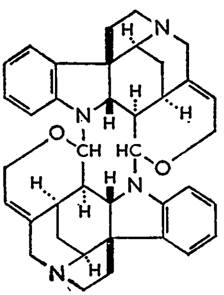
313. *The Structure of Caracurine-II: X-Ray Analysis of Caracurine-II Dimethiodide*

By A. T. McPhail and G. A. Sim

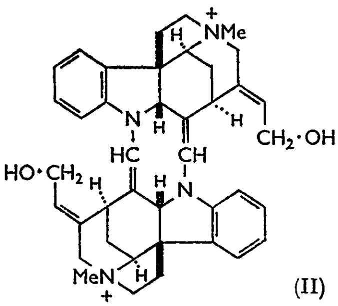
The alkaloid caracurine-II, isolated from *Strychnos toxifera*, has been shown by an *X*-ray study of the dimethiodide to have structure (III). The crystals of the dimethiodide are orthorhombic, space group $P2_12_12_1$, with four molecules of $C_{40}H_{44}I_2N_4O_2$ in the unit cell of dimensions $a = 18{\cdot}59$, $b = 27{\cdot}44$, $c = 7{\cdot}52$ Å. Phase determination was based initially on the iodine atoms and Fourier methods were employed for the assignment of co-ordinates to the carbon, nitrogen, and oxygen atoms.

The bark of *Strychnos toxifera* from British Guiana is the source of a number of quaternary alkaloids. In 1949 King reported the isolation of toxiferines I—XII,[1] while at a later date Battersby and his colleagues [2] re-examined the bark and showed that toxiferine-IX is identical with the dimethochloride of the tertiary base caracurine-II which Asmis, Schmid, and Karrer had isolated from Venezuelan *Strychnos toxifera*.[3]

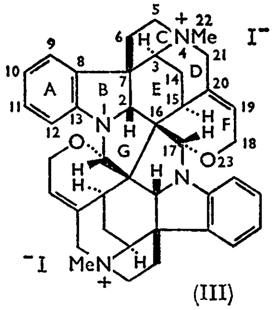
It was clear that caracurine-II is closely related to a number of other curare alkaloids, for treatment of caracurine-V (I) with aqueous acid in the presence of oxygen yields caracurine-VII and caracurine-II,[4] while similar treatment of toxiferine-I [5,6] (II) affords hemitoxiferine-I and caracurine-II dimethochloride.[6]



(I)



(II)



(III)

At the suggestion of Professor A. R. Battersby we undertook an *X*-ray investigation of the structure of caracurine-II while chemical and spectroscopic studies continued at Bristol and Zurich. Initially we examined crystals of the dimethochloride and dimethobromide which are isomorphous and monoclinic: good crystals of the chloride were obtained but the bromide proved much less suitable and though we were able to assign co-ordinates to the halogen ions the limited intensity data available frustrated our attempts to solve the crystal structure.

We next obtained crystals of the dimethiodide which proved not to be isomorphous with the chloride and bromide, but to belong to the orthorhombic system. The crystals, like those of the bromide, gave only a limited number of reflexions and the crystal-structure determination was effected with a total of 1285 $|F_o|$ values. The phase-determining heavy-atom method [7] was employed and a number of three-dimensional electron-density

---

[1] King, *J.*, 1949, 3263.

[2] Battersby, Binks, Hodson, and Yeowell, *J.*, 1960, 1848.

[3] Asmis, Schmid, and Karrer, *Helv. Chim. Acta*, 1954, **37**, 1983.

[4] Asmis, Bächli, Schmid, and Karrer, *Helv. Chim. Acta*, 1954, **37**, 1993.

[5] Bernauer, Berlage, von Philipsborn, Schmid, and Karrer, *Helv. Chim. Acta*, 1958, **41**, 2293; Battersby and Hodson, *Proc. Chem. Soc.*, 1958, 287; Boekelheide, Ceder, Crabb, Kawazoe, and Knowles, *Tetrahedron Letters*, 1960, No. 26, 1; Arnold, Hesse, Hiltebrand, Melera, von Philipsborn, Schmid, and Karrer, *Helv. Chim. Acta*, 1961, **44**, 620.

[6] Battersby and Hodson, *J.*, 1960, 786.

[7] 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.

distributions were evaluated. The course of the analysis is described in the Experimental section.

Our final results establish the constitution and relative stereochemistry of caracurine-II dimethiodide to be as in (III). The studies at Bristol and Zurich reached identical conclusions and preliminary reports of the independent investigations have been published together.[8]

TABLE 1

Atomic co-ordinates and temperature factors

	x/a	y/b	z/c	B		x/a	y/b	z/c	B
N(1)	0·3496	0·3632	0·2751	3·1	N(1′)	0·4765	0·2736	0·2479	3·7
C(2)	0·4265	0·3765	0·3116	3·0	C(2′)	0·4175	0·2669	0·1268	3·4
C(3)	0·4817	0·4650	0·2205	4·1	C(3′)	0·4466	0·2319	−0·1796	3·3
N(4)	0·5489	0·4694	0·2702	3·6	N(4′)	0·3839	0·2254	−0·3014	4·2
C(5)	0·5474	0·4488	0·4529	4·2	C(5′)	0·3281	0·2104	−0·1801	4·7
C(6)	0·4856	0·4416	0·5220	3·9	C(6′)	0·3589	0·1890	−0·0026	3·2
C(7)	0·4291	0·4293	0·3498	3·1	C(7′)	0·4305	0·2312	0·0175	3·8
C(8)	0·3518	0·4380	0·3842	3·4	C(8′)	0·4872	0·1979	0·1150	2·5
C(9)	0·3138	0·4834	0·4519	4·6	C(9′)	0·5149	0·1518	0·1082	5·8
C(10)	0·2425	0·4813	0·4592	3·8	C(10′)	0·5698	0·1396	0·2364	3·8
C(11)	0·2068	0·4411	0·4158	5·8	C(11′)	0·5822	0·1712	0·3612	3·0
C(12)	0·2366	0·3952	0·3707	5·5	C(12′)	0·5638	0·2135	0·3689	3·3
C(13)	0·3125	0·3983	0·3411	4·5	C(13′)	0·5035	0·2274	0·2497	4·9
C(14)	0·4637	0·4440	0·0281	4·6	C(14′)	0·4777	0·2858	−0·2093	4·3
C(15)	0·5148	0·3914	0·0338	2·4	C(15′)	0·4183	0·3222	−0·1699	2·2
C(16)	0·4693	0·3503	0·1452	3·7	C(16′)	0·4086	0·3172	0·0454	3·1
C(17)	0·5215	0·3149	0·2067	3·7	C(17′)	0·3452	0·3500	0·0823	5·4
C(18)	0·6302	0·3284	0·0855	4·3	C(18′)	0·2823	0·3771	−0·1714	2·9
C(19)	0·6434	0·3795	0·1589	4·5	C(19′)	0·2967	0·3991	−0·2898	5·2
C(20)	0·5892	0·4011	0·1028	4·1	C(20′)	0·3560	0·3066	−0·2646	3·7
C(21)	0·6068	0·4571	0·1618	4·3	C(21′)	0·3529	0·2713	−0·3870	3·4
C(22)	0·5477	0·5249	0·2873	6·3	C(22′)	0·3910	0·1826	−0·4271	3·7
O(23)	0·5771	0·2966	0·0846	3·4	O(23′)	0·3291	0·3878	−0·0320	4·4
I(24)	0·5107	0·5633	−0·1980	†	I(24′)	0·1849	0·1788	−0·6185	†

† For the iodide ions anisotropic temperature factors were employed. These were of the form

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

with parameters

	b_{11}	b_{22}	b_{33}	b_{12}	b_{23}	b_{13}
I(24)	0·01089	0·00282	0·03170	−0·00027	0·00031	−0·00112
I(24′)	0·00867	0·00502	0·03229	−0·00020	0·00073	0·00129

The final three-dimensional electron-density distribution is shown in Fig. 1 as superimposed contour sections drawn parallel to (001) and covering the region of one molecule; the corresponding atomic arrangement is explained in Fig. 2. The interatomic distances and valency angles calculated from the final atomic co-ordinates (see Table 1) are listed in Table 2. The standard deviations of the final atomic co-ordinates are about 0·008 Å for the iodide ions and 0·07 Å for the carbon nitrogen, and oxygen atoms; from these results the average estimated standard deviation (e.s.d.) of a carbon–carbon bond length is about 0·10 Å and the average e.s.d. of a valency angle about 5°.

Examination of the bond lengths, valency angles, non-bonded interactions, etc., shows that the molecule probably does not deviate from two-fold symmetry (C_2) in the crystal.

The average bond length in the benzene rings, 1·38 Å, and the average carbon–carbon single bond length, 1·54 Å, do not differ significantly from accepted values. The average sp^3-carbon–nitrogen bond length of 1·46 Å is not different from the usual carbon–nitrogen single bond length of 1·47 Å,[9] whereas the average sp^2-carbon–nitrogen distance, as in other alkaloids, is considerably smaller. Because of the large standard deviations of the bond lengths, none of the differences between chemically equivalent bonds is significant.

