		8	10	6	90
		9	9	4	90
		10	19	15	90
		11	10	8	270
0	10	0	7	6	0
		1	6	2	0
		2	25	23	180
		3	50	48	0
		4	37	33	0
		5	34	26	0
		6	9	3	0
0	10	8	14	12	0
		9	16	15	180
		10	10	7	180
		11	5	5	180
0	11	1	45	43	270
		2	19	17	270
		3	13	7	270
		4	31	27	270
		5	38	34	90
		7	19	13	90
		9	8	4	90
		10	6	6	90
		11	7	6	270
0	12	3	21	14	0
		4	7	2	0
		5	10	9	0
		7	10	8	180
		8	9	5	180
		9	11	8	180
		10	8	6	180
0	13	1	15	9	270
		2	29	18	90
		4	15	13	90
		5	14	10	90
		6	12	9	90
		7	16	11	90
		8	8	5	270
		9	7	4	90
		10	7	7	270
0	14	0	41	35	0
		1	16	17	0
		2	11	11	0
		3	11	8	0
		5	9	7	0
		6	19	13	180
		8	9	7	180
		9	6	5	180
0	15	1	7	8	270
		2	23	16	90
		4	17	10	90
		5	6	3	90
		8	10	11	270
0	16	0	11	5	0
		2	7	6	0
		4	6	5	180
		6	13	11	180
0	17	1	13	8	90
		2	12	8	90
0	18	0	6	6	0
		1	4	3	180
1	0	1	49	47	270
		2	104	115	180
		3	109	120	90
		4	46	34	180
		5	58	49	90
		6	11	8	180
		7	5	3	270
		8	11	7	0
		9	15	13	270
		10	9	9	0
1	0	11	11	11	270
		12	8	6	0
1	1	0	21	17	90
		1	62	70	27
		2	11	17	198
		3	74	78	286
		4	63	57	154
		5	76	69	157
		6	21	23	241
		7	46	33	182
		8	24	27	330
		9	16	17	166
		10	28	32	355
		11	12	12	345
		12	3	4	87
		13	15	12	11
		14	7	6	161
1	2	0	125	144	90
		1	31	27	136
		2	39	28	238
		3	120	116	93
		4	78	79	257
		5	48	46	48
		6	38	41	265
		7	31	19	47
		8	23	21	331
		9	30	30	275
		10	3	8	89
		11	14	19	242
		12	11	9	87
		13	2	4	145
		14	6	6	74
1	3	0	16	25	90
		1	63	68	92
		2	121	109	211
		3	32	36	221
		4	28	28	185
		5	58	60	175
		6	17	14	274
		7	6	5	263
		8	47	46	3
		9	15	11	83
		10	22	19	1
		11	20	19	28
		12	12	11	30
1	4	0	65	77	90
		1	46	60	182
		2	47	56	100
		3	22	15	70
		4	46	40	80
		5	34	33	313
		6	59	56	274
		7	13	11	312
		8	37	31	275
		9	7	1	328
		10	3	5	206
		11	3	5	218
		12	17	11	90
	5	0	9	10	270
		1	30	27	177
1	5	2	82	79	155
		3	37	41	272
		4	57	67	171
		5	52	49	345
		6	18	14	123
		7	24	26	354
		8	21	17	341
		9	15	11	32
		10	21	18	25
		11	11	12	137
		12	12	10	336
1	6	0	45	50	90
		1	40	41	245
		2	37	36	5
		3	48	44	280
		4	30	27	284
		5	15	12	188
		6	38	34	280
		7	16	19	19
		8	25	27	239
		9	16	11	104
		10	11	11	125
		11	15	10	70
		12	3	6	106
		13	6	5	215
1	7	0	17	13	270
		1	47	47	183
		2	15	17	233
		3	9	7	319
		4	23	24	139
		5	23	24	320
		6	24	24	118
		7	38	34	10
		8	12	9	126
		9	11	6	17
		11	9	8	134
		13	10	9	187
1	8	0	12	7	270
		1	28	26	292
		2	21	17	355
		3	41	43	304
		4	3	5	230
		5	25	26	279
		6	23	26	68
		7	23	24	15
		8	16	13	129
		9	28	26	107
		11	16	12	72
		12	6	4	128
1	9	0	29	32	270
		1	43	46	173
		2	33	34	313
		3	22	21	98
		4	20	19	0
		5	44	47	3
		6	11	8	36
		7	28	27	4
		8	3	5	143
		9	13	11	325
		10	11	7	197
1	9	12	10	8	225
1	10	0	44	44	270
		1	23	22	251
		2	22	22	304
		3	22	26	273
		4	13	7	322
		5	24	22	238
		6	10	8	41
		7	11	10	126
		8	9	7	115
		9	11	11	132
1	11	0	11	13	90
		1	20	19	128
		2	22	20	308
		3	17	14	173
		4	14	12	49
		5	16	17	166
		6	16	15	355
		7	6	10	297
		8	21	15	158
		9	3	4	265
		10	16	11	174
1	12	0	42	50	270
		2	12	12	264
		3	21	22	80
		4	18	18	97
		5	11	9	129
		6	27	24	96
		8	13	10	95
		9	7	6	239
		10	4	4	254
1	13	0	23	24	90
		1	9	8	137
		2	22	23	351
		3	9	10	80
		4	22	22	16
		5	13	10	153
		6	3	6	261
		7	8	6	204
		8	11	7	184
		9	9	5	211
		10	4	6	155
1	14	0	3	7	90
		1	11	11	18
		2	3	4	234
		3	21	20	80
		4	3	7	129
		5	10	8	101
		6	14	12	104
		8	9	7	98
1	15	1	19	18	10
		2	3	5	20
		3	3	6	13
		4	3	6	300
		5	3	5	159
		6	2	4	313
		7	4	6	174
		8	4	4	268
1	16	0	3	4	270
		1	10	8	105
1	16	3	16	11	83
1	17	0	6	4	90
		1	10	6	345
		2	7	6	180
		3	6	4	295
		4	8	5	211
		5	7	6	205
1	18	0	8	7	90
		1	1	3	208
		2	4	4	125
2	0	0	143	200	0
		1	6	7	90
		2	134	137	0
		3	78	78	90
		4	40	32	180
		5	54	49	270
		6	28	26	180
		7	54	52	270
