Cyclization in the Cleavamine Series: X-ray Analysis of N(a)-Acetyl-7-ethyl-5-desethyl-aspidospermidine N(b)-Methiodide

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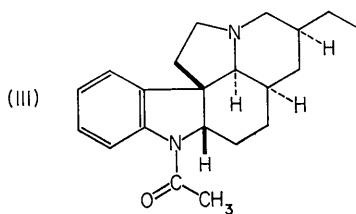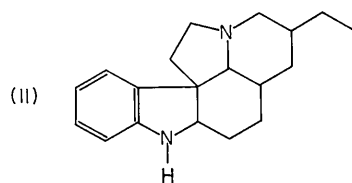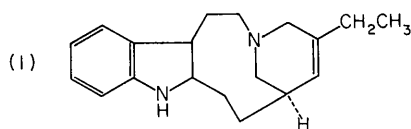*Department of Chemistry, University of British Columbia, Vancouver 8, B.C., Canada*

Transannular cyclization of the iminium salt of dihydrocleavamine yields a compound with an *Aspidosperma* skeleton. X-ray analysis of the N-acetyl methiodide derivative has established the structure as N(a)-acetyl-7-ethyl-5-desethyl-aspidospermidine N(b)-methiodide. Crystals of the methiodide are orthorhombic, $a = 9.32$, $b = 11.28$, $c = 19.70$ Å, $Z = 4$, space group $P2_12_12_1$. The intensities of about 1350 reflexions (1018 observed) were measured with a scintillation counter and Mo $K\alpha$ radiation. The iodine position was determined by Patterson methods; y_I was close to zero, but although this gave rise to a false mirror plane all the carbon, nitrogen and oxygen atoms were located on successive three-dimensional electron-density distributions. The positional and anisotropic thermal parameters were refined by least squares, the final R value being 0.066. The absolute configuration was determined by the anomalous dispersion method.

The structure analysis has established the absolute stereochemistry at all the asymmetric centres in the *Aspidosperma* skeleton. The bond distances, valency angles and intermolecular separations are all normal. One of the six-membered rings has a boat conformation.

Introduction

In a study of the chemistry of the *Vinca* alkaloid catharanthine, we were able to establish the structure, including the absolute configuration, of cleavamine (I), one of the acid-rearrangement products of this *Iboga*-type alkaloid (Kutney, Trotter, Tabata, Kerigan & Camerman, 1963; Camerman & Trotter, 1964). The

(I)

(II)

(III)

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close structural relationship of cleavamine to the alkaloid quebrachamine suggested its use as an excellent model for evaluating some of the reactions proposed in the biosynthesis of *Aspidosperma* alkaloids (Kutney & Piers, 1964). Transannular cyclization of dihydrocleavamine, *via* its iminium salt, yielded a compound whose physical and chemical properties suggested structure (II); this compound, which has m.p. 128–129°, $[\alpha]_D = -105°$ (CHCl$_3$), possesses five asymmetric centres, and we have undertaken an X-ray analysis of its N(a)-acetyl-N(b)-methiodide derivative to determine its structure. Our results establish the structure, including the absolute configuration, of the N(a)-acetyl derivative as N(a)-acetyl-7-ethyl-5-desethyl-aspidospermidine (III).

Experimental

Crystals of the methiodide are colourless prisms elongated along *a*, with (010) and (001) developed. The density was measured by flotation in aqueous potassium iodide, and the unit-cell dimensions and space group were determined from various rotation, Weissenberg and precession photographs, and on the General Electric Spectrogoniometer.

Crystal data (λ, Cu $K\alpha = 1.5418$ Å; λ, Mo $K\alpha = 0.7107$ Å). N(a)-Acetyl-7-ethyl-5-desethyl-aspidospermidine N(b)-methiodide [the parent 7-ethyl-5-desethyl-aspidospermidine has m.p. 128–129 °C, $[\alpha]_D = -105°$ (CHCl$_3$)].

C$_{22}$H$_{31}$N$_2$OI; mol. wt. 466·3; m.p. 281–282 °C (decomp.).

Orthorhombic, $a = 9.32 \pm 0.03$, $b = 11.28 \pm 0.03$, $c = 19.70 \pm 0.04$ Å.

Table 1. *Measured and calculated structure amplitudes*

Unobserved reflexions, for which F_o is listed as 0, have threshold values in the range 8–14