---

[8] Battersby, Hodson, Rao, and Yeowell, *Proc. Chem. Soc.*, 1961, 412; Battersby, Yeowell, Jackman, Schroeder, Hesse, Hiltebrand, von Philipsborn, Schmid, and Karrer, *Proc. Chem. Soc.*, 1961, 413; McPhail and Sim, *ibid.*, p. 416.

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

In order to analyse the conformation of the molecule we calculated, by the method of Schomaker *et al.*,[10] the mean planes through various sets of atoms; the deviations of the atoms from these planes are shown in Table 3. The cyclohexane rings E and E′ do not adopt the normal chair conformation but are considerably flattened; atoms 2, 7, 3, 15, and 16 are closely coplanar while the average displacement of atom 14 from the plane of these atoms is 0·93 Å. The piperidine rings D and D′ are in the boat conformation with atoms 3, 4, 15, and 20 coplanar and atoms 14 and 21 displaced, by average amounts of 0·57 and 0·72 Å, respectively, from the plane through 3, 4, 15, and 20. In rings C and C′ atoms 3, 4, 5, and 7 are coplanar and the average displacement of atom 6 is 0·61 Å. The atoms of

TABLE 2

Interatomic distances (Å) and angles

Intramolecular bonded distances

N(1)–C(2)	1·50	C(8)–C(13)	1·35	N(1′)–C(2′)	1·44	C(8′)–C(13′)	1·33
N(1)–C(13)	1·28	C(9)–C(10)	1·33	N(1′)–C(13′)	1·36	C(9′)–C(10′)	1·44
N(1)–C(17′)	1·50	C(10)–C(11)	1·33	N(1′)–C(17)	1·44	C(10′)–C(11′)	1·30
C(2)–C(7)	1·48	C(11)–C(12)	1·42	C(2′)–C(7′)	1·30	C(11′)–C(12′)	1·21
C(2)–C(16)	1·65	C(12)–C(13)	1·43	C(2′)–C(16′)	1·52	C(12′)–C(13′)	1·49
C(3)–N(4)	1·31	C(14)–C(15)	1·73	C(3′)–N(4′)	1·49	C(14′)–C(15′)	1·52
C(3)–C(7)	1·69	C(15)–C(16)	1·64	C(3′)–C(7′)	1·51	C(15′)–C(16′)	1·63
C(3)–C(14)	1·59	C(15)–C(20)	1·50	C(3′)–C(14′)	1·60	C(15′)–C(20′)	1·42
N(4)–C(5)	1·49	C(16)–C(17)	1·45	N(4′)–C(5′)	1·44	C(16′)–C(17′)	1·51
N(4)–C(21)	1·39	C(17)–O(23)	1·47	N(4′)–C(21′)	1·53	C(17′)–O(23′)	1·38
N(4)–C(22)	1·53	C(18)–C(19)	1·53	N(4′)–C(22′)	1·51	C(18′)–C(19′)	1·40
C(5)–C(6)	1·27	C(18)–O(23)	1·32	C(5′)–C(6′)	1·57	C(18′)–O(23′)	1·39
C(6)–C(7)	1·70	C(19)–C(20)	1·24	C(6′)–C(7′)	1·77	C(19′)–C(20′)	1·43
C(7)–C(8)	1·48	C(20)–C(21)	1·63	C(7′)–C(8′)	1·58	C(20′)–C(21′)	1·34
C(8)–C(9)	1·52	C(16)–C(16′)	1·63	C(8′)–C(9′)	1·37		

Intramolecular non-bonded distances

N(1) ··· C(14)	3·59	C(6) ··· C(14)	3·74	N(1′) ··· C(14′)	3·45	N(4′) ··· C(16′)	3·66
N(1) ··· C(15)	3·65	C(6) ··· C(16)	3·79	N(1′) ··· C(15′)	3·58	C(5′) ··· C(14′)	3·47
N(1) ··· C(17)	3·50	C(6) ··· C(21)	3·55	N(1′) ··· C(17′)	3·45	C(5′) ··· C(15′)	3·50
N(1) ··· N(1′)	3·42	C(6) ··· C(22)	3·11			C(5′) ··· C(20′)	2·77
N(1) ··· C(2′)	3·13	C(7) ··· C(21)	3·67	N(1′) ··· C(2)	3·01	C(6′) ··· C(14′)	3·79
N(1) ··· C(18′)	3·60	C(7) ··· C(22)	3·46	N(1′) ··· C(18)	3·45	C(6′) ··· C(16′)	3·65
C(2) ··· N(4)	3·43	C(7) ··· C(17′)	3·35	C(2′) ··· N(4′)	3·47	C(6′) ··· C(21′)	3·67
C(2) ··· C(5)	3·18	C(7) ··· O(23′)	3·60	C(2′) ··· C(5′)	3·24	C(6′) ··· C(22′)	3·25
C(2) ··· C(20)	3·47	C(14) ·· C(22)	3·34	C(2′) ··· C(20′)	3·34	C(7′) ··· C(21′)	3·54
C(2) ··· C(2′)	3·32	C(14) ·· C(17′)	3·41			C(7′) ··· C(22′)	3·67
N(4) ··· C(16)	3·71	C(14) ·· O(23′)	2·97			C(7′) ··· C(17)	3·19
C(5) ··· C(14)	3·56	C(15) ·· C(17′)	3·37			C(7′) ··· O(23)	3·30
C(5) ··· C(15)	3·58	C(15) ·· O(23′)	3·47			C(14′) ·· C(22′)	3·65
C(5) ··· C(20)	3·04	C(16) ·· C(21)	3·89			C(14′) ·· C(17)	3·33
		C(17) ·· C(17′)	3·54			C(14′) ·· O(23)	2·90
						C(15′) ·· C(17)	3·43
						C(15′) ·· O(23)	3·59
						C(16′) ·· C(21′)	3·64

Intermolecular distances (<4 Å)

I(24′) ··· C(18)$_{\rm I}$	3·66	C(22) ··· C(10′)$_{\rm II}$	3·84	C(5′) ··· C(18)$_{\rm V}$	3·90	I(24) ·· C(9′)$_{\rm IV}$	3·96
C(22) ··· C(9′)$_{\rm II}$	3·75	I(24) ··· C(22′)$_{\rm IV}$	3·87	C(10) ··· C(10)$_{\rm III}$	3·91	C(9) ··· C(10)$_{\rm III}$	3·97
O(23′) ·· C(10)$_{\rm III}$	3·83	I(24′) ·· C(19)$_{\rm V}$	3·89	C(11′) ·· C(12)$_{\rm VI}$	3·95		

Shortest $N^+ \cdots I^-$ *distances*

N(4) ··· I(24)	4·42	N(4) ··· I(24)$_{\rm VII}$	4·81
N(4′) ··· I(24′)	4·58	N(4′) ·· I(24)$_{\rm IV}$	4·86

The subscripts refer to the following positions:

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

---

[10] Schomaker, Waser, Marsh, and Bergman, *Acta Cryst.*, 1959, **12**, 600.

TABLE 2 (*Continued*)