		8	26	24	180
		9	30	32	270
		10	7	5	0
		12	7	8	0
		14	7	5	0
2	1	0	68	111	180
		1	67	62	271
		2	59	97	87
		3	150	134	183
		4	36	31	107
		5	10	9	269
		6	22	20	77
		7	23	22	294
		8	38	40	253
		9	22	21	333
		10	22	19	243
		11	12	10	7
		12	7	11	193
		13	5	5	91
		14	7	7	143
2	2	0	7	18	0
		1	105	91	67
		2	79	73	345
		3	77	71	180
		4	14	10	233
		5	49	44	220
		6	41	39	212
		7	3	4	87
		8	22	21	173
		9	12	11	328
		10	11	11	148
		11	8	10	42
		12	12	11	11
		13	5	8	92
		14	3	4	309
2	3	0	84	86	180
		1	97	116	72
		2	79	59	127
		3	17	11	69
		4	23	15	206
		5	62	59	261
		6	39	41	16
2	3	7	33	32	265
		8	27	27	322
		9	14	12	319
		10	3	9	106
		11	10	8	81
		12	10	10	207
		13	12	9	116
		14	4	4	206
2	4	0	31	27	180
		1	82	82	187
		2	61	66	250
		3	42	45	164
		4	58	56	311
		5	54	55	161
		6	27	26	219
		7	6	7	3
		8	19	15	95
		9	21	14	356
		10	8	7	97
		11	16	18	18
		12	5	5	68
		13	5	6	141
2	5	0	94	92	180
		1	58	58	103
		2	33	28	228
		3	31	29	353
		4	70	68	295
		5	40	41	327
		6	49	42	355
		7	46	41	282
		8	13	15	343
		9	15	20	195
		10	12	15	78
		11	10	8	138
		13	6	5	87
2	6	0	32	30	180
		1	31	30	279
		2	57	53	198
		3	58	59	178
		4	40	38	270
		5	12	11	142
		6	27	28	313
		8	24	20	53
		9	14	14	6
		10	19	20	133
		11	6	8	311
		12	6	5	156
		13	8	7	248
2	7	0	9	6	0
		1	37	41	60
		2	45	45	273
		3	38	36	341
		4	42	42	288
		5	12	13	282
		6	3	6	134
		7	3	6	173
		8	14	11	92
		9	11	12	124
		10	16	15	104
		11	7	8	172
2	7	12	12	10	98
2	8	0	37	41	180
		1	39	36	283
		2	22	18	194
		3	28	31	317
		4	17	16	73
		5	21	19	105
		6	31	29	39
		7	25	24	73
		8	21	19	357
		9	6	6	38
		10	3	3	133
		11	7	8	274
		12	8	6	178
2	9	0	32	34	0
		1	26	23	313
		2	23	24	244
		3	20	21	33
		4	26	25	272
		5	29	31	36
		6	20	21	237
		7	11	7	91
		8	11	10	97
		9	6	5	149
		10	14	12	113
		11	7	6	196
2	10	0	17	23	180
		1	26	26	319
		2	34	33	83
		3	27	25	13
		4	33	32	25
		5	31	33	21
		6	16	15	19
		7	12	11	123
		8	8	10	277
		9	13	9	181
2	11	0	12	10	0
		1	33	31	291
		2	11	12	309
		3	19	19	279
		4	20	16	276
		5	13	15	38
		6	14	13	188
		7	16	14	103
		8	15	13	181
		10	2	5	37
		11	5	5	262
2	12	0	21	19	0
		1	14	13	37
		2	21	22	99
		3	28	28	17
		4	13	11	127
		5	3	3	336
		6	3	3	237
		7	11	9	167
		8	12	10	254
		9	9	6	201
		10	10	9	227
2	13	0	12	12	0
		1	11	9	318
2	13	2	3	5	4
		3	9	7	168
		4	8	8	105
		5	11	10	144
		6	8	10	110
		7	15	12	116
		8	2	4	215
		9	5	5	98
2	14	0	34	28	0
		1	16	15	110
		2	6	7	348
		3	11	12	13
		4	8	8	88
		5	12	11	264
		6	14	12	152
		7	9	7	303
		8	6	5	202
		9	7	8	205
2	15	1	3	7	222
		2	13	14	69
		3	10	10	178
		4	10	9	120
		6	2	3	212
		7	2	3	337
		8	5	6	257
2	16	0	8	9	0
		1	3	7	95
		2	6	6	23
		5	7	6	251
		6	11	11	197
2	17	0	2	3	180
		1	2	4	105
		2	2	3	86
		3	5	3	153
		4	5	6	64
2	18	0	6	6	0
		1	5	5	195
		2	3	4	246
3	0	1	75	79	90
		2	67	62	180
		3	80	76	90
		4	31	32	180
		5	41	43	90
		6	35	36	180
		7	29	33	270
		8	25	23	0
		9	10	10	270
		10	28	27	0
		11	10	13	270
		12	10	13	0
		14	3	4	180
3	1	0	69	96	90
		1	56	47	262
		2	44	42	309
		3	17	11	327
		4	36	37	200
		5	23	23	230
		6	28	59	263
		7	31	33	127
		8	27	29	258
3	1	9	2	3	184
		10	15	14	5
		11	8	9	29
		12	9	6	111
		13	8	9	4
		14	5	7	71
3	2	0	73	80	90
		1	42	46	158
		2	93	102	152
		3	55	48	117
		4	96	81	239
		5	41	43	30
		6	26	29	211
		7	27	24	17
		8	30	32	322
		9	12	14	236
		10	5	5	3
		11	10	14	189
		12	8	7	18
		13	8	11	192
3	3	0	44	39	90
		1	46	44	259
		2	43	44	165
		3	64	61	255
		4	29	28	212
		5	47	38	226
		6	15	13	265
		7	13	16	115
		8	25	22	27
		9	30	30	114
		10	15	20	36
		11	15	14	73
		12	7	8	55
3	4	0	33	34	90
		1	79	88	173
		2	78	91	64
		3	37	41	122
		4	4	9	245
		5	49	53	346
		6	28	28	249
		7	30	27	4
		8	15	10	295
		9	21	23	3
		10	14	13	77