h	k	l	F_{obs}	F_{calc}
0	0	2	114.2	92.3
0	0	4	44.5	47.6
0	0	6	52.6	54.6
0	0	8	154.4	148.4
0	0	10	106.3	115.8
0	0	12	0.	11.4
0	0	14	28.9	37.4
0	0	16	0.	9.8
0	0	18	48.4	54.8
0	0	20	23.4	24.0
0	0	22	0.	13.5
0	0	24	0.	8.1
0	1	1	7.0	3.3
0	1	2	138.9	131.1
0	1	3	16.8	22.3
0	1	4	221.7	219.7
0	1	5	42.7	39.3
0	1	6	143.4	143.4
0	1	7	7.5	3.9
0	1	8	32.3	32.4
0	1	9	39.3	31.1
0	1	10	62.5	78.0
0	1	11	30.5	31.1
0	1	12	54.6	56.5
0	1	13	9.3	8.3
0	1	14	62.7	65.5
0	1	15	0.	2.8
0	1	16	47.9	49.8
0	1	17	0.	3.4
0	1	18	0.	1.6
0	1	19	0.	1.8
0	1	20	0.	11.7
0	1	21	0.	5.6
0	1	22	0.	11.3
0	1	23	0.	3.3
0	1	24	0.	16.1
0	2	0	297.2	309.2
0	2	1	68.6	68.5
0	2	2	88.6	86.2
0	2	3	103.7	96.7
0	2	4	91.3	92.1
0	2	5	38.2	38.2
0	2	6	90.0	82.1
0	2	7	31.4	27.8
0	2	8	111.4	124.7
0	2	9	0.	5.9
0	2	10	85.2	94.2
0	2	11	8.6	8.5
0	2	12	43.7	48.7
0	2	13	20.8	21.8
0	2	14	11.0	14.5
0	2	15	0.	0.6
0	2	16	23.7	28.2
0	2	17	17.4	16.7
0	2	18	53.3	55.9
0	2	19	0.	0.9
0	2	20	21.5	23.2
0	2	21	0.	7.0
0	2	22	0.	17.6
0	2	23	0.	1.9
0	3	1	62.3	52.8
0	3	2	113.7	115.9
0	3	3	45.8	44.0
0	3	4	106.4	109.3
0	3	5	17.2	17.6
0	3	6	104.7	106.1
0	3	7	0.	1.3
0	3	8	16.2	9.0
0	3	9	17.0	20.9
0	3	10	0.	4.6
0	3	11	30.1	27.5
0	3	12	62.2	68.5
0	3	13	24.3	26.1
0	3	14	44.8	55.9
0	3	15	18.4	13.0
0	3	16	23.5	27.0
0	3	17	0.	2.3
0	3	18	0.	2.8
0	3	19	0.	12.3
0	3	20	0.	2.6
0	3	21	0.	0.6
0	3	22	0.	14.6
0	3	23	0.	1.4
0	4	0	141.3	133.3
0	4	1	12.8	12.9
0	4	2	66.6	70.0
0	4	3	57.1	58.1
0	4	4	15.8	26.4
0	4	5	48.3	49.5
0	4	6	57.4	56.4
0	4	7	16.1	17.6
0	4	8	86.1	89.7
0	4	9	0.	3.7
0	4	10	76.8	78.4
0	4	11	9.8	11.1
0	4	12	25.8	28.9
0	4	13	44.2	46.5
0	4	14	23.0	25.9
0	4	15	19.6	20.7
0	4	16	0.	10.0
0	4	17	0.	5.1
0	4	18	41.2	43.0
0	4	19	0.	1.0
0	4	20	0.	13.3
0	4	21	0.	0.4
0	4	22	0.	3.6
0	4	23	0.	0.5
0	5	1	26.0	25.8
0	5	2	92.3	87.7
0	5	3	45.7	43.4
0	5	4	121.2	122.7
0	5	5	0.	3.5
0	5	6	86.9	89.8
0	5	7	15.3	11.3
0	5	8	0.	0.5
0	5	9	19.2	19.0
0	5	10	21.9	22.4
0	5	11	22.4	20.8
0	5	12	45.5	48.0
0	5	13	17.5	16.8
0	5	14	11.3	12.8
0	5	15	0.	3.4
0	5	16	24.1	23.2
0	5	17	0.	11.2
0	5	18	0.	5.5
0	5	19	0.	11.1
0	5	20	0.	11.2
0	5	21	0.	2.5
0	5	22	0.	9.4
0	6	0	160.7	166.9
0	6	1	14.9	15.8
0	6	2	67.9	68.3
0	6	3	0.	8.7
0	6	4	0.	0.2
0	6	5	46.6	43.8
0	6	6	34.2	35.0
0	6	7	25.6	22.7
0	6	8	56.0	54.9
0	6	9	0.	1.1
0	6	10	38.2	37.1
0	6	11	0.	5.0
0	6	12	21.8	16.4
0	6	13	42.4	40.6
0	6	14	29.0	28.7
0	6	15	39.0	35.8
0	6	16	0.	3.6
0	6	17	0.	3.5
0	6	18	24.4	25.5
0	6	19	0.	1.3
0	6	20	0.	8.1
0	6	21	0.	4.7
0	7	1	45.7	46.7
0	7	2	60.2	57.5
0	7	3	0.	7.3
0	7	4	77.7	75.0
0	7	5	16.1	15.3
0	7	6	60.7	59.6
0	7	7	0.	2.1
0	7	8	14.4	11.6
0	7	9	0.	1.2
0	7	10	14.2	16.6
0	7	11	0.	5.4
0	7	12	53.5	54.1
0	7	13	0.	5.6
0	7	14	15.7	14.8
0	7	15	0.	8.2
0	7	16	36.4	34.6
0	7	17	0.	5.3
0	7	18	0.	2.7
0	7	19	0.	3.5
0	7	20	0.	16.9
0	8	0	70.5	74.0
0	8	1	15.2	14.8
0	8	2	50.4	50.2
0	8	3	13.8	17.3
0	8	4	9.8	7.0
0	8	5	25.9	27.5
0	8	6	31.2	33.2
0	8	7	0.	11.0
0	8	8	48.9	49.1
0	8	9	0.	11.4
0	8	10	15.9	17.2
0	8	11	0.	13.3
0	8	12	0.	7.5
0	8	13	0.	10.9
0	8	14	0.	4.3
0	8	15	0.	9.7
0	8	16	0.	11.6
0	8	17	0.	1.0
0	8	18	19.2	17.9
0	8	19	0.	2.7
0	9	1	27.6	24.6
0	9	2	60.6	60.5
0	9	3	18.8	19.7
0	9	4	35.3	33.9
0	9	5	0.	7.9
0	9	6	41.7	42.3
0	9	7	0.	6.5
0	9	8	11.1	11.6
0	9	9	29.9	25.1
0	9	10	15.8	15.0
0	9	11	0.	8.0
0	9	12	47.7	43.2
0	9	13	0.	0.9
0	9	14	13.2	14.9
0	9	15	0.	4.2
0	9	16	16.5	17.5
0	9	17	0.	3.6
0	9	18	0.	3.9
0	10	0	37.8	36.9
0	10	1	16.1	16.8
0	10	2	24.1	18.8
0	10	3	0.	3.0
0	10	4	0.	7.0
0	10	5	0.	12.1
0	10	6	20.6	18.7
0	10	7	0.	2.4
0	10	8	29.1	28.2
0	10	9	0.	1.1
0	10	10	32.6	24.7
0	10	11	0.	2.1
0	10	12	0.	4.8
0	10	13	0.	5.3
0	10	14	0.	0.3
0	10	15	0.	7.4
0	10	16	0.	6.6
0	11	1	0.	2.7
0	11	2	27.3	26.9
0	11	3	0.	16.0
0	11	4	27.3	28.8
0	11	5	0.	0.8
0	11	6	33.2	33.1
0	11	7	0.	2.6
0	11	8	0.	9.7
0	11	9	18.3	20.1
0	11	10	0.	4.1
0	11	11	0.	3.9
0	11	12	0.	4.8
0	11	13	0.	8.3
0	11	14	0.	14.1
0	12	0	24.9	26.8
0	12	1	0.	7.5
0	12	2	0.	5.5
0	12	3	0.	2.2
0	12	4	0.	9.5
0	12	5	0.	9.3
0	12	6	0.	14.6
0	12	7	0.	11.0
0	12	8	13.1	14.3
0	12	9	0.	0.1
0	12	10	0.	11.2
0	12	11	0.	4.4
0	12	12	13.8	11.6
0	13	1	23.3	22.3
0	13	2	19.2	22.0
0	13	3	19.9	17.6
0	13	4	14.1	15.9
0	13	5	0.	5.3
0	13	6	0.	14.1
0	13	7	0.	2.3
0	13	8	0.	8.6
0	14	0	32.2	26.0
1	0	1	84.6	79.4
1	0	2	32.0	37.9
1	0	3	122.2	128.6
1	0	4	68.1	70.2
1	0	5	165.3	156.7
1	0	6	50.5	63.3
1	0	7	67.0	71.5
1	0	8	0.	14.2
1	0	9	14.5	11.9
1	0	10	41.6	42.2
1	0	11	19.0	27.0
1	0	12	47.1	46.9
1	0	13	72.2	79.0
1	0	14	26.1	29.6
1	0	15	46.6	53.5
1	0	16	0.	7.2
1	0	17	0.	4.4
1	0	18	16.5	9.4
1	0	19	0.	8.1
1	0	20	0.	1.0
1	0	21	21.2	24.3
1	0	22	14.5	12.3
1	0	23	17.0	14.1
1	0	24	0.	6.4
1	1	0	13.9	2.7
1	1	1	54.3	67.2
1	1	2	30.4	28.2
1	1	3	75.0	70.8
1	1	4	31.0	26.6
1	1	5	54.4	46.9
1	1	6	31.4	31.6
1	1	7	72.7	75.3
1	1	8	51.3	50.4
1	1	9	93.8	96.3
1	1	10	44.5	46.4
1	1	11	81.1	83.0
1	1	12	34.2	34.3
1	1	13	19.3	16.9
1	1	14	18.9	22.8
1	1	15	41.3	34.8
1	1	16	0.	3.3
1	1	17	32.1	33.9
1	1	18	21.2	20.2
1	1	19	17.1	19.5
1	2	0	73.0	71.9
1	2	1	21.3	20.9
1	2	2	19.6	17.2
1	2	3	163.7	183.4
1	2	4	107.9	103.1
1	2	5	149.4	151.5
1	2	6	62.4	61.6
1	2	7	85.1	86.6
1	2	8	23.2	18.7
1	2	9	35.4	30.0
1	2	10	20.1	19.9
1	2	11	50.3	54.0
1	2	12	25.9	26.0
1	2	13	62.8	66.1
1	2	14	18.3	16.4
1	2	15	52.5	52.5
1	2	16	19.6	19.5
1	2	17	0.	6.6
1	2	18	0.	5.7
1	3	0	206.8	199.6
1	3	1	187.6	183.2
1	3	2	54.7	47.0
1	3	3	95.8	94.4
1	3	4	46.8	40.9
1	3	5	21.2	20.6
1	3	6	39.3	35.8
1	3	7	70.3	75.3
1	3	8	48.3	46.9
1	3	9	106.7	107.1
1	3	10	36.6	36.3
1	3	11	52.8	56.5
1	3	12	18.9	17.0
1	3	13	0.	4.3
1	3	14	27.2	27.0
1	3	15	25.1	27.5
1	3	16	15.5	11.1
1	3	17	30.8	33.9
1	3	18	0.	10.9
1	4	0	62.6	62.6
1	4	1	26.1	25.7
1	4	2	20.6	20.0
1	4	3	124.8	125.1
1	4	4	74.3	74.3
1	4	5	120.1	121.5
1	4	6	47.2	47.1
1	4	6	0.	47.1
1	4	7	75.9	79.9
1	4	8	16.3	17.4
1	4	10	0.	9.6
1	4	11	50.0	55.3
1	4	12	16.2	16.5
1	4	13	66.2	69.7
1	4	14	19.2	17.4
1	4	15	55.0	58.3
1	4	16	20.6	19.9
1	4	17	0.	3.3
1	5	0	75.1	69.9
1	5	1	86.4	91.9
1	5	2	13.6	12.4
1	5	3	89.4	87.6
1	5	4	37.1	42.6
1	5	5	36.9	37.4
1	5	6	42.8	39.1
1	5	7	60.4	62.0
1	5	8	41.2	41.0
1	5	9	93.3	95.6
1	5	10	21.0	20.5