Interbond angles

C(2)N(1)C(13)	105°	C(9)C(10)C(11)	122°	C(2′)N(1′)C(13′)	100°	C(9′)C(10′)C(11′)	117°
C(2)N(1)C(17′)	107	C(10)C(11)C(12)	127	C(2′)N(1′)C(17)	114	C(10′)C(11′)C(12′)	129
C(13)N(1)C(17′)	122	C(11)C(12)C(13)	112	C(13′)N(1′)C(17)	121	C(11′)C(12′)C(13′)	116
N(1)C(2)C(7)	108	N(1)C(13)C(8)	114	N(1′)C(2′)C(7′)	111	N(1′)C(13′)C(8′)	118
N(1)C(2)C(16)	102	N(1)C(13)C(12)	123	N(1′)C(2′)C(16′)	103	N(1′)C(13′)C(12′)	122
C(7)C(2)C(16)	124	C(18)C(13)C(12)	123	C(7′)C(2′)C(16′)	117	C(8′)C(13′)C(12′)	118
N(4)C(3)C(7)	116	C(3)C(14)C(15)	99	N(4′)C(3′)C(7′)	116	C(3′)C(14′)C(15′)	109
N(4)C(3)C(14)	120	C(14)C(15)C(16)	108	N(4′)C(3′)C(14′)	108	C(14′)C(15′)C(16′)	103
C(7)C(3)C(14)	101	C(14)C(15)C(20)	112	C(7′)C(3′)C(14′)	103	C(14′)C(15′)C(20′)	107
C(3)N(4)C(5)	102	C(16)C(15)C(20)	115	C(3′)N(4′)C(5′)	102	C(16′)C(15′)C(20′)	112
C(3)N(4)C(21)	123	C(2)C(16)C(15)	110	C(3′)N(4′)C(21′)	117	C(2′)C(16′)C(15′)	118
C(3)N(4)C(22)	96	C(2)C(16)C(17)	112	C(3′)N(4′)C(22′)	114	C(2′)C(16′)C(17′)	124
C(5)N(4)C(21)	118	C(2)C(16)C(16′)	105	C(5′)N(4′)C(21′)	103	C(2′)C(16′)C(16)	104
C(5)N(4)C(22)	108	C(15)C(16)C(17)	106	C(5′)N(4′)C(22′)	104	C(15′)C(16′)C(17′)	103
C(21)N(4)C(22)	108	C(15)C(16)C(16′)	120	C(21′)N(4′)C(22′)	114	C(15′)C(16′)C(16)	109
N(4)C(5)C(6)	117	C(17)C(16)C(16′)	104	N(4′)C(5′)C(6′)	113	C(17′)C(16′)C(16)	97
C(5)C(6)C(7)	106	C(16)C(17)O(23)	120	C(5′)C(6′)C(7′)	96	C(16′)C(17′)O(23′)	120
C(2)C(7)C(3)	118	C(16)C(17)N(1′)	102	C(2′)C(7′)C(3′)	130	C(16′)C(17′)N(1)	106
C(2)C(7)C(6)	111	O(23)C(17)N(1′)	106	C(2′)C(7′)C(6′)	114	O(23′)C(17′)N(1)	116
C(2)C(7)C(8)	99	C(19)C(18)O(23)	137	C(2′)C(7′)C(8′)	105	C(19′)C(18′)O(23′)	121
C(3)C(7)C(6)	88	C(18)C(19)C(20)	101	C(3′)C(7′)C(6′)	94	C(18′)C(19′)C(20′)	122
C(3)C(7)C(8)	125	C(15)C(20)C(19)	141	C(3′)C(7′)C(8′)	109	C(15′)C(20′)C(19′)	120
C(6)C(7)C(8)	116	C(15)C(20)C(21)	117	C(6′)C(7′)C(8′)	100	C(15′)C(20′)C(21′)	127
C(7)C(8)C(9)	130	C(19)C(20)C(21)	101	C(7′)C(8′)C(9′)	140	C(19′)C(20′)C(21′)	109
C(7)C(8)C(13)	111	N(4)C(21)C(20)	104	C(7′)C(8′)C(13′)	99	N(4′)C(21′)C(20′)	107
C(9)C(8)C(13)	119	C(17)O(23)C(18)	107	C(9′)C(8′)C(13′)	120	C(17′)O(23′)C(18′)	116
C(8)C(9)C(10)	116			C(8′)C(9′)C(10′)	117		

TABLE 3

Deviations (Å) of the atoms from various planes

Atoms included in derivation of mean plane		Atoms omitted		Atoms included in derivation of mean plane		Atoms omitted	
C(3)	0·00	C(14)	0·73	C(3′)	−0·05	C(14′)	0·71
N(4)	0·00	C(21)	0·63	N(4′)	0·05	C(21′)	0·50
C(15)	0·00			C(15′)	0·05		
C(20)	0·00			C(20′)	−0·05		
C(2)	0·01	C(14)	1·02	C(2′)	0·02	C(14′)	0·83
C(7)	−0·02			C(7′)	−0·05		
C(3)	0·01			C(3′)	0·03		
C(15)	−0·01			C(15′)	−0·02		
C(16)	0·00			C(16′)	0·02		
C(3)	−0·07	C(6)	−0·46	C(3′)	−0·05	C(6′)	−0·76
N(4)	0·07			N(4′)	0·02		
C(5)	−0·04			C(5′)	−0·02		
C(7)	0·04			C(7′)	0·05		
N(1)	−0·04	C(17′)	−0·66	N(1′)	−0·01	C(17)	−0·51
C(2)	0·05			C(2′)	0·01		
C(16)	−0·05			C(16′)	−0·01		
C(16′)	0·03			C(16)	0·01		
C(15)	−0·03	C(16)	−1·31	C(15′)	0·05	C(16′)	−1·28
C(18)	0·06	C(17)	−1·57	C(18′)	−0·06	C(17′)	−1·43
C(19)	−0·10	O(23)	−0·45	C(19′)	0·11	O(23′)	−0·33
C(20)	0·04			C(20′)	−0·11		
C(21)	0·04			C(21′)	0·00		

rings G and G′ exhibit a similar feature, atoms 1, 2, 16, and 16′ being coplanar while the remaining atom, 17′, is an average distance of 0·59 Å from the plane.

The non-planarity of the five-membered rings is reflected in the average valency angles in these rings. The average valency angle in rings C and C′ is 105° and in rings G and G′ is 104°, in excellent agreement with the values reported for, *e.g.*, hydroxy-L-proline (106°),[11]

---

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

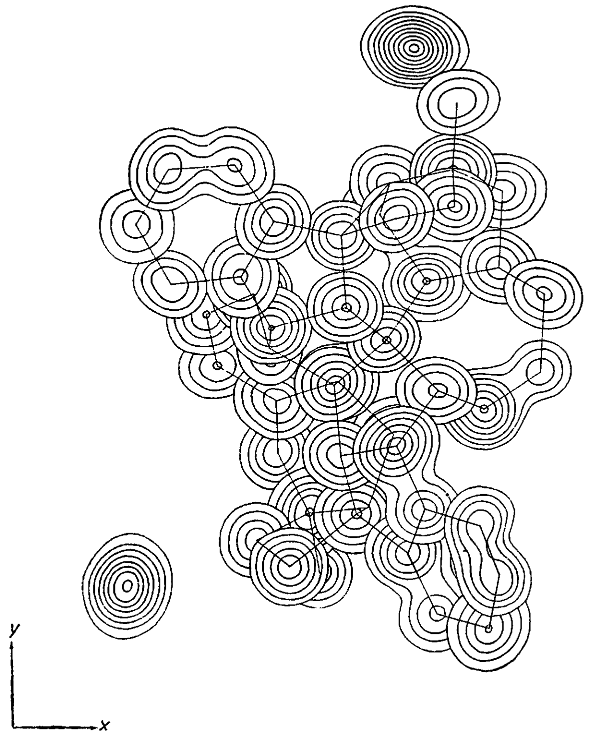


FIG. 1. The final three-dimensional electron-density distribution for caracurine-II dimethiodide, shown by means of superimposed contour sections drawn parallel to (001). Contour interval 1eÅ^{-3} except around the iodide ions where it is 5 eÅ^{-3}

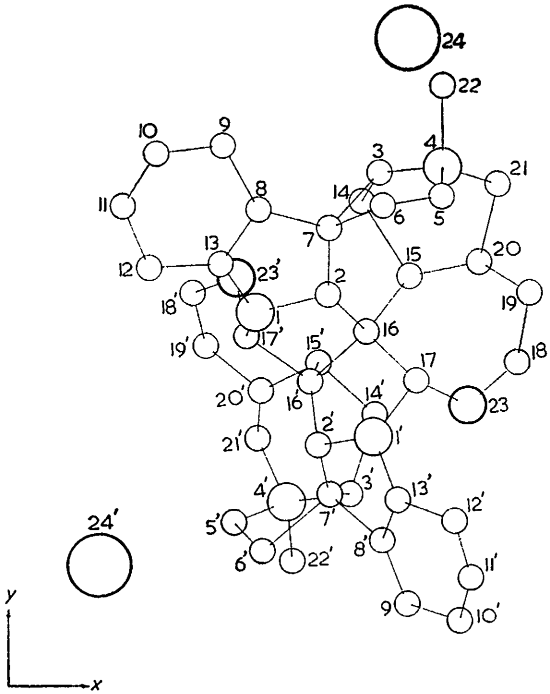


FIG. 2. The arrangement of atoms corresponding to Fig. 1

clerodin bromolactone (106°),[12] and isoclovene hydrochloride (105°).[13] When the five-membered ring is fused to an aromatic ring or incorporates a double bond the average valency angle is usually slightly larger than in the above examples. Thus in echitamine bromide [14] the average valency angle in the five-membered ring fused to the benzene ring is 107° and in that not fused to the benzene ring 104°, while in bromogeigerin acetate [15] the average valency angle in the cyclopentenone ring is 107° and in the γ-lactone ring 105°. The value of 107° for the average valency angle in rings B and B′ of caracurine-II dimethiodide conforms to this pattern. The average valency angle in the cyclohexane and piperidine rings, 112°, is slightly greater than tetrahedral. The average valency angle in the seven-membered rings F and F′ is 117°.

The planes of the indoline ring systems are mutually inclined at an angle of 58°.

The conformation of a model of the caracurine-II dimethiodide molecule constructed with standard bond lengths and valency angles differs to some extent from the conformation of the actual molecule in the crystal. A list of some of the non-bonded distances in the model and in the crystal molecule is given in Table 4; comparison of these distances shows that the considerable strain inherent in the model molecule is relieved to some extent in the actual molecule by the rotation of both halves of the molecule away from each other about the 16–16′ bond as axis. The non-bonded separations 14 · · · 14′, 14 · · · 15′, 14 · · · 16′, for example, which are extremely short in the model are increased considerably in the actual molecule.