		11	7	5	172
		12	11	10	108
		13	10	7	180
3	5	0	16	16	90
		1	36	37	297
		2	16	19	202
		3	57	56	294
		4	24	24	159
		5	33	35	299
		6	13	13	76
		7	12	11	30
		8	19	21	67
		9	26	22	59
		10	10	11	351
		11	11	12	75
		12	6	7	330
3	6	1	41	46	262
		2	19	16	284
		3	25	27	251
		4	40	41	355
		5	30	31	318
		6	17	12	299
		7	17	13	35
		8	21	20	196
		9	15	15	23
		10	15	16	188
		11	11	11	141
		13	6	7	208
3	7	0	59	68	270
		1	62	61	203
		2	21	21	233
		3	22	18	291
		4	37	41	113
		5	17	21	328
		6	40	37	111
		7	33	36	6
		8	16	15	72
		9	8	6	103
		10	2	5	314
		11	2	3	131
		13	3	4	156
3	8	0	21	19	90
		1	27	27	321
		2	37	33	341
		3	8	8	226
		4	30	32	340
		5	26	23	300
		6	10	12	201
		7	9	7	92
		8	11	12	141
		9	10	9	95
		10	18	15	198
		11	5	6	88
3	9	0	41	45	270
		1	45	31	181
		2	41	41	289
		3	26	21	101
		4	16	15	339
		5	21	21	36
		6	26	19	130
		7	12	9	355
		8	20	19	104
		9	2	3	282
		10	8	7	239
		11	14	12	256
		12	8	7	260
3	10	0	13	11	270
		1	10	10	35
		2	26	27	338
		3	14	14	280
		4	23	23	8
		5	27	25	166
		6	8	6	66
		7	16	18	164
		8	10	10	87
		9	11	9	139

TABLE 7. (*Continued.*)

h	k	l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α°
3	10	10	8	7	160
		11	4	4	308
3	11	0	16	19	270
		1	7	9	245
		2	28	18	355
		3	28	31	104
		4	15	12	18
		5	7	7	176
		6	10	12	42
		7	6	8	322
		8	10	11	157
		9	14	12	279
		10	11	9	179
		11	7	8	250
3	12	0	18	23	270
		1	16	19	1
		2	15	19	181
		3	2	3	40
		4	2	4	93
		5	16	16	153
		6	11	14	122
		7	13	10	177
		8	3	4	73
		9	3	3	179
3	13	0	10	12	90
		1	8	7	56
		2	10	13	35
		3	15	17	85
		4	14	14	345
		5	13	12	111
		6	7	7	251
		7	6	6	208
		8	7	5	253
		9	5	6	279
3	14	1	15	18	13
		2	14	13	192
		3	8	9	103
		4	8	9	201
		5	7	8	152
		6	10	10	138
		7	2	5	187
		8	5	5	26
3	15	0	8	10	90
		1	10	9	28
		2	2	5	27
		3	5	6	94
		5	6	7	154
		6	9	8	265
		7	5	5	149
3	16	1	2	3	163
		2	6	6	163
		3	3	5	67
		4	4	4	173
		5	1	4	39
		6	3	4	179
3	17	0	7	8	90
		1	5	5	308
		2	6	7	157
		3	7	8	270
		4	5	6	204
4	0	0	89	101	0
		1	176	155	90
		2	85	68	180
		3	51	47	90
		4	17	12	0
		5	78	77	270
		6	15	12	180
		7	44	48	270
		9	13	17	270
		11	6	4	90
		12	4	4	180
		13	6	6	90
4	1	0	19	22	180
		1	83	90	102
		2	27	22	204
		3	69	67	184
		4	23	22	116
		5	39	40	200
		6	21	24	298
		7	20	21	316
		8	19	19	335
		9	23	24	356
		10	13	19	229
		11	13	16	6
4	2	0	31	22	0
		1	74	84	107
		2	115	111	290
		3	23	22	118
		4	43	44	254
		5	70	70	229
		6	20	22	229
		7	17	15	252
		8	12	14	174
		9	5	6	250
		10	8	11	71
		11	10	12	102
		12	7	7	70
		13	7	6	95
4	3	0	43	45	180
		1	10	4	182
		2	50	52	175
		3	27	26	132
		4	28	29	71
		5	8	8	140
		6	30	29	346
		7	10	17	236
		8	33	38	10
		9	13	9	6
		11	5	7	8
		12	7	8	162
4	4	0	48	53	0
		1	47	50	201
		2	31	45	275
		3	15	12	341
		4	83	81	294
		5	7	9	355
		6	15	18	274
		7	9	13	88
		8	25	29	92
		9	12	15	278
4	4	10	19	18	87
4	5	0	114	114	180
		1	72	75	359
		2	62	65	211
		3	32	29	290
		4	38	39	340
		5	44	47	329
		6	39	39	353
		7	16	19	227
		8	20	25	57
		10	8	9	123
		11	9	12	155
		12	7	6	170
4	6	0	5	4	180
		1	30	34	277
		2	51	61	232
		3	21	25	161
		4	39	39	264
		5	12	15	144
		7	26	29	67
		8	13	12	95
		9	15	19	28
		10	11	10	92
		11	4	6	310
		12	3	5	107
		13	9	10	243
4	7	0	12	14	0
		1	19	22	18
		2	11	11	308
		3	40	49	7
		4	16	20	251
		5	27	31	351
		6	20	20	359
		7	11	13	119
		8	13	18	322
		9	15	17	188
		11	11	11	186
		12	7	9	152
4	8	0	6	7	180
		1	52	53	268
		2	19	22	205
		3	11	15	289
		4	21	20	108
		5	19	21	73
		6	17	22	68
		7	19	19	99
		8	3	6	7
		9	6	7	122
		11	4	5	232
		12	6	7	187
4	9	0	15	17	0
		1	22	23	346
		2	17	19	326
		3	39	45	29
		4	8	13	224
		5	29	30	32
		6	13	13	184
		8	10	9	149
		9	9	11	184
		10	7	9	40
4	9	11	10	9	177
4	10	1	9	9	289
		2	31	36	84
		3	6	9	284
		4	30	34	33