1	5	11	49.1	50.4
1	5	12	34.6	33.2
1	5	13	38.3	36.5
1	5	14	0.	9.7
1	5	15	34.2	35.0
1	5	16	0.	11.5
1	5	17	32.2	33.5
1	6	0	54.5	56.2
1	6	1	47.8	46.1
1	6	2	40.2	42.6
1	6	3	63.5	65.2
1	6	4	31.0	31.0
1	6	5	86.5	90.1
1	6	6	34.2	34.0
1	6	7	47.9	50.4
1	6	8	32.1	34.0
1	6	9	29.2	29.3
1	6	10	26.2	27.8
1	6	11	37.6	36.6
1	6	12	17.5	15.9
1	6	13	48.5	49.5
1	6	14	22.1	23.4
1	6	15	36.0	35.5
1	7	0	44.5	44.4
1	7	1	56.2	55.9
1	7	2	14.9	13.2
1	7	3	52.7	51.3
1	7	4	39.4	40.4
1	7	5	31.0	32.5
1	7	6	29.1	26.9
1	7	7	41.3	40.3
1	7	8	24.2	26.0
1	7	9	72.1	72.8
1	7	10	29.4	29.7
1	7	11	41.7	37.7
1	7	12	0.	14.4
1	7	13	27.8	26.3
1	7	14	0.	6.8
1	8	0	20.7	16.6
1	8	1	16.0	14.2
1	8	2	26.1	30.6
1	8	3	52.3	49.4
1	8	4	27.3	27.4
1	8	5	56.9	56.6
1	8	6	29.7	29.3
1	8	7	33.0	33.8
1	8	8	29.3	22.8
1	8	9	15.4	13.7
1	8	10	26.1	25.0
1	8	11	22.8	22.6
1	8	12	20.5	21.9
1	9	0	31.3	29.6
1	9	1	38.2	37.6
1	9	2	14.6	13.6
1	9	3	44.8	43.2
1	9	4	34.9	32.6
1	9	5	17.2	16.7
1	9	6	28.8	27.2
1	9	7	32.3	29.8
1	9	8	15.0	9.7
1	9	9	36.4	35.3
1	9	10	0.	9.4
1	10	0	31.0	29.6
1	10	1	15.0	11.8
1	10	2	28.1	27.9
1	10	3	28.5	26.0
1	10	4	18.9	17.4
1	10	5	30.6	26.4
1	10	6	16.0	16.5
1	10	7	20.4	19.7
1	11	1	26.7	26.3
1	11	2	23.7	22.3
1	11	3	25.2	25.0
1	11	4	20.7	19.9
1	11	5	19.5	18.1
1	11	9	23.5	24.5
2	0	0	152.7	152.6
2	0	1	226.1	229.9
2	0	2	168.2	171.9
2	0	3	0.	2.7
2	0	4	60.7	57.1
2	0	5	20.7	22.2
2	0	6	60.6	59.2
2	0	7	50.2	51.9
2	0	8	96.4	103.4
2	0	9	147.5	146.8
2	0	10	79.5	88.6
2	0	11	14.6	15.6
2	0	12	16.1	21.5
2	0	13	0.	0.2
2	0	14	0.	8.3
2	0	15	0.	6.3
2	0	16	15.6	20.4
2	0	17	21.1	24.8
2	0	18	40.7	45.7
2	0	19	35.0	35.9
2	0	20	0.	6.7
2	0	21	0.	12.9
2	0	22	0.	2.5
2	0	23	0.	4.6
2	1	0	29.1	28.7
2	1	1	52.6	55.6
2	1	2	137.4	143.4
2	1	3	93.4	98.1
2	1	4	126.7	120.7
2	1	5	95.6	98.4
2	1	6	81.0	86.9
2	1	7	67.7	67.5
2	1	8	24.8	28.8
2	1	9	13.3	9.2
2	1	10	37.8	40.2
2	1	11	38.6	43.7
2	1	12	57.1	55.2
2	1	13	35.7	34.2
2	1	14	38.5	40.7
2	1	15	50.3	52.4
2	1	16	15.6	18.1
2	1	17	0.	4.3
2	1	18	0.	11.9
2	2	0	149.6	150.4
2	2	1	116.4	124.6
2	2	2	97.6	100.0
2	2	3	98.9	96.0
2	2	4	46.2	44.9
2	2	5	13.0	12.2
2	2	6	71.7	64.0
2	2	7	52.1	53.1
2	2	8	91.3	92.0
2	2	9	105.5	105.2
2	2	10	73.4	74.1
2	2	11	39.5	41.3
2	2	12	27.0	30.4
2	2	13	30.5	30.9
2	2	14	14.4	8.4
2	2	15	29.6	31.6
2	2	16	24.2	24.7
2	2	17	36.1	36.1
2	2	18	26.9	27.2
2	3	0	50.4	47.7
2	3	1	17.5	9.7
2	3	2	76.1	74.7
2	3	3	60.7	62.1
2	3	4	92.1	94.8
2	3	5	95.6	95.1
2	3	6	75.0	76.7
2	3	7	53.4	55.1
2	3	8	17.2	18.9
2	3	9	14.2	16.3
2	3	10	36.7	33.7
2	3	11	27.0	27.8
2	3	12	30.5	32.8
2	3	13	46.8	47.5
2	3	14	20.4	20.0
2	3	15	36.2	35.1
2	3	16	26.6	26.1
2	3	17	0.	7.4
2	4	0	106.2	104.4
2	4	1	96.1	94.1
2	4	2	46.6	45.9
2	4	3	71.5	71.0
2	4	4	58.2	57.5
2	4	5	33.7	35.4
2	4	6	79.5	80.6
2	4	7	18.9	22.4
2	4	8	67.3	70.2
2	4	9	67.6	69.6
2	4	10	37.1	39.0
2	4	11	39.8	42.9
2	4	12	24.1	27.2
2	4	13	0.	2.9
2	4	14	0.	8.0
2	4	15	31.6	31.7
2	4	16	20.1	20.2
2	4	17	21.1	22.1
2	5	0	0.	5.7
2	5	1	28.9	30.5
2	5	2	94.8	85.4
2	5	3	88.8	93.7
2	5	4	49.2	53.2
2	5	5	45.3	47.1
2	5	6	53.2	57.6
2	5	7	36.0	37.5
2	5	8	22.9	23.4
2	5	9	20.5	20.8
2	5	10	23.0	20.3
2	5	11	33.6	35.7
2	5	12	27.5	27.8
2	5	13	31.7	34.1
2	5	14	19.8	19.9
2	5	15	25.9	23.0
2	5	16	0.	7.4
2	6	0	59.5	57.9
2	6	1	54.4	53.5
2	6	2	59.0	58.6
2	6	3	53.7	54.2
2	6	4	31.7	31.0
2	6	5	21.6	22.9
2	6	6	41.6	39.8
2	6	7	30.4	34.5
2	6	8	45.1	48.3
2	6	9	37.4	35.2
2	6	10	32.4	33.1
2	6	11	30.9	31.0
2	6	12	0.	8.5
2	6	13	0.	12.2
2	6	14	26.3	24.3
2	6	15	17.0	15.4
2	7	0	24.6	26.5
2	7	1	14.1	9.4
2	7	2	72.5	74.3
2	7	3	54.4	56.2
2	7	4	36.7	32.2
2	7	5	25.5	24.7
2	7	6	49.4	51.2
2	7	7	39.6	37.1
2	7	8	0.	9.1
2	7	9	0.	10.3
2	7	10	21.5	23.9
2	7	11	21.6	19.8
2	7	12	31.0	31.2
2	7	13	25.7	22.7
2	8	0	43.6	41.1
2	8	1	32.1	28.7
2	8	2	43.7	48.4
2	8	3	30.9	27.8
2	8	4	15.3	14.4
2	8	5	14.2	16.1
2	8	6	17.0	16.1
2	8	7	24.2	25.8
2	8	8	32.4	29.0
2	8	9	28.5	28.9
2	8	10	36.6	38.3
2	8	11	0.	10.3
2	8	12	0.	0.9
2	9	0	45.0	46.3
2	9	1	21.6	22.1
2	9	2	38.6	35.2
2	9	3	32.5	32.0
2	9	4	25.5	26.9
2	9	5	30.2	31.5
2	9	6	36.6	35.6
2	9	7	31.5	30.8
2	9	8	0.	11.4
2	9	9	0.	10.1
2	10	0	29.5	27.9
2	10	1	26.0	23.2
2	10	2	25.1	23.4
2	10	3	15.1	12.1
2	10	4	0.	8.2
2	10	5	0.	4.8
2	10	6	18.7	17.0
2	11	2	22.4	19.8
2	11	3	19.5	17.2
2	11	4	22.2	22.4
2	11	5	25.8	25.3
3	0	1	31.4	35.3
3	0	2	44.0	43.1
3	0	3	39.4	39.2
3	0	4	138.3	139.5
3	0	5	30.8	31.4
3	0	6	124.5	128.8
3	0	7	9.9	20.5
3	0	8	0.	4.1
3	0	9	0.	9.6
3	0	10	0.	0.1
3	0	11	34.1	33.1
3	0	12	59.6	66.8
3	0	13	0.	14.8
3	0	14	47.5	52.0
3	0	15	24.2	27.5
3	0	16	29.5	29.5
3	0	17	14.0	10.5
3	0	18	0.	2.3
3	0	19	0.	0.1
3	0	20	14.6	17.2
3	0	21	0.	3.8
3	0	22	14.8	16.7
3	0	23	0.	6.0
3	1	0	112.8	109.2
3	1	1	58.3	56.5
3	1	2	126.7	121.3
3	1	3	0.	9.3
3	1	4	17.5	17.7
3	1	5	44.4	39.1
3	1	6	56.6	61.3
3	1	7	56.6	55.1
3	1	8	67.5	66.8
3	1	9	19.6	24.5
3	1	10	45.7	50.7
3	1	11	12.1	11.4
3	1	12	34.0	32.9
3	1	13	0.	14.9
3	1	14	0.	14.3
3	1	15	19.5	20.5
3	1	16	29.0	32.7
3	1	17	14.5	12.6
3	2	0	0.	7.4
3	2	1	11.3	16.0
3	2	2	102.9	107.9
3	2	3	22.8	28.3
3	2	4	123.0	123.0
3	2	5	50.0	55.9
3	2	6	101.5	103.2
3	2	7	24.8	34.7
3	2	8	11.3	14.7
3	2	9	11.3	17.4
3	2	10	25.2	26.0
3	2	11	30.1	27.9
3	2	12	55.2	59.6
3	2	13	28.1	31.5
3	2	14	50.8	51.9
3	2	15	29.3	32.3
3	2	16	19.6	18.5
3	2	17	0.	8.3
3	3	0	83.7	89.2
3	3	1	53.2	54.0
3	3	2	72.9	77.6
3	3	3	71.3	73.7
3	3	4	26.8	30.2
3	3	5	33.3	33.1
3	3	6	60.3	64.0
3	3	7	31.1	28.9
3	3	8	76.8	82.1
3	3	9	17.7	14.7
3	3	10	72.4	73.1
3	3	11	39.1	41.0
3	3	12	27.3	23.7
3	3	13	0.	7.7
3	3	14	0.	11.7
3	3	15	36.9	36.8
3	3	16	0.	20.2
3	3	17	27.0	28.0
3	4	0	32.7	32.3
3	4	1	0.	2.4
3	4	2	95.3	97.7
3	4	3	62.6	55.9
3	4	4	90.4	87.4
3	4	5	49.4	47.9
3	4	6	89.8	93.8
3	4	7	30.8	31.8
3	4	8	23.5	29.1
3	4	9	18.1	17.0
3	4	10	0.	15.6
3	4	11	34.4	36.4
3	4	12	41.6	43.7
3	4	13	35.3	38.0
3	4	14	50.6	50.6
3	4	15	0.	15.9
3	4	16	17.9	19.2
3	5	0	75.1	75.5
3	5	1	41.2	44.6
3	5	2	89.8	93.1
3	5	3	38.5	37.3
3	5	4	26.0	26.5
3	5	5	0.	17.2
3	5	6	50.8	48.6
3	5	7	35.3	33.3
3	5	8	62.7	59.6
3	5	9	22.9	24.3
3	5	10	63.6	63.2
3	5	11	31.8	33.5
3	5	12	38.1	36.9
3	5	13	18.1	16.6
3	5	14	0.	1.7
3	5	15	16.9	17.1
3	6	0	0.	4.0