TABLE 4

Comparison of intramolecular non-bonded separations (Å) in the crystal molecule and a model molecule

	Model molecule *	Crystal molecule *		Model molecule *	Crystal molecule *		Model molecule *	Crystal molecule *
N(1) · · · N(1′)	3·7	3·42	C(13) · · · O(23′)	2·5	2·75	C(15) · · · C(15′)	2·8	3·03
N(1) · · · C(2′)	3·5	3·07	C(14) · · · C(15′)	2·6	3·61	C(15) · · · C(17′)	3·7	3·40
C(3) · · · C(15)	3·7	4·90	C(14) · · · C(14′)	2·8	4·70	C(15) · · · O(23′)	4·3	3·53
C(7) · · · O(23′)	3·8	3·45	C(14) · · · C(16′)	3·0	3·42	C(15) · · · C(2′)	3·6	3·93
C(11) · · O(23′)	2·8	3·31	C(14) · · · C(17′)	3·6	3·37	C(16) · · · O(23′)	3·5	3·15
C(12) · · C(18′)	3·7	4·09	C(14) · · · O(23′)	3·8	2·94			

* The value listed for a separation X · · · Y is the average of the two separations, X · · · Y and X′ · · · Y′.

The distance between the two quaternary centres in the molecule is 8·5 Å, whereas in toxiferine-I and (+)-tubocurarine the corresponding separations have been estimated [16] at about 14 Å; this distinction is noteworthy in view of the high physiological activity of the latter alkaloids and the relatively low activity of caracurine-II dimethochloride.

The arrangement of the molecules in the unit cell as viewed along the *c* axis is shown in Fig. 3. The shortest contact between a positively charged nitrogen atom and a negatively charged iodide ion is 4·42 Å, close to the minimum $N^+ \cdots I^-$ distances in *N*-methylgelsemicine hydriodide (4·39 Å),[17] morphine hydriodide (4·38 Å),[18] and macusine-A iodide (4·52 Å).[19] The closest carbon · · · iodine approaches, 3·66, 3·87, 3·89, and 3·96 Å, are similar to the values of 3·81 and 3·99 Å in (+)-de(oxymethylene)lycoctonine hydriodide monohydrate,[20] 3·81 Å in *N*-methylgelsemicine hydriodide,[17] and 3·93 and 3·95 Å in macusine-A iodide.[19]

---

[12] Paul, Sim, Hamor, and Robertson, *J.*, 1962, 4133.

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

[14] Hamilton, Hamor, Robertson, and Sim, *J.*, 1962, 5061.

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

[16] Battersby and Hodson, *Quart. Rev.*, 1960, **14**, 77.

[17] Przybylska, *Acta Cryst.*, 1962, **15**, 301.

[18] Mackay and Hodgkin, *J.*, 1955, 3261.

[19] McPhail, Robertson, and Sim, *J.*, 1963, 1832.

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

The two iodide ions in the asymmetric crystal unit are in rather different environments and the co-ordination of each appears to account for the anisotropic thermal motion of these ions. The electrostatic attraction between I(24) and the three quaternary nitrogen atoms at distances of less than 5 Å is mainly in the y and z directions; accordingly, for I(24) the value of B_{11}, 10·4 Å^2, is distinctly greater than the values of B_{22}, 5·9 Å^2, and B_{33}, 5·0 Å^2. For I(24′) the ionic forces appear to be greatest in the z direction and least in the y direction; the anisotropic thermal parameters, B_{11} = 8·3 Å^2, B_{22} = 10·5 Å^2, and B_{33} = 5·1 Å^2, are in good agreement with this.

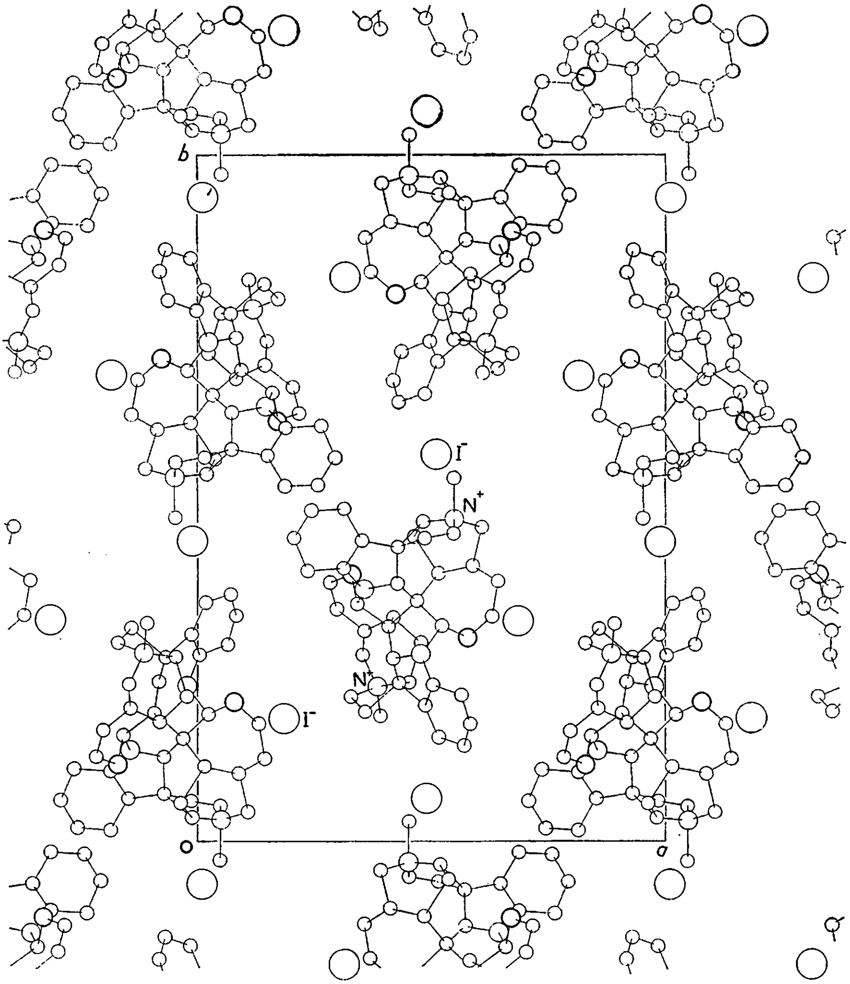


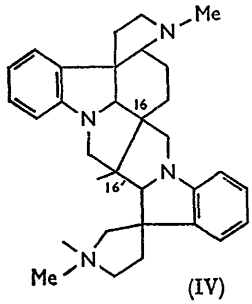
FIG. 3. The crystal structure as viewed along the c axis

EXPERIMENTAL

Crystal Data.—Caracurine-II dimethiodide, $C_{40}H_{44}I_2O_2N_4$; *M*, 866·6. Orthorhombic, a = 18·59, b = 27·44, c = 7·52 Å, U = 3836 Å^3, D_m = 1·505 g. cm.$^{-3}$, Z = 4, D_c = 1·502 g. cm.$^{-3}$, space group $P2_12_12_1 - D_2^4$. Absorption coefficient for *X*-rays (λ = 1·542 Å) μ = 134·5 cm.$^{-1}$. Total number of electrons in the unit cell = $F(000)$ = 1736.

Experimental Measurements.—Rotation, oscillation, and Weissenberg photographs were taken with Cu-K_α ($\lambda = 1{\cdot}542$ Å) radiation; precession photographs were taken with Mo-K_α ($\lambda = 0{\cdot}7107$ Å) radiation. The cell dimensions were determined from the rotation and precession photographs. For the intensity survey small crystals were employed, completely bathed in a uniform X-ray beam, and no correction for absorption was applied. The intensities were estimated visually from equi-inclination Weissenberg photographs of the $hk0$–$hk5$ layers; the multiple-film technique was employed. The usual correction factors (Lorentz, polarization, and rotation) were applied and 1285 independent structure amplitudes were derived. The exposures were such that the various layers were approximately on the same relative scale; the absolute scale of each layer was obtained at a later stage by correlation with the calculated structure amplitudes, $|F_c|$.