		5	12	11	57
		6	7	6	60
		7	11	12	80
		8	3	5	256
		9	7	6	230
		10	4	7	259
		11	7	7	272
4	11	0	33	37	0
		1	7	7	347
		2	11	13	53
		3	14	18	321
		4	15	19	180
		5	3	6	325
		6	23	26	185
		7	6	4	98
		8	14	15	191
4	12	1	11	12	23
		2	14	18	43
		3	26	30	55
		4	17	21	137
		5	7	9	67
		6	5	6	79
		7	3	4	156
		8	11	10	255
		9	2	3	186
		10	11	11	262
4	13	0	28	29	0
		1	9	10	238
		2	11	15	306
		3	15	18	175
		4	3	5	335
		5	6	7	144
		6	10	10	174
4	14	0	3	6	0
		1	12	14	95
		2	9	7	74
		3	7	8	173
		4	6	9	85
		5	9	11	278
		6	3	5	117
		7	10	7	285
		8	9	4	278
4	15	0	3	4	0
		2	8	9	99
		3	14	16	184
		5	2	4	177
		6	6	4	227
		7	6	6	291
4	16	1	9	11	85
		2	4	5	327
		5	10	10	256
		6	5	6	193
4	17	0	2	3	180
		1	4	6	174
		2	3	4	145
4	17	3	8	8	195
5	0	1	14	12	270
		2	98	84	180
		3	2	7	90
		4	38	39	180
		5	13	1	270
		6	7	2	180
		7	6	5	270
		8	10	12	0
		9	9	12	270
		10	19	24	0
		12	9	9	0
5	1	0	19	32	90
		1	41	50	241
		2	34	36	18
		3	114	90	242
		4	48	39	277
		5	13	15	261
		6	55	52	267
		7	13	13	126
		8	41	41	248
		9	10	11	24
		10	4	5	122
		11	6	8	96
		12	7	12	87
5	2	0	52	53	90
		1	67	68	175
		2	57	52	154
		3	53	50	215
		4	50	55	148
		5	14	18	6
		6	26	31	159
		7	28	31	33
		8	23	23	21
		9	12	12	148
		10	9	10	343
		11	9	9	166
		12	5	7	345
		13	5	7	205
5	3	0	98	92	90
		1	44	33	320
		2	36	28	194
		3	69	61	287
		4	16	17	155
		5	35	41	280
		6	17	16	269
		7	24	25	63
		8	22	25	73
		9	31	30	89
		10	7	7	97
		11	13	18	97
		12	4	5	108
5	4	0	10	5	90
		1	73	65	184
		2	8	9	239
		3	29	31	26
		4	23	24	146
		5	44	48	24
		6	16	21	211
		7	30	36	5
5	4	8	13	14	39
		9	22	20	357
		11	7	7	219
		12	5	8	89
		13	8	8	155
5	5	0	3	5	270
		1	41	40	315
		2	42	37	304
		3	47	51	260
		4	24	28	71
		5	19	14	266
		6	27	28	34
		7	13	14	89
		8	9	9	122
		9	19	20	60
		11	12	14	78
		12	6	8	269
5	6	0	96	64	270
		1	26	26	189
		2	11	17	293
		3	20	16	272
		4	48	44	353
		5	6	2	333
		6	20	21	37
		7	31	34	349
		8	15	15	213
		10	16	15	183
		11	7	7	220
		12	5	5	263
		13	5	10	187
5	7	0	52	54	270
		1	33	32	168
		2	52	55	263
		3	12	16	282
		4	41	40	96
		5	8	12	260
		6	27	32	74
		7	5	10	296
		8	22	22	95
		9	6	5	198
5	8	0	12	13	90
		1	7	5	144
		2	50	55	8
		3	8	3	78
		4	34	34	354
		5	6	6	339
		6	8	5	215
		7	4	6	291
		8	23	23	188
		9	6	5	183
		10	11	12	179
5	9	0	21	26	270
		1	19	19	46
		2	23	24	254
		3	9	7	166
		4	4	7	170
		5	12	13	111
		6	23	23	116
		7	10	9	167
		8	14	14	91
5	9	9	10	8	280
		11	12	9	275
5	10	0	6	3	270
		1	22	22	346
		2	21	25	336
		3	16	16	63
		4	13	11	61
		5	25	26	160
		6	7	7	52
		7	14	16	155
		8	6	7	197
		9	3	5	207
		10	9	8	173
5	11	0	9	6	270
		1	13	13	99
		2	9	10	253
		3	19	19	88
		4	6	8	50
		5	14	13	82
		6	4	6	37
		7	7	8	295
		9	11	9	263
5	12	1	25	26	4
		2	12	14	182
		3	10	10	13
		4	4	6	121
		5	14	16	186
		6	6	6	243
		7	13	14	171
		9	5	6	157
5	13	0	8	10	90
		1	6	6	98
		2	12	13	238
		3	17	20	88
		4	16	2	241
		5	6	8	80
		6	10	10	267
		7	3	5	167
		8	7	6	335
		9	5	8	278
5	14	0	4	7	90
		1	10	9	19
		2	13	13	195
		3	6	8	151
		4	16	16	170
		5	10	11	185
		7	5	4	234
		8	5	5	16
5	15	0	11	13	90
		2	5	7	70
		3	8	8	116
		5	4	5	10
		6	7	6	271
5	16	1	5	6	155
		2	4	6	140
		3	6	7	300
		4	9	9	186
5	17	0	11	13	90
		1	6	4	253
		2	4	5	133
5	17	3	5	5	274
6	0	0	65	78	180
		1	58	66	90
		2	17	23	180
		3	35	39	90
		4	11	14	180
		5	49	44	270
		6	27	26	0
		7	46	44	270
		8	24	24	0
		9	7	12	270
		11	10	11	90
		12	5	1	180
6	1	0	20	30	180
		1	17	20	274
		2	64	48	270
		3	80	76	167
		4	56	45	235
		5	8	10	90
		6	22	20	340
		7	25	23	319
		8	14	10	23
		9	25	22	359
		11	10	8	21
		12	7	8	175
6	2	0	35	31	180
		1	82	83	84
		2	94	85	292
		3	39	32	156
		4	55	50	253
		5	39	37	331
		6	10	11	259
		7	17	20	254
		8	6	7	313
		9	7	7	236
		10	12	13	111