Table 1 (cont.)

continued:—

h	k	l	Fobs	Fcalc
3	6	1	39.8	42.8
3	6	2	53.0	51.C
3	6	3	46.8	43.6
3	6	4	80.8	80.9
3	6	5	23.6	22.9
3	6	6	79.5	76.4
3	6	7	C.	12.2
3	6	8	14.2	13.C
3	6	9	2.3	34.6
3	6	10	C.	11.5
3	6	11	16.1	13.6
3	6	12	36.1	38.3
3	6	13	29.8	29.C
3	6	14	27.5	25.7
3	7	0	69.8	91.1
3	7	1	13.3	9.1
3	7	2	65.1	72.1
3	7	3	33.1	34.C
3	7	4	17.2	16.1
3	7	5	27.1	27.8
3	7	6	40.5	43.7
3	7	7	34.2	31.C
3	7	8	46.2	48.5
3	7	9	C.	5.5
3	7	10	35.9	35.7
3	7	11	15.4	17.3
3	7	12	28.1	25.4
3	7	13	0.	8.6
3	8	0	25.8	41.C
3	8	1	26.2	26.4
3	8	2	30.9	27.8
3	8	3	26.0	25.9
3	8	4	52.4	51.1
3	8	5	17.7	18.7
3	8	6	39.3	34.5
3	8	7	19.4	19.2
3	8	8	C.	11.C
3	8	9	20.8	19.9
3	8	10	C.	7.5
3	8	11	18.2	15.2
3	9	0	34.9	33.9
3	9	1	21.C	17.4
3	9	2	47.C	42.7
3	9	3	34.3	32.8
3	9	4	20.8	19.5
3	9	5	21.9	19.3
3	9	6	32.3	31.2
3	9	7	16.8	12.5
3	9	8	32.1	30.8
3	9	9	19.3	20.6
3	10	0	24.5	23.2
3	10	1	16.1	11.4
3	10	2	24.6	23.5
3	10	3	16.C	14.7
3	11	2	19.3	19.4
3	11	3	25.2	26.1
4	C	0	26.0	20.4
4	C	1	104.6	111.3
4	C	2	0.	10.C
4	C	3	33.1	37.5
4	C	4	C.	4.5
4	C	5	20.1	18.7
4	C	6	C.	12.0
4	C	7	85.4	88.8
4	C	8	C.	4.2
4	C	9	115.7	118.7
4	C	10	18.1	23.0
4	C	11	93.2	101.7
4	C	12	C.	5.4
4	C	13	11.6	12.4
4	C	14	18.9	19.6
4	C	15	23.1	20.4
4	C	16	C.	5.4
4	C	17	4C.8	44.3
4	0	18	C.	2.0
4	0	19	3C.0	28.9
4	C	20	C.	0.4
4	C	21	C.	6.8
4	1	22	C.	3.6
4	1	0	5C.3	48.8
4	1	1	27.6	28.5
4	1	2	16.2	19.1
4	1	3	121.9	124.5
4	1	4	35.4	39.3
4	1	5	98.4	102.1
4	1	6	0.	8.C
4	1	7	83.1	83.7
4	1	8	0.	10.7
4	1	9	C.	10.6
4	1	10	22.1	18.9
4	1	11	50.8	50.9
4	1	12	12.7	12.1
4	1	13	47.1	47.2
4	1	14	C.	5.8
4	1	15	32.7	33.3
4	1	16	C.	47.6
4	2	0	48.5	47.6
4	2	1	131.1	13C.9

h	k	l	Fobs	Fcalc
4	2	2	28.4	28.1
4	2	3	61.9	62.4
4	2	4	27.4	21.P
4	2	5	28.2	29.C
4	2	6	41.4	41.3
4	2	7	87.8	86.8
4	2	8	21.5	23.1
4	2	9	101.9	1C3.5
4	2	10	16.8	20.C
4	2	11	60.8	61.7
4	2	12	20.7	19.7
4	2	13	20.4	19.8
4	2	14	27.9	29.5
4	2	15	C.	15.0
4	2	16	32.1	25.C
4	3	C	45.6	51.4
4	3	1	58.7	56.3
4	3	2	26.3	31.C
4	3	3	99.8	99.1
4	3	4	C.	13.7
4	3	6	19.8	17.1
4	3	7	58.5	56.7
4	3	8	16.1	15.9
4	3	9	13.4	14.5
4	3	10	20.3	22.3
4	3	11	42.7	43.C
4	3	12	C.	11.3
4	3	13	45.2	48.2
4	3	14	C.	10.3
4	3	15	35.0	32.1
4	3	16	0.	6.8
4	4	0	C.	2.8
4	4	1	104.9	105.C
4	4	2	58.5	55.7
4	4	3	49.6	52.9
4	4	4	29.7	29.9
4	4	5	26.9	26.4
4	4	6	39.4	41.C
4	4	7	7C.7	71.5
4	4	8	C.	6.5
4	4	9	63.2	66.3
4	4	10	C.	6.5
4	4	11	12.3	8.C
4	4	12	0.	9.3
4	4	13	C.	13.6
4	4	14	C.	14.C
4	4	15	C.	17.5
4	5	0	16.9	13.8
4	5	1	36.6	34.4
4	5	2	1C.1	10.1
4	5	3	55.5	60.9
4	5	4	12.3	8.C
4	5	5	63.2	59.6
4	5	6	13.1	16.7
4	5	7	51.3	50.C
4	5	8	16.5	17.5
4	5	9	C.	6.5
4	5	10	C.	8.7
4	5	11	44.2	45.4
4	5	12	0.	10.8
4	5	13	35.5	32.C
4	5	14	C.	9.5
4	6	C	3C.C	34.1
4	6	1	45.3	5C.2
4	6	2	26.2	29.2
4	6	3	16.4	9.3
4	6	4	26.6	27.3
4	6	5	C.	4.3
4	6	6	26.7	29.C
4	6	7	42.3	40.4
4	6	8	C.	8.2
4	6	10	C.	5.4
4	6	11	14.5	29.2
4	6	12	C.	9.2
4	6	13	C.	11.5
4	7	0	31.8	32.2
4	7	2	C.	10.C
4	7	3	51.9	46.C
4	7	4	18.3	17.3
4	7	5	41.9	40.1
4	7	6	C.	13.8
4	7	7	43.4	46.C
4	7	8	14.0	14.4
4	7	9	C.	3.2
4	7	10	20.1	20.2
4	7	11	39.2	37.5
4	8	0	27.0	28.6
4	8	1	4C.9	37.C
4	8	2	0.	7.1
4	8	3	17.1	16.2
4	8	4	C.	5.9
4	8	5	C.	4.5
4	8	6	21.3	20.4
4	8	7	28.9	24.2
4	8	8	C.	10.5
4	8	9	39.8	39.9
4	9	C	C.	8.6
4	9	1	28.C	26.1
4	9	2	12.8	9.8
4	9	3	46.1	44.4