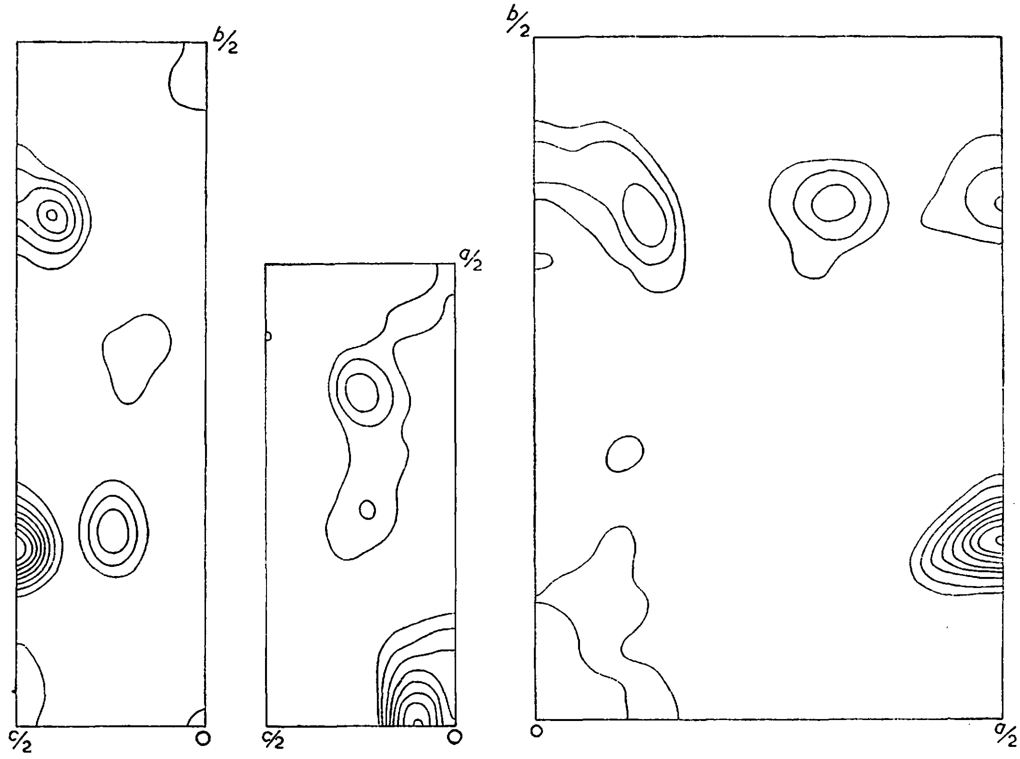
The crystal density was determined by flotation in aqueous zinc chloride.



(IV)

Structure Analysis.—The initial co-ordinates of the iodide ions were obtained by interpreting the three-dimensional Patterson function; sections at $U = \frac{1}{2}$, $V = \frac{1}{2}$, and $W = \frac{1}{2}$ are shown in Fig. 4.

On the basis of the iodide ions alone a first set of structure amplitudes and phase angles was calculated; the value of R was 40%. The first Fourier synthesis was then evaluated with the measured values of the structure amplitudes and the phases calculated from the iodide ion positions. The three-dimensional electron-density distribution was displayed as contoured sections drawn on sheets of glass and stacked in a frame and was thoroughly examined for recognizable molecular features. We were able to allocate co-ordinates to thirty-six atoms defining the partial skeleton (IV) and at this stage it was already clear that the alkaloid differed from caracurine-V and toxiferine-I by the presence of a carbon–carbon bond joining positions 16 and 16′.



(*a*) (*b*) (4*c*)

Fig. 4. Sections through the three-dimensional Patterson function $P(UVW)$, (*a*) at $U = \frac{1}{2}$, (*b*) at $V = \frac{1}{2}$, and (*c*) at $W = \frac{1}{2}$. Contour scale arbitrary

TABLE 5

Measured and calculated values of the structure factors

h	*k*	*l*	F_o	F_c	α
0	0	2	227	191	180
		4	83	74	180
0	1	2	56	69	90
		3	156	135	90
		4	158	108	270
		5	43	39	90
0	2	1	134	148	0
		2	14	19	180
		3	88	71	180
		4	99	104	0
		5	54	35	0
0	3	1	97	88	270
		2	285	269	90
		3	126	106	90
		4	11	15	90
		5	102	90	270
0	4	0	28	46	180
		1	446	414	0
		2	29	22	180
		4	63	54	0
		5	55	68	180
0	5	1	140	91	270
		2	225	232	270
		3	53	37	90
		4	61	51	90
		5	79	78	270
0	6	0	54	47	0
		1	167	100	0
		2	120	80	0
		3	68	69	180
		4	98	87	180
		5	42	45	0
0	7	1	139	157	270
		2	37	58	270
		3	34	47	90
		4	98	84	90
		5	35	32	90
0	8	0	351	338	180
		1	69	70	180
		2	55	41	0
		4	55	67	0
		5	36	46	0
0	9	1	38	64	90
		2	29	10	90
		3	112	117	270
		4	63	68	90
0	10	0	87	63	180
		1	17	37	0
		2	112	96	0
		3	34	62	0
		4	30	36	180
0	11	1	124	96	90
		2	71	100	270
		3	105	89	270
		5	53	52	90
0	12	0	61	34	180
		1	178	172	180
		2	39	37	0
		3	39	26	0
		4	37	56	180
0	12	5	36	48	0
0	13	2	14	41	90
		3	33	17	270
		4	33	24	270
		5	62	76	90
0	14	0	53	23	180
		1	75	64	180
		2	79	89	180
		3	32	20	0
		4	39	46	0
0	15	1	25	31	90
		2	113	113	90
		3	40	62	270
		4	57	60	270
0	16	0	100	124	0
		2	20	15	180
		4	19	5	180
0	17	1	35	32	270
		3	19	15	90
		4	45	44	270
		5	26	14	270
0	18	0	90	100	0
		1	47	28	0
		3	45	49	180
		4	28	10	180
0	19	1	50	68	270
		3	81	68	90
0	20	0	48	61	180
		1	46	53	0
		2	40	38	0
0	21	3	46	23	90
0	22	0	24	6	180
		1	39	43	0
0	23	2	35	45	270
0	24	0	80	90	180
		1	34	21	180
0	26	1	34	28	180
1	0	1	20	21	270
		2	256	247	0
		3	117	79	270
		4	27	15	0
		5	57	41	270
1	1	1	49	65	349
		2	181	175	354
		3	135	129	228
		4	58	45	301
		5	114	79	24
1	2	1	78	61	40
		2	105	101	102
		3	30	33	260
		4	51	43	292
		5	64	40	163
1	3	0	86	123	270
		1	45	53	242
		2	138	126	299
		3	54	55	177
		4	162	141	138
1	4	0	144	139	270
		1	142	144	172
		2	280	197	118
1	4	3	95	82	7
		4	28	27	20
		5	76	77	346
1	5	0	207	204	90
		1	94	72	138
		2	35	24	18
		3	23	28	61
		4	122	126	214
		5	26	28	239
1	6	0	80	64	270
		1	148	113	258
		2	118	108	39
		3	105	96	123
		4	30	17	329
		5	17	18	221
1	7	0	95	82	270
		1	34	59	237
		2	116	109	8
		3	184	150	316
		4	36	40	223
		5	87	71	165
1	8	0	78	64	90
		1	193	202	287
		2	67	87	195
		3	106	95	122
		4	26	21	175
		5	27	34	174
1	9	0	122	110	270
		1	29	31	89
		2	33	58	208
		3	97	88	24
		4	22	48	85
		5	79	88	207
1	10	0	67	58	90
		1	83	98	202
		2	107	99	308
		3	36	48	19
		4	32	41	81
		5	31	36	10
1	11	0	69	107	90
		1	32	27	96
		2	79	68	163
		3	55	62	26
		4	93	93	319
1	12	0	154	176	90
		1	57	69	61
		2	120	106	280
		4	41	30	49
		5	28	33	176
1	13	0	68	56	270
		1	39	59	260
		2	32	19	200
		3	49	59	222
		4	76	68	33
		5	23	24	61
1	14	0	41	15	90
		1	70	61	107
		2	92	88	213
		3	64	66	261
		5	21	15	105
1	15	2	40	39	164
		3	54	50	154
		5	35	45	329
1	16	0	49	59	270
		1	115	112	111
		2	49	49	350
		3	32	29	270
1	17	1	35	24	299
		2	24	17	350
		3	46	44	202
		4	19	24	219
		5	41	44	354
1	18	0	46	38	270
		1	88	71	69
		2	42	35	74
		3	40	48	221
		4	20	33	287
1	19	2	26	17	308
		3	21	25	220
		4	32	30	147
1	20	0	69	52	270
		2	79	73	105
		3	26	39	299
1	21	2	36	32	32
		4	29	30	180
1	22	1	39	29	244
		2	54	41	83
2	0	0	242	329	0
		1	107	106	270
		2	179	206	180
		3	18	18	270
		4	168	123	0
		5	41	35	90
2	1	0	75	84	0
		1	174	163	113
		2	96	93	116
		3	49	49	243
		4	181	154	311
		5	83	71	286
2	2	0	77	105	0
		1	237	231	30
		2	252	216	112
		3	75	66	260
		4	31	19	267
		5	22	18	236
2	3	0	24	17	180
		1	155	149	328
		2	100	72	278
		3	140	126	64
		4	59	63	254
		5	93	77	249
2	4	0	98	136	0
		1	133	106	5
		2	136	118	229
		3	155	141	169
		4	34	41	277
		5	47	30	300
2	5	0	153	121	0
2	5	1	81	87	245
		2	98	74	101
		3	142	158	126
		4	60	70	146
		5	48	45	299
2	6	0	210	235	180
		1	181	175	328
		2	81	72	48
		3	110	101	117
		4	18	7	128
		5	42	32	97
2	7	0	114	128	180
		1	81	70	72
		2	76	70	273
		3	36	32	238
		4	112	117	50
		5	68	56	239
2	8	0	132	144	180
		1	83	76	52
		2	65	75	19
		3	25	33	253
		4	71	61	190
		5	29	30	219
2	9	0	50	56	0
		1	45	40	338
		2	166	157	275
		3	75	83	359
		4	64	73	132
		5	57	53	100
2	10	0	136	160	180
		1	125	133	180
		2	102	108	300
		3	20	19	96
		4	21	16	197
		5	21	19	300
2	11	0	19	4	180
		1	64	53	80
		2	22	41	73
		3	103	96	212
		4	38	26	51
		5	49	56	70
2	12	0	76	73	180
		1	89	85	200
		2	87	89	90
		3	66	79	31
		4	38	34	83
		5	20	23	31
2	13	0	62	77	180
		1	120	112	118
		2	39	33	20
		3	84	92	283
		4	17	40	329
		5	43	40	90
2	14	0	132	138	0
		1	87	81	139
		2	68	54	218
		3	25	27	297
		5	30	10	200
2	15	0	23	37	0
		1	23	12	190
2	15	2	59	49	109
		3	18	18	22
		4	71	71	237
		5	25	35	107
2	16	0	36	37	0
		1	34	41	207
		2	39	47	229
		3	30	28	216
		4	23	27	12
2	17	0	22	23	0
		1	33	38	190
		2	54	53	84
		3	39	38	115
		4	44	37	272
		5	34	29	288
2	18	0	56	43	0
		1	91	84	356
		2	42	45	111
		3	29	12	215
		4	32	29	334
2	19	0	32	23	0
		1	33	22	318
		3	70	56	64
2	20	1	49	26	33
		2	27	43	17
		3	34	34	205
		4	21	23	177
2	21	3	41	31	85
		4	39	38	106
2	22	1	42	25	311
		4	21	16	12
2	24	0	49	47	180
3	0	1	167	99	270
		2	150	107	180
		3	154	139	270
3	1	0	59	90	90
		1	201	155	61
		2	105	93	179
		3	156	145	158
		4	45	52	159
		5	64	54	342
3	2	0	268	339	270
		1	270	258	99
		2	111	112	72
		3	35	37	27
		4	100	80	83
		5	59	45	309
3	3	0	129	149	90
		1	66	69	187
		2	160	164	342
		3	55	53	4
		4	98	82	194
		5	57	48	22
3	4	0	57	44	90