		11	8	10	137
		12	5	6	63
		13	6	7	92
6	3	0	23	33	180
		1	36	34	247
		2	45	48	159
		3	45	37	200
		4	32	28	344
		5	25	24	119
		6	33	33	2
		7	25	24	102
		8	27	28	0
		9	10	7	26
		10	7	8	28
		12	9	8	171
6	4	0	32	23	180
		1	37	36	315
		2	24	22	313
		3	37	37	358
		4	54	56	271
		5	20	16	96
		6	24	24	312
		7	11	12	223
		8	25	23	93
6	4	9	14	16	258
		10	15	18	97
		11	12	10	209
6	5	0	98	84	180
		1	41	30	322
		2	27	28	177
		3	39	31	321
		4	44	37	16
		5	25	28	29
		6	43	39	27
		7	10	8	32
		9	13	16	138
		10	9	7	167
6	6	0	15	12	0
		1	46	46	276
		2	38	34	320
		3	12	9	346
		4	27	29	230
		5	26	26	17
		7	24	22	72
		8	14	12	102
		9	10	9	116
		10	7	10	60
		11	5	6	268
6	7	0	13	17	180
		1	36	36	336
		2	20	22	114
		3	37	37	2
		4	12	9	104
		5	26	30	13
		6	11	14	18
		7	9	9	264
		8	8	11	319
		9	16	15	190
		10	10	9	233
		11	12	11	198
		12	7	7	188
6	8	1	29	33	257
		2	12	14	339
		3	13	13	353
		4	17	15	119
		5	23	17	116
		6	17	16	167
		7	18	19	88
		8	13	15	196
		9	9	8	158
6	9	0	17	18	0
		1	27	26	28
		3	20	19	15
		4	9	7	43
		5	21	24	359
		6	18	18	181
		7	9	6	148
		8	6	2	177
		9	11	11	192
		11	7	6	181
6	10	0	18	16	0
		2	43	38	94
		3	20	23	180
		4	21	19	106
6	10	5	11	10	132
		6	10	7	165
		7	10	12	78
		8	10	7	241
		9	10	8	295
		11	6	7	301
6	11	0	24	23	0
		1	18	16	46
		2	21	20	21
		3	16	17	48
		4	16	13	146
		5	6	6	340
		6	16	16	175
		7	8	5	192
		8	20	16	197
6	12	2	15	16	63
		3	16	16	123
		4	13	16	60
		8	9	6	307
6	13	0	14	16	0
		2	10	10	343
		3	12	11	188
		5	8	9	244
		6	9	11	228
		7	5	4	340
6	14	0	9	9	180
		1	10	11	105
		2	8	8	125
		3	6	6	218
		4	6	8	83
		5	13	11	243
		6	7	6	351
		7	9	7	271
		8	5	7	289
6	15	0	6	7	180
		2	5	6	269
		3	9	7	204
		4	6	4	171
		5	9	8	218
6	16	0	9	9	180
		1	13	14	98
		4	7	7	223
		5	7	8	291
7	0	1	20	19	90
		2	51	50	180
		3	30	29	270
		4	29	25	180
		5	23	17	270
		6	7	5	0
		7	6	2	90
		9	21	25	90
		10	12	14	0
		11	10	10	90
7	1	0	17	25	90
		1	41	46	200
		2	25	19	325
		3	34	25	246
		4	15	10	48
		5	28	29	316
		6	36	34	293
7	1	7	16	13	64
		8	18	15	224
		9	7	8	72
		12	15	13	102
		13	4	5	151
7	2	0	20	26	270
		1	42	46	194
		2	49	51	166
		3	47	45	265
		4	58	52	145
		5	34	32	330
		6	29	34	114
		7	27	26	8
		8	22	26	49
		9	7	6	99
		11	9	10	98
7	3	0	25	25	90
		1	17	21	274
		2	36	33	16
		3	39	37	278
		4	24	26	326
		5	27	24	332
		6	12	11	255
		7	17	16	359
		8	8	10	168
		9	22	27	74
		10	8	10	193
		11	10	9	136
		12	6	4	166
7	4	0	46	54	270
		1	42	46	159
		2	24	23	304
		3	10	9	256
		4	15	13	202
		5	36	34	27
		6	30	29	103
		7	15	18	339
		8	15	13	87
		9	6	7	354
		11	11	9	192
7	5	0	31	32	270
		1	26	24	266
		2	22	24	342
		3	18	19	272
		4	23	26	355
		5	9	12	306
		6	16	14	68
		7	12	13	150
		8	10	10	175
		9	14	17	95
		10	13	12	153
		11	4	5	77
		12	7	6	248
7	6	1	40	37	121
		2	17	17	245
		3	19	22	96
		4	34	38	10
		5	12	9	84
		6	13	13	3
		7	5	8	284
7	6	8	11	9	130
		9	6	6	264
		10	11	10	192
		11	9	8	219
		12	5	5	266
7	7	0	43	43	270
		1	19	23	330
		2	25	23	318
		3	13	10	51
		4	37	36	58
		5	32	30	222
		6	37	35	93
		7	15	16	192
		8	12	13	96
		9	8	9	191
7	8	1	13	11	25
		2	30	28	6
		3	12	16	103
		4	23	28	341
		5	20	19	19
		6	15	15	190
		8	7	6	159
		9	11	12	275
		10	10	12	171
		11	8	7	306
7	9	0	18	17	270
		1	22	25	352
		2	24	25	252
		3	10	8	97
		4	5	6	158
		5	18	18	179
		6	12	12	135
		7	11	12	188
		8	10	12	75
		9	8	6	255
		10	3	5	274
		11	6	5	311
7	10	0	8	11	90
		1	17	14	46
		3	9	9	50
		5	15	16	115
		6	5	8	217
		7	10	13	191
		8	7	6	244
		10	5	5	185
7	11	1	10	9	77
		2	11	11	192
		3	24	26	85
		4	11	12	175
		5	6	6	96
		6	5	6	215
		9	7	7	267
		10	6	8	353
7	12	0	18	19	90
		1	18	18	18
		2	11	13	134
		4	4	6	274
		5	7	7	181
		6	11	11	241
		7	14	15	169

TABLE 7. (*Continued.*)