h	k	l	Fobs	Fcalc
4	9	4	C.	3.7
4	9	5	31.9	31.4
4	9	6	C.	12.7
4	11	3	29.4	28.7
4	11	5	19.1	19.6
5	C	1	4C.9	46.C
5	C	2	31.3	82.7
5	C	3	23.6	23.5
5	C	4	1C1.0	99.2
5	C	5	4C.7	4C.3
5	C	6	18.0	19.5
5	C	7	C.	8.9
5	C	8	C.	3.4
5	C	9	39.1	1C.5
5	C	1C	27.0	30.3
5	C	11	0.	1C.7
5	C	12	39.5	38.1
5	C	13	29.0	27.8
5	C	14	44.5	5C.9
5	C	15	16.4	14.C
5	C	16	C.	11.8
5	C	17	C.	9.7
5	C	20	C.	3.5
5	C	21	C.	1.8
5	1	0	137.6	14C.8
5	1	1	38.3	40.5
5	1	2	44.6	65.4
5	1	3	38.9	33.C
5	1	5	C.	10.7
5	1	6	48.4	41.1
5	1	7	2C.5	28.5
5	1	8	56.4	53.1
5	1	9	C.	7.2
5	1	10	44.7	43.3
5	1	11	C.	21.6
5	1	12	C.	7.7
5	1	13	C.	4.5
5	1	14	18.4	19.3
5	2	0	37.1	39.8
5	2	1	26.7	26.6
5	2	2	47.1	47.2
5	2	3	39.8	4C.4
5	2	4	92.8	92.7
5	2	5	41.5	37.3
5	2	7	21.C	18.2
5	2	8	C.	4.4
5	2	9	C.	7.9
5	2	10	14.3	18.9
5	2	11	14.3	18.5
5	2	12	49.3	45.2
5	2	13	C.	10.6
5	2	14	5C.2	46.5
5	3	1C	65.C	84.3
5	3	2	29.C	31.C
5	3	3	45.7	44.C
5	3	4	21.3	22.C
5	3	5	C.	7.6
5	3	6	45.4	45.7
5	3	7	11.8	12.3
5	3	8	63.2	61.3
5	3	9	16.3	15.7
5	3	10	48.5	42.C
5	3	11	23.7	23.6
5	3	12	14.2	34.6
5	3	13	0.	3.3
5	3	14	11.2	18.5
5	4	0	C.	2.2
5	4	1	25.6	26.5
5	4	2	45.5	42.3
5	4	3	26.5	27.C
5	4	4	53.C	91.1
5	4	5	21.5	21.9
5	4	6	55.8	62.2
5	4	7	21.3	22.C
5	4	8	C.	11.2
5	4	10	18.3	19.7
5	4	11	17.2	13.5
5	4	12	47.9	48.3
5	4	13	15.6	15.6
5	4	14	24.1	23.6
5	5	0	49.0	88.9
5	5	1	C.	32.3
5	5	2	64.1	62.0
5	5	3	43.0	23.5
5	5	4	14.8	18.1
5	5	5	15.0	13.1
5	5	6	4C.9	4C.9
5	5	7	17.6	19.7
5	5	8	55.2	52.8
5	5	9	0.	12.6
5	5	10	38.7	37.5
5	5	11	15.1C	11.4
5	5	12	27.8	26.5
5	5	13	15.C	17.7
5	6	0	2C.3	32.3

h	k	l	Fobs	Fcalc
5	6	1	2C.1	28.1
5	6	2	5C.7	47.8
5	6	3	33.1	38.7
5	6	4	7C.5	68.3
5	6	5	2C.6	20.9
5	6	6	46.6	46.2
5	6	7	12.1	6.6
5	6	8	12.3	11.4
5	6	9	15.2	13.6
5	6	10	C.	10.2
5	6	11	C.	9.6
5	7	C	55.6	45.1
5	7	1	19.1	39.H
5	7	2	61.9	60.6
5	7	3	C4.0	23.5
5	7	4	71.7	24.7
5	7	5	18.6	17.4
5	7	6	49.9	41.6
5	7	7	27.6	31.3
5	7	8	33.8	29.7
5	7	9	C.	4.P
5	8	0	U.	0.7
5	8	1	77.4	2C.C
5	8	2	31.C	2C.1
5	8	3	26.1	25.6
5	8	4	17.1	17.4
5	H	5	17.3	13.7
5	H	6	5C.9	26.3
5	H	7	C.	3.8
5	9	0	5.9	4C.6
5	9	1	15.2	22.7
6	C	0	3.6	49.4
6	C	1	56.4	42.5
6	C	2	4C.1	3.4
6	C	3	13.0	33.7
6	C	4	14.C	9.1
6	C	5	33.9	34.5
6	C	6	C.	13.C
6	C	7	42.9	38.9
6	C	8	6C.9	59.6
6	C	9	7C.0	71.3
6	C	1C	54.3	56.5
6	C	11	14.9	14.7
6	C	12	43.9	43.7
6	C	13	n.	11.C
6	C	14	C.	0.4
6	C	15	C.	13.5
6	C	16	0.	6.6
6	C	17	18.5	22.3
6	C	18	23.5	18.4
6	C	19	17.7	17.4
6	1	10	C.	9.3
6	1	2	23.2	19.7
6	1	3	27.3	21.5
6	1	4	61.9	56.7
6	1	5	53.6	48.5
6	1	6	45.3	45.5
6	1	7	18.5	18.5
6	1	8	12.1	24.7
6	1	9	17.9	19.1
6	1	10	C.	7.6
6	1	11	13.5	16.5
6	1	12	13.4	14.C
6	1	13	36.C	37.P
6	2	1	79.3	79.7
6	2	2	12.2	52.5
6	2	3	18.7	17.6
6	2	4	30.9	28.5
6	2	5	13.2	16.5
6	2	7	29.2	24.H
6	2	8	43.1	53.1
6	2	9	12.7	11.5
6	2	10	49.5	49.0
6	2	11	22.4	24.3
6	2	12	23.9	27.8
6	3	0	C.	7.8
6	3	1	25.C	17.8
6	3	2	34.0	34.2
6	3	3	61.5	54.7
6	3	4	4C.7	39.3
6	3	5	54.9	52.3
6	3	6	5C.3	48.C
6	3	7	34.2	38.4
6	3	8	18.6	5.5
6	3	9	3C.1	27.3
6	3	10	C.	7.8
6	3	11	29.4	28.2
6	3	12	26.3	25.3
6	3	13	25.6	21.8
6	4	0	53.5	45.C
6	4	1	63.6	58.P
6	4	2	35.7	34.4
6	4	3	25.0	29.8
6	4	4	2C.1	20.4
6	4	5	29.C	29.4
6	4	6	29.2	33.4
6	4	7	14.5	10.1
6	4	8	38.1	33.1