TABLE 5 (*Continued*)

h	k	l	F_o	F_c	α
		1	108	97	326
		2	139	153	101
		3	73	64	102
		4	113	101	271
		5	17	20	219
3	5	0	31	40	270
		1	125	99	15
		2	147	138	8
		3	32	38	245
		4	88	74	134
		5	73	49	166
3	6	0	57	46	270
		1	208	214	269
		2	51	59	126
		3	14	11	330
		4	66	66	112
		5	68	68	56
3	7	0	35	42	270
		1	111	105	129
		2	79	83	170
		3	107	108	19
		4	65	63	188
		5	60	54	188
3	8	0	72	64	270
		1	88	58	332
		2	32	33	12
		3	113	112	76
		4	22	23	81
		5	22	23	280
3	9	0	66	66	90
		1	101	98	220
		2	66	48	57
		3	109	125	347
		4	43	46	323
		5	51	40	155
3	10	0	154	161	90
		1	80	99	272
		2	109	91	275
		3	18	11	107
		4	24	42	280
		5	32	30	179
3	11	0	30	27	270
		1	46	72	9
		2	21	23	156
		3	31	32	114
		4	67	79	9
		5	22	31	171
3	12	0	49	40	90
		1	18	18	201
		2	89	95	261
		3	28	36	326
		4	33	54	101
3	13	0	53	34	270
		1	24	19	99
		2	106	115	182
		3	45	40	127
		4	39	48	22
		5	41	27	317
3	14	0	38	36	90
		1	100	116	85
		2	78	83	283
		3	28	19	182
		5	33	8	98
3	15	1	35	29	286
		2	25	37	14
		3	47	39	194
		5	47	58	15
3	16	0	21	25	90
		1	81	73	88
		3	45	65	276
		4	33	44	247
3	17	0	30	12	270
		1	25	43	333
		2	28	27	338
		3	46	57	191
		4	31	34	146
3	18	0	79	104	270
		1	35	38	88
		2	36	43	110
		3	20	31	302
		4	20	13	90
3	19	0	28	28	90
		3	26	17	161
		4	25	28	216
3	20	0	38	41	270
		2	27	34	69
		4	21	19	315
3	21	2	64	68	4
3	22	1	45	48	292
		2	32	42	106
		4	21	17	205
3	24	1	31	21	294
		2	43	19	6
4	0	0	146	140	0
		1	117	107	90
		2	143	135	180
		3	105	64	270
		4	76	68	0
		5	84	55	270
4	1	0	156	124	0
		1	27	23	298
		2	125	122	88
		3	76	57	338
		4	139	106	224
		5	27	20	263
4	2	0	215	217	0
		1	33	71	325
		2	77	61	261
		3	75	66	183
		4	51	47	305
		5	48	43	89
4	3	0	99	64	180
		1	71	87	241
		2	28	34	209
		3	144	142	130
		4	60	50	272
		5	84	71	306
4	4	0	43	46	0
		1	163	192	325
		2	119	101	105
		3	34	29	164
		4	33	36	344
		5	36	27	5
4	5	0	75	33	0
		1	137	131	334
		2	64	53	185
		3	103	99	55
		4	120	101	37
		5	78	59	250
4	6	0	161	146	180
		1	98	124	34
		2	64	52	21
		3	73	77	199
		4	47	55	228
		5	94	62	274
4	7	0	127	133	0
		1	37	35	303
		2	62	72	298
		3	16	17	200
		4	111	108	134
		5	28	39	272
4	8	0	79	95	180
		1	85	89	280
		2	115	124	324
		3	69	81	101
		4	34	35	217
		5	41	33	103
4	9	0	62	79	180
		1	70	43	153
		2	55	41	278
		3	55	61	212
		4	44	55	63
		5	32	42	48
4	10	0	72	93	180
		1	114	123	156
		2	33	62	54
		3	67	77	10
		4	46	51	126
4	11	0	90	116	180
		1	116	119	7
		2	19	24	230
		3	57	73	308
		4	16	25	66
		5	61	72	127
4	12	0	32	18	180
		1	49	52	167
		2	56	61	253
		3	17	22	334
		4	17	7	335
		5	24	29	287
4	13	0	78	48	0
		1	61	80	173
		2	21	17	44
		3	41	40	253
		4	41	49	185
		5	32	43	56
4	14	0	77	83	0
		1	46	54	227
		2	22	33	213
		3	44	41	359
		4	29	18	88
		5	25	39	106
4	15	0	64	92	35
		1	29	39	151
		2	38	27	85
		4	48	66	308
		5	22	19	65
4	16	0	39	40	0
		1	43	43	104
		2	47	58	126
		3	39	50	258
		4	19	13	94
		5	26	11	79
4	17	1	41	26	205
		2	22	24	73
		3	28	23	0
		4	47	49	237
4	18	0	37	43	0
		1	40	45	358
		2	45	45	241
		3	29	19	186
		4	38	43	330
4	19	0	48	67	0
		1	34	20	231
		3	26	28	92
		4	21	20	262
4	20	1	61	37	358
		2	31	40	59
		4	29	32	225
4	21	0	33	42	180
		2	34	24	213
		3	27	33	73
4	22	0	43	57	180
		1	37	31	343
4	25	1	31	11	189
4	26	1	34	28	184
5	0	1	310	239	90
		2	86	96	180
		3	73	68	90
		5	56	50	270
5	1	0	19	0	92
		1	78	64	113
		2	149	128	343
		3	34	45	156
		4	57	56	130
		5	97	91	350
5	2	0	58	38	90
		1	49	70	118
		2	75	69	100
		3	112	108	261
		4	47	48	319
		5	45	48	15
5	3	0	168	149	90
		1	164	163	16
		2	73	82	325
		3	138	119	196
		4	76	81	219
		5	75	56	157
5	4	0	231	263	270
		1	77	96	312
		2	134	132	86
		3	63	62	159
		4	58	57	88
		5	13	18	212
5	5	0	92	72	270
		1	207	179	188
		2	45	44	225
		3	101	90	346
		4	36	47	163
		5	20	21	5
5	6	0	81	66	270
		1	50	29	308
		2	72	68	132
		3	58	63	70
		5	20	28	339
5	7	0	50	45	270
		1	65	76	99
		2	156	155	4
		3	33	61	38
		4	37	48	155
		5	51	56	203
5	8	0	54	61	90
		1	154	169	279
		2	84	81	352
		3	29	24	279
		4	35	35	263
		5	30	22	44
5	9	0	55	22	90
		1	37	50	342
		2	107	112	135
		3	67	58	324
		4	29	43	327
		5	44	58	157
5	10	0	40	32	90
		1	57	60	265
		2	48	63	295
		3	50	60	129
		4	60	73	99
		5	36	32	180
5	11	0	75	59	270
		1	90	114	209
		2	112	107	196
		3	39	60	8
		4	45	58	25
		5	26	21	14
5	12	0	120	145	90
		1	53	57	162
		2	46	48	260
		3	27	42	25
		5	24	11	347
5	13	0	25	5	90
		1	32	41	333
		2	25	15	77
		3	40	41	158
		4	26	24	316
		5	25	25	247
5	14	0	68	71	90
		1	49	43	129
		2	52	54	294
		3	49	70	279
		4	19	18	13
5	15	1	37	46	338
		2	53	57	204
		3	69	87	183
		4	19	24	322
		5	26	31	26
5	16	0	40	61	270
		1	81	92	87
		2	17	26	204
		3	24	16	239
5	17	0	42	16	270
		2	29	32	350
		4	32	32	155
5	18	1	39	41	92
		2	56	51	115
		4	29	31	255
5	19	0	29	14	90
		2	27	48	23
		4	25	33	195
5	20	0	29	44	270
		2	37	42	84
		3	22	27	237
		4	21	12	7
5	21	2	24	16	325
5	22	0	37	30	270
		1	37	32	283
		3	31	34	104
5	23	0	39	42	270
6	0	0	226	262	0
		1	139	134	270
		2	87	90	180
		3	111	71	90
		5	37	53	90
6	1	0	80	62	180
		1	73	85	232
		2	36	48	161
		3	59	59	95
		4	55	63	310
		5	45	37	32
6	2	0	44	21	0
		1	71	67	53
		2	58	48	97
		3	161	139	209
		4	47	42	330
		5	17	12	311
6	3	0	109	98	0
		1	52	54	28
		2	140	110	109
		3	110	94	53
		4	47	45	247
		5	69	60	248
6	4	0	62	56	180