h	*k*	*l*	$\lvert F_o \rvert$	$\lvert F_c \rvert$	α°
7	12	8	5	5	288
7	13	1	4	8	100
		2	11	11	183
		3	7	7	100
		4	12	9	229
		5	8	11	64
		6	4	5	220
		7	5	4	286
		8	7	7	0
7	14	0	4	6	90
		2	7	7	156
		3	10	10	226
		4	9	8	184
		6	5	5	264
7	15	1	7	8	153
		2	9	9	90
		4	3	5	251
		5	3	5	341
		6	6	7	267
7	16	0	6	5	90
		1	7	7	203
		3	8	8	287
		4	6	6	191
7	17	0	4	7	90
		1	6	5	247
8	0	0	76	73	180
		1	16	23	90
		2	35	34	180
		3	19	16	90
		4	18	12	0
		5	13	16	270
		6	23	22	0
		7	30	28	270
		8	8	4	0
		12	10	9	180
8	1	0	40	54	180
		1	23	24	219
		2	43	41	263
		3	25	21	192
		4	26	20	272
		5	21	22	101
		6	20	20	278
		7	16	14	52
		8	21	21	86
		9	18	17	19
		10	10	10	96
8	2	0	50	55	180
		1	49	45	95
		2	26	23	236
		3	57	45	6
		4	18	15	302
		5	34	28	339
		6	39	36	346
		7	13	10	33
		8	12	8	346
		9	12	13	182
		12	6	7	151
8	3	0	9	7	0
		1	47	55	261
		2	22	19	264
8	3	3	30	22	327
		4	15	14	287
		5	19	17	129
		6	40	38	328
		7	22	21	95
		8	16	18	16
		9	12	10	63
		10	7	5	23
		12	12	11	150
8	4	0	4	7	0
		1	15	15	343
		2	23	21	244
		3	49	44	3
		4	27	23	272
		5	6	8	297
		6	11	7	83
		7	10	9	227
		9	18	17	227
		11	8	8	168
8	5	0	25	22	180
		1	34	32	306
		2	31	29	112
		3	9	9	279
		4	48	45	60
		5	31	26	28
		6	16	12	359
		7	27	26	102
		8	8	3	147
		9	10	11	154
		10	8	7	260
		11	11	9	251
8	6	0	24	23	0
		1	48	42	316
		2	21	18	3
		3	37	33	0
		4	19	21	275
		5	17	17	326
		6	16	19	186
		7	12	12	144
		8	11	11	133
		9	12	10	180
		11	7	5	232
8	7	0	6	8	180
		1	14	12	315
		2	29	27	131
		3	40	36	14
		4	25	25	105
		5	10	5	97
		6	16	12	139
		9	9	8	209
		10	9	8	246
8	8	0	33	29	0
		2	29	29	321
		3	7	8	182
		4	11	9	128
		5	15	12	55
		6	15	17	147
		7	16	17	103
		8	15	15	189
8	9	0	20	17	0
8	9	1	13	14	62
		2	21	17	74
		4	25	23	121
		5	16	16	309
		6	9	6	175
		8	10	7	288
		10	9	10	274
8	10	0	11	9	0
		2	25	21	75
		3	16	17	147
		4	24	23	137
		5	18	18	144
		6	10	8	190
		9	8	7	331
		10	5	6	316
8	11	1	23	24	82
		2	10	13	15
		3	9	7	50
		5	8	10	313
		7	8	8	259
8	12	0	14	12	180
		1	11	10	160
		2	12	11	43
		3	17	15	170
		4	7	9	104
		5	11	11	200
		7	7	5	322
		9	4	7	340
8	13	0	8	8	0
		1	10	9	84
		5	12	10	254
		7	10	9	298
8	14	0	8	7	180
		1	7	8	102
		2	7	6	218
		5	7	6	242
		6	5	5	16
		7	4	7	256
8	15	2	11	10	251
		3	6	5	214
		4	8	8	242
8	16	0	10	9	180
		1	7	7	66
		2	5	6	199
9	0	1	2	5	270
		2	9	11	180
		3	47	47	270
		4	21	24	180
		5	20	19	270
		7	16	17	90
		8	15	15	180
		9	24	30	90
		10	6	7	0
		11	4	7	90
9	1	0	13	13	270
		1	21	29	201
		2	25	22	34
		3	11	6	272
		4	23	20	324
		5	41	36	5
9	1	6	16	16	17
		7	24	23	38
		8	5	5	4
		9	8	10	0
		10	6	7	150
		11	5	8	168
		12	4	3	122
9	2	0	36	48	270
		1	10	14	168
		2	25	23	252
		3	41	36	272
		4	11	14	134
		5	9	7	314
		6	16	18	106
		7	23	20	321
		8	8	7	41
		9	9	9	115
		11	6	7	91
		12	6	8	274
9	3	0	3	8	90
		1	10	11	181
		2	47	43	355
		3	16	10	140
		4	43	46	345
		6	14	10	253
		7	10	8	20
		8	22	21	163
		9	7	6	104
		10	14	15	179
		11	5	6	153
9	4	0	42	33	270
		1	37	32	246
		2	34	33	307
		3	25	20	289
		4	20	18	83
		5	5	7	273
		6	33	32	98
		7	7	6	64
		8	12	17	91
		12	5	9	285
9	5	1	15	13	268
		2	19	20	318
		3	18	18	248
		4	8	15	334
		6	7	3	345
		7	15	15	161
		8	10	11	161
		10	9	10	162
		12	3	7	208
9	6	1	32	29	96
		2	7	3	207
		3	40	36	103
		4	12	11	34
		5	28	24	164
		6	18	17	88
		7	6	8	351
		9	10	10	253
		11	4	5	255
9	7	1	54	51	3
		2	17	14	345
9	7	3	11	13	321
		4	26	23	67
		5	11	12	178
		6	13	12	53
		7	21	24	178
		11	6	7	347
9	8	0	25	20	270
		1	23	24	50
		2	17	18	282
		3	16	17	67
		5	23	22	74
		6	7	9	256
		7	10	11	259
		9	13	13	274
		10	4	4	243
		11	3	6	302
9	9	0	13	7	270
		1	18	18	39
		2	12	12	230
		3	10	12	210
		4	5	7	191
		5	10	10	160
		6	5	6	356
		7	12	16	189
9	10	0	26	29	90
		1	7	7	45