h	k	l	Fobs	Fcalc
6	4	9	54.5	52.4
6	4	10	41.9	28.7
6	4	11	C.	18.0
6	4	12	19.4	15.5
6	5	0	27.C	27.1
6	5	1	14.1	17.6
6	5	2	71.7	21.7
6	5	3	41.9	33.8
6	5	4	34.4	30.5
6	5	5	36.C	31.4
6	5	6	32.3	29.2
6	5	7	24.4	24.8
6	5	8	24.8	16.7
6	5	9	C.	13.7
6	5	11	2C.0	25.2
6	6	C	38.1	38.4
6	6	1	32.1	25.6
6	6	2	C.	10.1
6	6	3	26.0	24.1
6	6	4	2C.5	20.1
6	6	5	25.7	22.9
6	6	6	0.	14.9
6	6	7	26.1	20.4
6	6	8	C.	23.8
6	6	9	23.H	24.C
6	6	9	42.1	39.7
6	7	0	C.	3.4
6	7	1	15.C	13.2
6	7	2	14.5	12.9
6	7	3	33.5	33.3
6	7	4	24.5	21.6
6	7	5	25.2	22.7
6	7	6	18.4	16.8
6	7	7	18.C	16.8
6	8	C	28.1	24.3
6	8	1	11.9	27.5
7	C	1	24.4	21.1
7	C	2	22.6	14.3
7	C	3	64.6	54.2
7	C	4	4C.3	43.9
7	C	5	78.8	79.8
7	C	6	23.6	20.3
7	C	7	24.5	21.6
7	C	8	18.9	8.8
7	C	9	18.4	21.9
7	C	10	C.	5.4
7	C	11	24.2	21.2
7	C	12	24.7	26.6
7	C	13	29.9	26.2
7	C	14	C.	2.7
7	C	15	28.2	26.7
7	C	16	C.	4.C
7	C	17	C.	2.9
7	C	18	C.	5.5
7	C	19	C.	1.3
7	1	0	3C.2	37.6
7	1	1	67.6	54.7
7	1	2	2C.C	12.7
7	1	3	33.1	27.1
7	1	5	2C.5	24.C
7	1	6	19.7	14.1
7	1	8	25.9	23.1
7	1	9	56.7	54.1
7	1	10	7C.0	24.9
7	1	11	C.	5.7
7	2	C	C.	9.6
7	2	1	19.6	15.C
7	2	2	13.3	18.1
7	2	3	8.2	54.7
7	2	4	44.9	28.5
7	2	5	13.2	56.5
7	2	6	30.0	26.4
7	2	7	27.9	25.3
7	2	8	18.7	17.C
7	2	9	C.	9.4
7	2	10	C.	4.5
7	2	11	16.0	13.9
7	3	1	18.6	5.3
7	3	2	5C.C	42.8
7	3	3	23.C	22.2
7	3	4	42.7	37.1
7	3	5	17.4	20.3
7	3	6	36.5	38.6
7	3	7	26.7	23.6
7	3	8	21.7	22.1
7	3	9	44.7	39.4
7	3	10	19.7	18.4
7	4	0	C.	11.C
7	4	1	13.2	7.9
7	4	2	25.2	26.3
7	4	3	55.0	51.6
7	4	4	21.5	23.3
7	4	5	46.6	41.C
7	4	6	29.2	27.1
7	4	7	31.7	28.2
7	4	8	19.4	18.6
7	4	9	C.	13.0
7	5	0	31.8	30.6
7	5	1	61.1	55.7
7	5	2	12.4	7.1

h	k	l	Fobs	Fcalc
7	5	3	28.0	23.1
7	5	4	C.	10.6
7	5	5	2C.5	22.9
7	5	6	29.3	28.2
7	5	7	22.9	19.9
7	5	8	17.1	18.1
7	6	0	18.7	15.9
7	6	1	0.	2.8
7	6	2	24.3	21.3
7	6	3	47.8	43.3
7	6	4	25.1	21.2
7	6	5	44.0	38.7
7	6	6	22.3	16.7
7	7	0	31.3	26.9
7	7	1	24.5	21.2
8	C	0	7C.4	66.9
8	C	1	0.	7.7
8	C	2	51.3	45.3
8	C	3	17.4	17.3
8	C	4	14.7	12.0
8	C	5	C.	4.7
8	C	6	25.4	21.2
8	C	7	C.	5.5
8	C	8	41.2	34.2
8	C	9	C.	5.4
8	C	10	44.C	40.4
8	C	11	C.	8.1
8	C	12	21.6	16.7
8	C	13	C.	0.7
8	C	14	C.	1.4
8	C	15	18.8	13.7
8	C	16	16.6	11.C
8	C	17	C.	2.2
8	1	0	C.	7.3
8	1	1	C.	18.8
8	1	2	35.5	35.4
8	1	3	C.	6.6
8	1	4	41.5	29.2
8	1	5	C.	14.C
8	1	6	61.9	55.3
8	1	7	C.	3.1
8	2	0	76.0	77.6
8	2	1	0.	12.3
8	2	2	38.5	33.6
8	2	3	C.	18.2
8	2	4	C.	11.C
8	2	5	19.3	26.8
8	2	6	17.7	13.2
8	2	7	C.	5.5
8	3	0	C.	4.5
8	3	1	35.9	32.9
8	3	3	54.8	13.C
8	3	4	47.C	38.5
8	3	5	C.	9.9
8	3	6	47.3	40.5
8	4	0	54.3	46.9
8	4	1	14.2	14.1
8	4	2	28.0	18.4
8	4	3	C.	8.5
8	4	8	22.6	19.C
8	8	C	9C.8	21.8
9	C	1	C.	6.2
9	C	2	C.	3.5
9	C	3	54.4	46.9
9	C	4	2C.7	15.8
9	C	5	41.5	31.4
9	C	6	C.	11.8
9	C	7	1.3	16.1
9	C	8	C.	5.4
9	C	9	C.	2.9
9	C	11	71.6	19.7
9	C	12	C.	5.6
9	C	13	74.2	22.1
9	C	14	C.	5.6
9	1	1	38.8	27.2
9	1	3	37.8	24.2
9	3	1	21.3	17.6
9	3	2	23.C	20.5
9	3	3	42.7	37.1
9	3	4	C.	13.3
10	C	1	37.7	25.C
1C	C	2	42.C	37.9
1C	C	3	22.4	12.4
1C	C	3	22.5	17.7
10	C	4	C.	7.9
10	C	5	C.	4.5
10	C	6	C.	2.0
10	C	7	C.	10.4
10	C	8	22.5	16.9
10	C	9	18.4	11.7
10	C	10	16.4	14.C
10	C	11	15.4	9.8
10	2	3	29.5	13.C
10	3	3	2C.9	15.6
11	0	1	C.	3.5
11	C	2	0.	7.9
11	C	3	18.0	9.6
11	C	4	28.2	16.8
11	C	5	C.	8.4
11	0	6	24.0	17.1

$U = 2071$ Å^3.

$D_m = 1\cdot493$, $Z = 4$, $D_x = 1\cdot495$ g.cm^{-3}.

Absorption coefficients for X-rays,

$\mu(\text{Cu } K\alpha) = 125$ cm^{-1}.

$\mu(\text{Mo } K\alpha) = 16$ cm^{-1}.

$F(000) = 952$.

Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd. Space group $P2_12_12_1$ (D_2^4).

The intensities of all reflexions with $2\theta(\text{Mo } K\alpha) \leq 51°$ (corresponding to a minimum interplanar spacing $d = 0\cdot83$ Å) were measured on a General Electric XRD 5 Spectrogoniometer, with a scintillation counter, approximately monochromatic Mo $K\alpha$ radiation (zirconium filter and pulse height analyser), and the moving-crystal moving-counter technique (Furnas, 1957). In the range $0 < 2\theta \leq 40°$, about 80% of the reflexions had intensities above background, but most of the higher-order reflexions had negligible intensities. 1018 re-

flexions were observed, and during the analysis, structure factors were calculated in addition for all the unobserved reflexions with $2\theta < 40°$. All the intensities were corrected for background, Lorentz and polarization factors were applied, and the structure amplitudes were derived. The crystal used for the intensities was mounted with **a** parallel to the φ axis of the goniostat, and had dimensions 0·3 mm, 0·2 mm, 0·2 mm parallel to **a**, **b**, **c** respectively; absorption was negligible, and no corrections were applied.

Structure analysis

The position of the iodine was determined from the three axial Patterson projections as (0·94, 0·00, 0·44), and a three-dimensional Fourier series was summed with phases based on the iodine atom. The resulting electron-density distribution had of course a false mirror plane at $y = 0$, but it was possible to pick out some of the light atoms. The dihydroindole nucleus lay approximately in the plane $y = 0$, so there was little ambiguity about its position, but it was possible to include only three atoms with $y \neq 0$. A second electron-density distribution, with phases based on fourteen atoms, while it still contained some residual false symmetry, gave positions for all the atoms in the molecule. A third distribution (Fig. 1) showed the whole molecule with no false detail. Structure factors were calculated with the scattering factors for I⁻, C, N and O of *International Tables for X-ray Crystallography* (1962), that for I⁻ being derived from the I curve and corrected for anomalous dispersion. R was 0·205 for the 1018 observed reflexions.