TABLE 5 (*Continued*)

h	*k*	*l*	F_o	F_c	α
		1	134	161	355
		2	105	88	230
		3	22	25	23
		4	55	50	284
		5	27	24	254
6	5	0	93	101	0
		1	60	54	258
		2	70	70	249
		3	56	63	150
		4	32	31	70
		5	39	49	285
6	6	0	34	2	180
		1	29	32	279
		2	67	67	35
6	6	3	76	79	139
		4	86	79	195
		5	15	18	107
6	7	0	87	87	180
		1	89	91	305
		2	90	87	259
		3	30	61	135
		4	62	62	55
6	8	0	133	161	180
		1	39	53	59
		2	88	84	349
		3	15	18	123
		4	16	17	350
		5	55	64	276
6	9	0	66	69	0
		1	56	68	47
		2	20	21	50
		3	25	34	282
		4	45	66	113
6	10	0	45	53	180
		1	33	33	159
		2	46	52	299
		3	62	66	28
		4	34	37	86
6	11	0	37	29	180
		1	50	63	100
		2	52	64	286
		3	57	63	237
		4	21	32	134
		5	30	53	85
6	12	1	99	103	179
		2	35	43	87
		4	22	31	150
6	13	0	57	55	180
		2	38	37	63
		4	35	40	281
		5	31	47	100
6	14	0	40	31	0
		1	57	55	146
		2	52	56	201
		3	30	37	317
		4	30	42	59
6	15	0	34	28	0
		1	22	29	100
		2	37	50	72
		3	34	55	308
		4	24	22	245
6	16	0	67	74	0
		1	23	33	346
		2	31	24	167
		4	20	3	224
		5	29	35	95
6	17	0	27	22	180
		1	33	44	200
		2	23	15	293
		3	21	18	61
		4	35	33	252
6	18	0	35	45	0
		2	27	30	105
		3	30	34	205
6	18	4	21	19	314
6	19	0	31	27	0
		1	25	21	262
		2	36	42	114
		3	34	33	59
		4	21	28	333
6	20	1	33	44	23
6	21	3	22	17	49
7	0	1	34	65	90
		2	72	73	0
		3	26	46	270
		4	25	35	0
		5	15	9	90
7	1	0	33	55	90
		1	77	69	290
		2	68	67	314
		3	99	104	228
		4	59	55	196
		5	59	64	28
7	2	0	53	71	270
		1	120	128	39
		2	126	132	160
		3	65	75	223
		4	50	42	28
		5	33	29	188
7	3	0	82	57	270
		1	33	41	66
		2	64	67	334
		4	91	92	125
		5	15	26	37
7	4	0	34	47	270
		1	33	45	120
		2	96	114	98
		3	28	35	77
		4	42	38	242
		5	61	76	355
7	5	0	90	93	90
		1	107	96	118
		2	29	33	44
		3	38	41	63
		4	68	77	223
		5	31	33	233
7	6	0	77	90	270
		1	72	103	278
		2	85	83	15
		3	27	29	196
		4	25	14	326
		5	19	22	67
7	7	0	32	30	270
		1	47	61	289
		2	14	20	81
		3	97	107	298
		4	35	20	151
		5	50	67	153
7	8	1	84	94	307
		2	36	42	199
		3	68	74	130
		4	29	28	190
		5	20	14	228
7	9	0	102	106	270
7	9	2	48	41	76
		3	71	87	40
		4	49	40	27
7	10	0	106	109	90
		1	37	55	198
		2	43	60	326
		3	48	67	19
		5	24	22	24
7	11	0	112	92	90
		2	46	39	188
		4	26	41	306
		5	35	36	177
7	12	0	35	8	90
		2	75	83	304
		4	19	23	73
7	13	0	45	44	270
		1	60	68	281
		2	33	38	164
		4	27	34	19
		5	29	32	43
7	14	0	43	52	90
		1	59	60	99
		2	42	54	183
		4	24	17	203
		5	18	25	207
7	15	0	37	7	90
		2	22	28	265
		3	47	51	146
		4	20	31	23
7	16	1	33	40	133
		2	18	30	305
		3	29	39	288
		4	20	25	24
7	17	0	51	58	90
		3	30	30	212
		4	21	41	229
7	18	0	29	40	270
		2	27	32	79
		4	21	4	325
7	19	2	28	35	354
		4	29	36	156
7	20	0	32	22	270
		2	57	59	124
7	21	1	34	36	112
8	0	0	64	49	180
		1	26	2	269
		2	39	63	180
		3	29	30	270
		4	99	87	0
8	1	0	36	64	0
		1	74	88	142
		2	60	62	111
		3	38	33	274
		4	22	32	291
		5	55	60	285
8	2	0	98	106	0
		1	98	125	6
		3	15	25	319
		4	54	49	195
		5	16	16	149
8	3	0	59	65	0
		1	17	12	261
		2	113	108	269
		3	29	28	87
		4	32	25	278
		5	16	18	234
8	4	0	57	20	0
		1	35	8	114
		2	19	48	126
		3	69	98	166
		4	16	23	272
		5	30	30	314
8	5	0	100	105	0
		1	95	99	292
		2	117	103	109
		3	68	74	95
		4	29	25	94
		5	16	14	267
8	6	0	90	125	180
		1	47	59	335
		2	50	65	9
		3	16	21	109
		4	34	33	323
		5	24	30	175
8	7	0	35	21	0
		1	68	83	80
		2	66	66	260
		3	24	35	239
		4	40	51	86
		5	34	45	275
8	8	0	26	17	180
		1	40	58	4
		2	54	51	352
		3	37	28	59
		4	58	69	180
		5	21	29	233
8	9	0	25	11	180
		1	53	64	331
		2	46	63	270
		4	25	20	70
		5	17	32	116
8	10	0	54	54	180
		1	89	101	191
		2	19	35	314
		4	29	28	48
		5	18	24	0
8	11	0	28	14	180
		1	45	40	8
		2	31	45	66
		3	44	37	243
		4	35	32	98
		5	29	44	72
8	12	0	44	26	180
		3	61	72	1
		4	27	37	53
8	13	0	84	84	180
		1	51	60	122
		2	21	25	16
		3	42	46	279
		4	44	41	256
8	14	0	56	75	0
		1	26	24	170
		2	42	39	209
		4	20	20	139
8	15	0	33	23	0
		2	26	15	110
8	16	2	19	28	193
		3	50	57	231
		4	21	24	339
8	17	2	30	27	85
		3	26	31	17
		4	21	32	296
8	18	1	46	48	18
		2	37	34	140
8	19	1	26	23	194
		4	25	21	296
8	20	1	34	28	314
8	21	3	22	19	89
9	0	1	63	73	90
		2	124	119	180
		3	47	54	270
		4	24	23	0
9	1	1	86	86	40
		2	34	51	302
		3	76	90	156
		4	38	37	136
		5	24	34	338
9	2	0	121	125	270
		1	89	101	111
		2	31	21	57
		4	29	38	39
		5	21	27	358
9	3	0	52	62	90
		1	44	22	136
		2	48	59	345
		3	27	26	285
		4	40	45	252
9	4	0	24	39	270
		1	86	90	344
		2	31	47	78
		3	75	70	154
		4	35	41	264
		5	17	15	82
9	5	0	58	81	270
		1	22	43	51
		2	96	85	16
		3	52	43	293
		4	33	50	159
9	6	0	43	54	270
		1	50	60	259
		2	42	35	137
		4	18	17	173
		5	30	42	34
9	7	0	32	4	270
		1	56	47	129
		2	16	18	120
		3	36	50	27
		4	18	14	131
		5	30	30	166
9	8	0	45	18	270
9	8	1	23	19	233
		2	79	83	345
		4	18	17	140
9	9	0	42	14	270
		1	58	65	238
		2	40	44	110
		4	35	36	288
9	10	0	73	76	90
		1	57	58	308
		2	26	29	256
		4	30	33	240
9	11	4	39	51	48
		5	23	35	179
9	12	1	63	68	197
		2	25	39	265
9	13	2	42	43	203
		3	32	37	100
		4	28	34	330
9	14	1	33	59	85
9	15	1	40	48	255
		2	19	15	267
		4	21	8	191
9	16	1	32	43	46
		2	31	27	182
9	17	0	47	38	90
		1	33	41	27
		2	24	22	264
9	18	0	43	43	270
		1	33	41	174
		2	20	23	84
9	19	1	30	40	121
		4	21	13	182
10	0	0	44	82	0
		1	70	78	90
		2	24	28	180
		3	25	47	270
		4	34	32	180
10	1	0	83	85	0