		2	5	7	60
		3	11	9	65
		4	10	11	194
		5	6	7	110
		6	9	12	256
		7	6	4	283
		8	10	8	245
		9	4	3	281
9	11	2	9	11	193
		4	13	16	199
		5	6	7	101
		6	7	5	199
		7	4	6	167
		8	8	7	352
		9	4	5	277
9	12	0	19	21	90
		1	6	5	42
		2	14	14	118
		3	5	6	228
		4	6	6	243
		6	5	8	280
		8	4	6	260
9	13	2	10	11	191
		4	7	9	172
		5	5	7	8
		6	4	3	277
		7	4	5	3
9	14	1	6	8	267
		3	8	8	250
		4	6	6	211
		5	5	7	255
		6	6	9	293
9	15	1	8	9	182
		2	4	3	153
9	15	4	4	5	191
10	0	0	92	88	180
		1	12	10	90
		2	20	22	180
		4	19	18	0
		5	15	10	90
		6	11	15	0
		9	5	6	90
		12	4	6	180
10	1	0	10	15	0
		1	4	10	293
		2	24	26	305
		3	12	11	324
		4	21	27	263
		5	14	14	93
		6	5	5	37
		7	19	18	71
		8	11	12	80
		9	7	6	104
		10	12	11	93
10	2	0	13	23	180
		1	21	23	22
		2	8	10	156
		3	36	31	356
		4	10	12	123
		5	35	34	13
		6	38	36	23
		7	5	2	272
		8	17	22	348
		9	9	11	155
		11	4	5	221
		12	4	7	192
10	3	0	47	41	0
		1	34	40	270
		2	36	29	262
		3	19	15	343
		4	43	32	318
		5	15	13	23
		6	11	10	122
		7	9	11	75
		8	7	7	3
10	4	1	24	24	329
		2	7	7	28
		3	19	20	322
		4	22	19	199
		5	17	16	8
		6	8	8	214
		7	10	11	265
		8	5	3	203
		9	12	14	189
		10	5	5	326
		11	6	7	190
10	5	0	8	7	180
		1	35	33	283
		2	34	27	93
		3	7	7	186
		4	23	22	98
		5	23	21	92
		6	8	5	222
		7	21	21	95
10	5	8	8	7	186
		11	8	10	263
10	6	1	24	25	22
		2	24	26	9
		3	26	23	2
		4	11	11	149
		5	5	7	330
		6	18	17	178
		7	8	7	182
		8	8	7	182
		9	10	10	181
10	7	0	9	7	180
		1	11	9	310
		2	10	10	50
		3	9	6	116
		4	27	27	121
		5	19	18	103
		6	10	11	87
		7	11	9	143
		10	8	9	283
10	8	0	26	25	0
		1	23	21	149
		2	23	23	347
		3	17	18	158
		4	8	9	138
		6	5	6	157
		7	5	4	324
10	9	0	8	6	0
		2	25	22	88
		3	9	5	194
		4	20	24	89
		5	9	7	284
		6	5	2	191
		7	10	12	293
		8	7	7	286
		9	4	0	283
		10	3	11	272
10	10	0	5	5	0
		1	5	3	189
		2	6	3	71
		3	8	11	191
		4	8	8	188
		5	7	9	186
		6	5	6	173
		9	4	5	328
10	11	0	9	10	180
		1	17	18	107
		3	5	5	3
		4	9	6	166
		5	10	9	261
		7	11	11	291
10	12	0	7	7	180
		1	9	10	148
		2	5	3	200
		3	14	14	165
		5	6	9	166
		7	6	4	330
10	13	1	8	8	100
		4	7	7	337
		5	6	6	271
10	13	6	4	3	287
10	14	0	4	5	180
		1	4	6	157
		2	7	7	208
		3	5	5	207
		4	4	3	286
11	0	1	19	21	270
		2	7	6	0
		3	20	23	270
		4	15	7	180
		5	19	18	270
		7	17	13	90
		8	11	15	180
		9	10	12	90
		10	8	8	180
11	1	0	15	24	270
		1	10	17	159
		2	11	8	245
		3	15	14	76
		4	8	9	2
		5	16	15	25
		6	17	16	35
		7	20	22	14
		10	7	7	176
11	2	0	27	32	270
		1	11	11	275
		2	19	16	278
		3	12	15	262
		4	27	24	63
		5	17	17	237
		6	6	5	34
		7	12	13	190
		9	8	9	150
		10	5	5	200
11	3	0	16	10	270
		1	2	6	144
		2	38	35	1
		3	17	15	80
		4	35	32	11
		5	3	5	33
		6	12	10	139
		8	13	13	144
		10	8	11	170
11	4	0	26	21	270
		1	17	15	351
		2	31	25	283
		3	32	27	265
		4	8	5	231
		5	10	9	104
		6	18	23	77
		7	10	12	179
		8	8	11	82
		10	5	6	315
11	5	0	10	10	270
		1	3	7	7
		2	9	4	326
		3	19	14	148
		4	16	17	342
		5	13	11	151
		6	8	4	102
11	5	7	11	13	195
		9	7	8	248
		10	7	8	183
11	6	0	7	0	267
		1	33	28	90
		2	7	12	194
		3	10	9	111
		4	27	22	116
		5	11	10	106
		6	6	9	92
		7	7	5	257
		8	5	6	70
11	7	0	10	6	90
		1	35	28	7
		2	12	13	95
		3	17	13	59
		4	6	6	16
		5	7	9	164
		6	6	9	284
		7	14	16	189
		8	6	5	278
11	8	0	22	19	270
		1	14	13	72
		2	10	11	143
		3	14	16	76
		4	5	7	223
		5	8	12	46
		7	10	9	212
		9	7	10	268
11	9	0	7	7	90
		1	13	14	10
		2	6	9	114
		3	6	1	61
		4	8	10	223
		5	9	10	206
11	10	0	6	10	90
		1	4	2	54
		2	7	10	91
		3	6	6	55
		4	10	9	223
		5	8	8	60
		6	9	8	237
		7	4	5	323
		8	6	7	265
11	11	0	4	6	270
		1	6	7	291
		2	7	9	171
		3	8	7	299
		4	11	11	221
11	12	0	10	10	90
		1	5	7	168
		2	9	8	129
		3	8	6	227
		4	3	4	267
		5	7	8	300
		6	7	9	251
11	13	1	3	5	203
		2	8	8	179
		4	4	6	184
		5	5	5	312
11	14	0	5	4	90