Refinement of positional and thermal parameters, and a scale factor, proceeded by (block-diagonal) least-squares on the IBM 7040 computer. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$. Since we considered
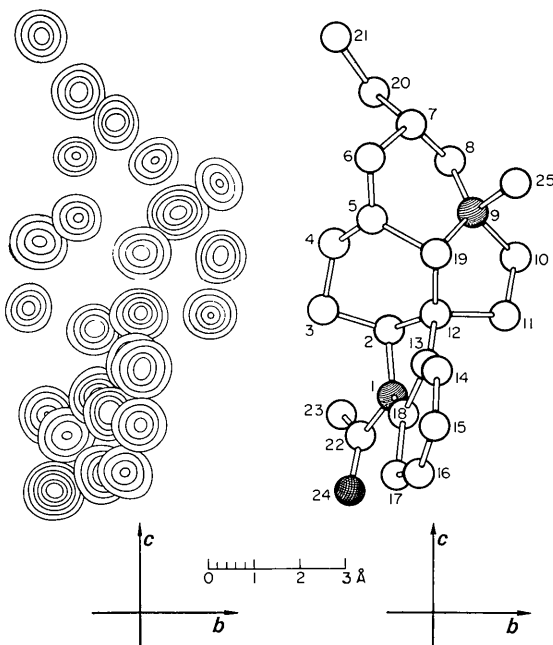
Fig. 1. Superimposed sections of the three-dimensional electron-density distribution, through the atomic centres parallel to (100); contours start at 2 e.Å⁻³, and are at intervals of 1 e.Å⁻³. The iodide ion is omitted. A drawing of the molecule is also shown. Both drawings show the correct absolute configuration, the positive direction of the *a* axis being towards the viewer.

Table 2. *Fractional positional parameters and standard deviations* (each × 10⁴), *isotropic thermal parameters and standard deviations* (Å²) *and anisotropic thermal parameters* (exp $\{-b_{ij}h_ih_j\}$; $b_{ij} \times 10^4$)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
I	9391	0074	4443	2	2	1	5·57	0·04	135	14	−16	101	−2	36
N(1)	3433	−0846	2379	21	17	10	3·49	0·68	85	23	−16	53	−1	20
C(2)	3339	−0836	3142	22	18	10	1·81	0·57	41	6	11	34	0	10
C(3)	3615	−2122	3395	27	22	13	3·52	0·87	127	20	5	59	−15	22
C(4)	3769	−2101	4188	26	22	12	3·37	0·82	90	3	−13	59	−7	18
C(5)	5082	−1370	4376	24	19	13	3·14	0·74	99	−2	−2	54	−5	18
C(6)	5321	−1291	5158	24	20	11	3·34	0·69	55	9	23	60	3	16
C(7)	4236	−0541	5518	20	16	12	2·36	0·62	19	−1	38	49	−2	19
C(8)	3330	0290	5059	24	20	11	3·27	0·70	79	−11	15	59	−6	21
N(9)	4277	0828	4519	20	14	9	2·97	0·49	64	−6	−20	48	8	19
C(10)	3203	1501	4048	26	20	11	2·73	0·74	82	−44	−21	52	−10	18
C(11)	4011	1370	3333	24	19	12	2·91	0·68	73	−14	−2	45	6	19
C(12)	4526	0057	3331	23	23	10	3·23	0·59	78	53	−5	52	5	22
C(13)	5599	−0132	2780	21	18	9	2·32	0·57	37	58	12	29	−6	19
C(14)	7029	0211	2759	25	22	11	3·68	0·79	85	−10	6	59	−12	27
C(15)	7765	0089	2121	26	32	11	4·63	0·79	128	−26	11	71	−6	28
C(16)	7039	−0283	1559	27	21	12	4·11	0·83	124	−26	37	54	6	27
C(17)	5580	−0586	1563	30	21	13	4·17	0·69	89	−59	−21	79	11	29
C(18)	4878	−0555	2193	26	20	12	2·92	0·76	70	−17	−9	44	0	22
C(19)	5141	−0092	4071	21	23	10	2·98	0·62	98	−38	−4	50	8	13
C(20)	2999	−1334	5903	29	23	13	4·11	0·80	94	52	10	80	−29	28
C(21)	3630	−1924	6554	30	24	14	4·66	1·02	131	9	11	83	−11	31
C(22)	2477	−1410	1958	27	21	13	3·10	0·77	69	16	−6	63	9	23
C(23)	1015	−1700	2230	29	23	14	4·40	0·96	89	28	−5	79	2	31
O(24)	2829	−1627	1364	20	16	9	4·63	0·58	132	28	−11	89	7	25
C(25)	5372	1700	4829	30	22	13	4·81	1·00	106	66	−55	71	6	30

that our measurements were reliable and accurate for all but the very weak reflexions, the weighting scheme used was $\sqrt{w} = 1$ when $|F_o| \geq 20$, $\sqrt{w} = F_o/20$ when $|F_o| < 20$. Four cycles with isotropic thermal parameters reduced R from 0·205 to 0·102, and $\Sigma w . \Delta F^2$ from 78×10^3 to 27×10^3, and two further cycles with anisotropic thermal parameters reduced these factors to 0·066 and 15×10^3 respectively. The final measured and calculated structure amplitudes ($R = 0.066$ for the 1018 observed reflexions) are listed in Table 1.

Coordinates and molecular dimensions

The final positional and anisotropic thermal parameters, from the sixth least-squares cycle, are given in Table 2; the isotropic thermal parameters from the fourth cycle, and the standard deviations of the positional parameters, calculated from the final least-squares residuals, are included.

The bond distances and valency angles in the molecule are given in Table 3, and a perspective drawing of the molecule is shown in Fig. 2. The most significant

Table 3. Bond distances and valency angles

Standard deviations are about 0·03 Å and 1·5°

C(13)–C(14)	1·389 Å	N(9)–C(8)	1·510 Å
C(14)–C(15)	1·439	N(9)–C(10)	1·561
C(15)–C(16)	1·363	N(9)–C(19)	1·583
C(16)–C(17)	1·403	N(9)–C(25)	1·544
C(17)–C(18)	1·403	Mean $N^+-C_{sp}{}^3$	1·55$_0$
C(18)–C(13)	1·421		
Mean $C_{ar}-C_{ar}$	1·40$_3$	N(1)–C(2)	1·507
C(12)–C(13)	1·491	N(1)–C(18)	1·434
C(22)–C(23)	1·501		
Mean $C_{sp}{}^2-C_{sp}{}^3$	1·49$_6$	N(1)–C(22)	1·374
C(2)–C(3)	1·556	C(24)–O(26)	1·239
C(3)–C(4)	1·570		
C(4)–C(5)	1·522		
C(5)–C(6)	1·558		
C(6)–C(7)	1·498		
C(7)–C(8)	1·554		
C(10)–C(11)	1·605		
C(11)–C(12)	1·559		
C(12)–C(2)	1·542		
C(12)–C(19)	1·575		
C(5)–C(19)	1·565		
C(7)–C(20)	1·645		
C(20)–C(21)	1·561		
Mean $C_{sp}{}^3-C_{sp}{}^3$	1·56$_2$		
C(13)–C(14)–C(15)	117·2°	C(13)–C(12)–C(19)	114·5°
C(14)–C(15)–C(16)	120·2	C(12)–C(2)–C(3)	114·5
C(15)–C(16)–C(17)	123·5	N(1)–C(2)–C(3)	107·7
C(16)–C(17)–C(18)	116·8	N(1)–C(2)–C(12)	101·7
C(17)–C(18)–C(13)	120·6	C(7)–C(20)–C(21)	110·3
C(18)–C(13)–C(14)	121·5	Mean angle at $C_{sp}{}^3$	109·$_5$
Mean angle at C_{ar}	120·$_0$		
		C(8)–N(9)–C(10)	103·9
C(2)–C(3)–C(4)	108·7	C(8)–N(9)–C(19)	115·2
C(3)–C(4)–C(5)	108·9	C(10)–N(9)–C(19)	108·3
C(4)–C(5)–C(19)	115·7	C(8)–N(9)–C(25)	111·3
C(4)–C(5)–C(6)	112·7	C(10)–N(9)–C(25)	110·4
C(19)–C(5)–C(6)	108·8	C(19)–N(9)–C(25)	107·6
C(5)–C(6)–C(7)	113·9	Mean angle at N^+	109·$_5$
C(6)–C(7)–C(8)	115·6		
C(6)–C(7)–C(20)	112·6	C(12)–C(13)–C(14)	128·7
C(8)–C(7)–C(20)	102·5	N(1)–C(18)–C(17)	131·2
C(7)–C(8)–N(9)	109·6	C(12)–C(13)–C(18)	108·9
N(9)–C(19)–C(5)	111·9	N(1)–C(18)–C(13)	108·3
N(9)–C(19)–C(12)	105·1	C(2)–N(1)–C(18)	107·9
C(5)–C(19)–C(12)	116·2	C(2)–N(1)–C(22)	124·6
N(9)–C(10)–C(11)	100·2	C(18)–N(1)–C(22)	124·1
C(10)–C(11)–C(12)	103·5	N(1)–C(22)–C(23)	118·3
C(11)–C(12)–C(13)	110·1	N(1)–C(22)–O(24)	119·3
C(11)–C(12)–C(19)	102·2	C(23)–C(22)–O(24)	122·4
C(11)–C(12)–C(2)	113·7		
C(2)–C(12)–C(13)	102·3		
C(2)–C(12)–C(19)	114·5		
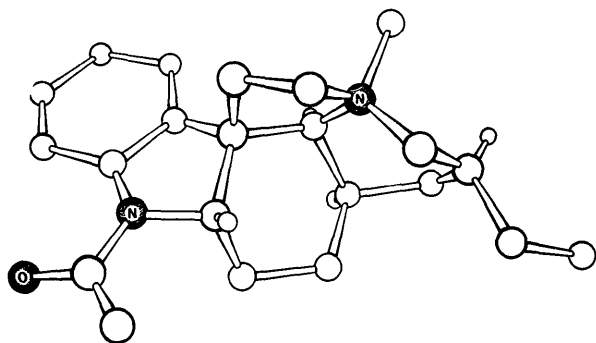
Fig. 2. Perspective drawing of the molecule; the correct absolute configuration is shown.
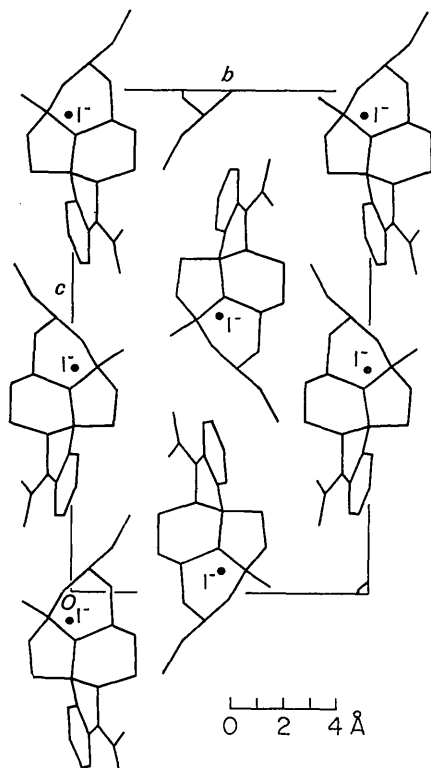
Fig. 3. Projection of the structure along [100], illustrating the packing of the molecules.