TABLE 5 (*Continued*)

h	*k*	*l*	F_o	F_c	α
		1	37	37	290
		2	31	30	184
		3	43	43	30
		4	31	43	222
10	2	0	32	10	180
		1	49	55	256
		2	62	60	251
		3	44	39	149
		4	18	28	305
10	3	0	23	14	180
		1	70	84	183
		2	25	28	148
		3	25	24	118
10	4	1	94	86	349
		2	66	59	100
		3	42	31	262
		5	22	29	157
10	5	0	26	12	0
		1	35	41	27
		2	28	38	218
		3	37	31	12
		4	37	46	20
10	5	5	33	47	257
10	6	0	44	0	180
		1	29	48	36
		2	36	39	3
		3	39	43	227
		4	44	58	219
		5	22	42	265
10	7	0	83	100	0
		1	36	51	312
		2	26	27	299
		3	27	27	150
		4	40	50	123
		5	26	27	43
10	8	0	74	104	180
		1	33	51	228
		2	38	44	326
		3	58	73	107
		4	19	24	34
10	9	0	34	49	180
		1	18	25	59
		2	27	32	146
		4	19	22	13
10	10	2	43	46	52
		3	47	50	17
		4	20	18	206
10	11	0	28	38	180
		1	56	50	35
		2	25	40	282
		3	25	29	299
		4	20	13	178
		5	19	19	88
10	12	0	25	40	0
		1	30	41	131
		2	37	46	257
		3	21	23	277
		4	20	27	90
10	13	0	37	39	180
		2	30	36	66
		4	21	30	192
10	14	0	38	17	180
		2	23	29	219
		3	21	24	14
		4	25	33	29
10	15	0	25	10	180
		3	15	20	198
10	16	0	26	38	0
10	17	1	26	13	272
		2	25	10	2
10	18	1	26	34	85
		2	20	27	179
11	0	1	65	63	90
11	1	0	38	62	90
		2	65	69	338
		3	19	23	248
		4	19	10	331
		5	18	34	17
11	2	1	27	38	48
		2	57	56	118
		3	52	63	218
		4	23	32	289
11	2	5	18	20	72
11	3	1	68	64	62
		3	57	66	180
		4	19	25	172
		5	29	27	210
11	4	0	72	90	270
		1	25	28	215
		2	27	12	46
		4	23	23	119
		5	18	23	357
11	5	0	18	12	270
		1	33	38	141
		4	34	45	226
		5	26	27	321
11	6	1	52	49	38
		3	52	37	99
		4	20	30	233
		5	18	27	295
11	7	2	51	62	28
		4	39	33	82
11	8	1	65	73	262
		3	35	29	306
		5	19	18	106
11	9	2	48	55	134
		3	32	31	53
		4	20	17	166
		5	23	37	188
11	10	0	29	14	270
		4	25	37	145
		5	19	19	309
11	11	0	24	22	90
		1	39	45	241
		2	23	29	148
		5	19	20	9
11	12	0	78	100	90
		2	19	7	18
11	13	0	31	15	270
		2	19	9	239
		3	43	42	149
		4	21	19	346
11	15	0	26	28	90
		2	42	47	236
11	16	0	28	32	270
		1	40	32	69
12	0	0	78	84	0
		2	28	4	180
		3	34	24	90
		4	20	16	180
		5	26	50	90
12	1	1	34	50	164
		4	28	34	317
12	2	1	36	42	68
		2	35	48	107
		3	42	35	234
12	3	0	29	36	0
		1	37	25	312
		2	18	17	114
		3	57	66	33
12	4	0	29	24	180
		1	32	48	15
12	4	2	31	33	284
		5	23	24	156
12	5	0	53	72	0
		1	35	29	182
		2	28	34	224
		3	32	33	180
12	6	1	30	34	267
		2	29	46	67
		3	41	34	93
12	7	1	23	31	324
		4	25	40	31
12	8	1	36	33	121
		2	26	36	3
		3	26	21	187
		4	20	20	38
		5	26	42	286
12	9	1	31	30	343
		3	21	10	354
		4	21	26	88
12	10	2	33	41	303
		3	21	33	27
12	11	0	37	11	0
		1	35	30	123
		3	30	32	209
		4	25	26	183
12	12	2	28	32	98
		4	25	25	106
12	13	0	37	44	180
12	14	1	26	24	160
		2	25	21	167
12	15	2	20	19	116
12	16	2	29	38	229
13	0	1	33	29	270
		3	49	42	270
13	1	1	33	33	319
		2	37	39	229
		4	20	22	303
13	2	1	68	67	59
13	3	1	41	45	128
		3	21	24	27
		4	20	13	150
13	4	1	31	38	160
		2	19	15	89
		3	21	17	183
13	5	1	31	37	59
		2	33	39	6
		4	29	30	244
13	6	0	37	39	270
		1	31	32	302
		3	21	26	216
13	7	0	32	29	270
		2	41	48	170
		4	33	20	92
13	8	3	48	51	100
13	9	0	41	39	270
		2	20	33	67
		4	21	15	0
13	10	1	25	26	197
		3	22	18	305
13	12	2	20	14	298
13	15	2	41	38	305
14	1	0	32	44	0
		1	35	38	128
		2	27	27	100
14	2	1	40	17	29
14	4	1	32	21	1
		2	36	38	50
		3	26	29	191
14	5	3	27	27	82
14	6	1	46	18	257
14	8	1	26	21	283
14	9	2	35	47	261
14	10	1	26	33	194
15	0	2	31	31	180
15	1	1	33	31	125
15	2	2	20	18	355
15	3	0	45	53	90
15	5	0	39	52	270
15	6	1	34	15	174
15	7	2	25	13	72
15	9	2	32	38	102
16	0	1	34	27	90
16	1	1	34	35	228
16	4	2	25	7	60
16	6	2	20	16	28

The thirty-six light atoms were included as carbon atoms in the calculation of a second set of structure amplitudes and phase angles. The value of R fell to 32·8%.

In the three-dimensional electron-density distribution derived from the improved phases the remaining carbon and oxygen atoms (apart from C-18) were located. The positions assigned to carbon atoms 11 and 12 appeared to be very approximate and these atoms were omitted from the subsequent structure-factor calculation. This yielded a value of R of 31·2%.

A third electron-density distribution was then calculated and improved co-ordinates obtained for all the atoms. On calculating a fourth set of structure factors the value of R decreased to 30·1%.

Three further rounds of structure-factor and Fourier calculations were carried out. Back-shift corrections for termination of series were derived from F_c syntheses and individual isotropic temperature factors were assigned. The value of R was reduced to 24·9%.

We next assigned anisotropic temperature factors to the iodide ions by least-squares calculations and obtained improved co-ordinates and isotropic temperature factors for the carbon, oxygen, and nitrogen atoms from difference Fourier syntheses. Four cycles of this refinement lowered the value of R to 18·6%.

The refinement procedure was concluded by one round of least-squares adjustment of the positional parameters of the light atoms. In view of the limited intensity data we did not feel justified in assigning anisotropic temperature factors to these atoms.

The final atomic co-ordinates, the isotropic temperature factors of the light atoms, and the anisotropic temperature factors of the iodide ions are listed in Table 1. The final values of $|F_o|$, $|F_c|$ and α are shown in Table 5; the final value of R is 18·1% over the 1285 independent reflexions. The theoretical atomic scattering factors used in all the structure-factor calculations were those of Berghuis *et al.*[21] for carbon, nitrogen, and oxygen and the Thomas–Fermi values for iodine.[22]

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

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

The individual results have been listed by McPhail.[23]

The extensive calculations were performed on the Glasgow University DEUCE computer with programmes devised by Dr. J. S. Rollett and Dr. J. G. Sime. We are grateful to Professor J. Monteath Robertson, F.R.S., for his encouragement and to Professor A. R. Battersby for supplies of caracurine-II dimethiodide and for helpful correspondence.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW W.2.

[Present address (G. A. S.): DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS, U.S.A.]

[*Received, April* 15*th*, 1964.]

---

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

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

[23] McPhail, Ph.D. Thesis, 1963, University of Glasgow.