		1	2	6	214
		3	5	8	264
12	0	0	34	36	180
		1	2	6	270
		2	24	21	180
		3	10	8	270
		4	23	21	0
		5	8	9	90
		6	13	15	0
		7	13	17	90
		9	3	4	90
12	1	0	6	7	0
		1	10	10	350
		2	25	21	357
		3	22	23	354
		4	11	12	226
		5	7	9	8
		8	7	10	83
		9	3	5	146
		10	7	8	97
12	2	0	5	4	180
		1	18	20	281
		2	13	15	160
		3	15	12	58
		4	16	16	66
		5	18	16	24
		6	9	11	34
		7	5	6	129
		8	7	9	19
		10	6	7	280
12	3	0	19	20	0
		1	29	27	233
		2	30	26	0
		3	11	12	350
		5	13	11	16
		6	4	8	173
		7	11	15	46
		8	14	12	165
		9	6	6	219
12	4	0	5	2	180
		1	28	20	336
		2	15	15	112
		3	16	17	359
		4	14	16	126
		5	4	7	23
		6	7	6	261
		8	10	9	224
12	5	1	6	9	246
		2	10	12	41
		3	14	12	158
		4	16	15	99
		5	14	15	144
		6	6	9	211
		7	17	17	104
		8	5	6	206
12	6	1	18	17	68
		2	25	20	44
		3	12	13	357
		4	13	12	99
12	6	5	4	6	301
		6	4	6	145
		7	9	7	223
		8	7	6	262
		9	3	6	196
		10	4	5	326
12	7	0	9	6	0
		1	22	22	194
		2	9	10	107
		3	5	3	92
		4	10	12	92
		5	12	15	166
		6	5	4	171
		9	5	3	326
12	8	0	6	8	0
		1	19	16	128
		2	12	10	30
		3	6	4	121
		7	13	14	264
		8	5	3	189
12	9	0	4	6	180
		1	7	8	116
		2	9	9	118
		3	9	9	231
		4	7	11	68
		5	12	10	263
12	10	0	4	6	0
		1	7	6	113
		2	5	7	255
		3	6	6	203
		4	15	14	223
		5	10	10	214
		7	5	6	289
12	11	0	12	12	180
		1	6	9	101
		2	9	8	163
		3	3	4	142
		6	2	4	35
		7	4	5	290
12	12	0	6	5	180
		1	5	5	145
		2	3	5	260
		3	4	7	157
12	13	0	3	4	180
		3	2	3	333
		4	4	6	325
12	14	0	5	7	180
13	1	0	18	18	270
13	2	0	12	15	270
13	3	0	6	8	270
13	5	0	7	4	270
13	8	0	13	11	90
13	9	0	6	12	90
14	0	0	26	25	180
		1	24	23	270
14	1	0	10	5	180
14	3	0	14	21	0
14	5	0	18	21	0
14	11	0	9	11	180
15	1	0	11	17	270
15	2	0	10	10	270
15	3	0	4	1	270
15	5	0	12	12	90
16	0	0	11	7	180
16	2	0	13	13	0
16	5	0	11	12	0
16	8	0	4	4	180
17	1	0	4	7	270
17	2	0	3	4	90
17	3	0	5	5	270
17	4	0	8	9	90
17	5	0	4	7	90
18	0	0	10	9	0
18	1	0	11	8	0
18	2	0	6	1	180

for the carbon, nitrogen, and oxygen atoms an isotropic value was deduced for each of these atoms from the anisotropic parameters. These isotropic values are in good agreement with those deduced from the second difference Fourier synthesis and they are listed with the anisotropic temperature-factor parameters for the bromide ion and the final atomic co-ordinates in Table 2.

The final set of structure factors based on the co-ordinates and temperature factors of Table 2 was then calculated; the value of R was 13·4%. The final values of $|F_o|$, $|F_c|$, and α are shown in Table 7, and the course of the analysis is summarized in Table 1. The final three-dimensional electron-density distribution evaluated on the basis of the phase constants of Table 7 is shown in Fig. 1 by means of superimposed contour sections drawn parallel to (001).

For the structure-factor calculations theoretical atomic scattering factors were used; those of Berghuis *et al.*[58] for carbon, oxygen, and nitrogen, and the Thomas–Fermi values [59] for bromine were chosen.

The standard deviations of the final atomic co-ordinates were derived from the least-squares residuals by application of the equation

$$\sigma^2(x_i) = \sum_j w_j(\Delta F_j)^2/[(n - s) \sum w_j(F_j/\partial x_i)^2].$$

The results are listed in Table 4.

Calculations were performed on the Glasgow University DEUCE computer with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. We thank the University of Glasgow for an I.C.I. Research Fellowship (to T. A. H.) and the Department of Scientific and Industrial Research for a maintenance grant (to J. A. H.).

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

[59] "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Borntraeger, Berlin, 1935, Vol. II, p. 572.