Table 4. *Shorter intermolecular distances*

All distances $\leq 4\cdot0$ Å were calculated;
only the crystallographically independent contacts $< 3\cdot7$ Å are listed

Atom (Molecule 1)	to	Atom in	Molecule	d
C(17)		C(11)	4	3·46 Å
C(17)		C(10)	4	3·68
C(3)		C(16)	4	3·62
C(3)		C(15)	4	3·55
O(24)		C(25)	4	3·45
C(15)		C(23)	2	3·65
C(8)		O(24)	3	3·17
C(7)		O(24)	3	3·53
C(20)		O(24)	3	3·55
C(21)		C(23)	5	3·62

Molecule	at	x	y	z
1		x	y	z
2		$1+x$	y	z
3		$\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$
4		$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
5		$\frac{1}{2}+x$	$-\frac{1}{2}-y$	$1-z$

intermolecular contacts are given in Table 4, and the molecular packing is illustrated in Fig. 3.

Absolute configuration

As a final step in the analysis the absolute configuration of the molecule was determined by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The procedure was exactly as for cleavamine methiodide (Camerman & Trotter, 1964), except that Cu $K\alpha$ radiation was used, and there were many reflexions with quite large differences between $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$. Some of the planes with the largest calculated differences were chosen at random, and the intensities were measured. The results, which are given in Table 5, unambiguously indicate that the parameters used to calculate the structure factors (those of Table 2 referred to a conventional right-handed set of axes) represent the true absolute configuration. (III), Fig. 1 and Fig. 2 also depict the correct absolute configuration.

Discussion

The present analysis has established the structure, including the absolute configuration, of the $N(a)$-acetyl

Table 5. *Determination of the absolute configuration*
Cu $K\alpha$ radiation

hkl	$I_o(hkl)$	$I_o(\bar{h}\bar{k}\bar{l})$	$\|F_c(hkl)\|$	$\|F_c(\bar{h}\bar{k}\bar{l})\|$	$\dfrac{I_o(hkl)}{I_o(\bar{h}\bar{k}\bar{l})}$	$\dfrac{\|F_c(hkl)\|^2}{\|F_c(\bar{h}\bar{k}\bar{l})\|^2}$
111	455	1568	52·7	84·2	0·29	0·39
112	143	294	22·0	32·6	0·49	0·46
113	1223	752	78·8	64·6	1·63	1·48
162	131	90	48·0	39·1	1·46	1·51
163	220	374	56·2	70·8	0·59	0·63
164	90	55	33·7	24·6	1·64	1·88
227	149	239	45·1	64·1	0·62	0·70
247	17	46	19·6	29·7	0·37	0·44
251	41	103	26·9	36·4	0·40	0·55
323	42	67	22·0	31·4	0·63	0·49
331	405	276	57·0	47·6	1·47	1·44
337	42	64	23·4	33·3	0·66	0·49
352	618	796	84·5	94·4	0·78	0·80

methiodide derivative of the trans-annular cyclization product of dihydrocleavamine. The compound is $N(a)$-acetyl-7-ethyl-5-desethyl-aspidospermidine $N(b)$-methiodide (Figs. 1, 2, 3), and the parent $N(a)$-acetyl compound is (III). The structure of the *Aspidosperma* skeleton was first established conclusively by X-ray analysis of (−)-aspidospermine $N(b)$-methiodide (Mills & Nyburg, 1960). This alkaloid possesses four asymmetric carbon centres, and the relative configuration at each centre is the same as that in the *Aspidosperma* skeleton in the molecule described in the present paper. Mills & Nyburg did not determine the absolute configuration of (−)-aspidospermine.

The general shape of the $N(a)$-acetyl-7-ethyl-5-desethyl-aspidospermidine molecule (III) is clear from Figs. 1 and 2. The molecule contains five asymmetric centres; H at C(2), and the C(12)–C(11) bond are β; the H atoms at C(5), C(7), C(19) are all α (so that the 7-ethyl group is β); the N-CH₃ in the methiodide derivative is α. The six-membered aromatic ring is planar; the indole five-membered ring and the other five-membered ring are each significantly non-planar; the ring C(2)(3)(4)(5)(19)(12) has a chair conformation, but the other six-membered ring has a boat conformation with atoms C(6), C(7), N(9), C(19) approximately in a plane, with C(5) and C(8) displaced in the same direction from this plane; the –CO . CH₃ group lies approximately in the aromatic plane. All these features are clear from Fig. 2.

The bond distances and valency angles in the molecule (Table 3) are all quite normal, and require no special comment. The intermolecular distances (Table 4) all correspond to normal van der Waals interactions; the shortest distance is a C $\cdots$ O separation of 3·17 Å, and the shortest C $\cdots$ C contact is 3·46 Å. The I⁻ ion is situated between the N⁺(9) atoms of molecules separated by translation a, but the distances are quite large, I⁻ $\cdots$ N⁺ = 4·63 and 4·84 Å; the shortest distance involving I⁻ is an I⁻ $\cdots$ C separation of 3·87 Å.

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The Crystal Structure of the Triclinic Modification of Quinhydrone

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A new triclinic modification of quinhydrone $C_6H_4O_2 . C_6H_4(OH)_2$, stable at room temperatures, was found to exist. The lattice parameters are $a = 7·652$, $b = 5·956$, $c = 6·770$ Å, $\alpha = 107°\ 37'$, $\beta = 121°\ 56'$ and $\gamma = 90°\ 17'$. In its crystal structure determination, the use of the P_0 function (K. Sakurai, 1958) was especially successful.

Hydroquinone and quinone molecules are linked by hydrogen bonds to form zigzag molecular chains. These chains are packed side by side by the charge transfer force to form a molecular sheet. The structure of each molecular sheet is similar to that in the monoclinic form, although the remarkable deformation of the hydroquinone molecule, which was reported for monoclinic quinhydrone, does not exist in the triclinic modification. From the direct integration of the charge density, the upper limit of the charge transfer from the hydroquinone molecule to the quinone molecule is estimated to be 0·21 in electron units.

Introduction

Quinhydrone is the well known aromatic molecular complex, consisting of p-benzoquinone $C_6H_4O_2$ and hydroquinone $C_6H_4(OH)_2$ with 1:1 molecular ratio. Its structure has been known to be monoclinic (Foz & Palacios, 1932; Palacios & Foz, 1935, 1936). The space group is $P2_1/c$ with two quinhydrone molecular