The Crystal Structure and Absolute Configuration of the Dihydrobromide of (+)-Haplophytine

By DAVID E. ZACHARIAS*

Crystallography Laboratory, University of Pittsburgh, Pittsburgh, Pa. 15213, U.S.A.

(Received 1 May 1969)

The dihydroindole alkaloid, haplophytine, from the plant *Haplophytine cimicidum* (Apocynaceae) forms a dihydrobromide, $C_{37}H_{42}Br_2N_4O_7$, which is monoclinic, space group C2 with $a = 25 \cdot 535$, $b = 7 \cdot 490$ and $c = 18 \cdot 861$ Å, $\beta = 101^{\circ} 19'$ with four molecules in the unit cell. Data were collected on a Picker fourcircle automated diffractometer with Cu K α radiation. The structure was solved with the heavy-atom technique and refined anisotropically by a full-matrix least-squares procedure to a final R index of 0.071. The hydrogen atom positions were not determined. The molecular ion consists of two large residues, one having the skeleton and absolute configuration of (-)-aspidospermine and the other a tetracyclic tetrahydro- β -carboline skeleton closely resembling the alkaloid eburnamine.

Introduction

Haplophytine is the major alkaloid of the Mexican insecticidal 'Cucaracha' (cockroach) plant Haplophyton *cimicidum* $A \cdot DC \cdot (Apocynaceae)$ and, together with the alkaloid cimicidine, it is responsible for the insectkilling property. When these two substances were isolated and partially characterized in the first reported chemical investigation, it was found that haplophytine possessed most of the insect-toxicity (Rogers, Snyder & Fischer, 1952; Snyder, Fischer, Walker, Els & Nussberger, 1954a, b; Snyder, Strohmayer & Mooney, 1958). More recent reports of chemical studies (Cava, Talapatra, Nomura, Weisbach, Douglas & Shoop, 1963; Cava, Talapatra, Yates, Rosenberger, Szabo, Douglas, Raffauf, Shoop & Weisbach, 1963) have described the isolation and characterization of seven minor alkaloids from this plant. Three of these, eburnamine (III), isoeburnamine, and O-methyleburnamine contain the tetrahydro- β -carboline skeleton (I) and the remaining four are of the aspidospermine type (II). The occurrence of both eburnamine- and aspidospermine-type alkaloids in this and in several other plant genera (Hunteria, Vinca (Catharanthus), Pleiocarpa and *Rhazia*) has led to the hypothesis that both arise from a common biogenetic precursor (Schnoes, Burlingame & Biemann, 1962). The chemistry of the Haplophytine alkaloids has been reviewed by Saxton (1965); that of the Aspidospermine alkaloids by Gilbert (1965, 1968) and that of the eburnamine-type (Hunteria) by Taylor (1965). The absolute configuration of (-)-aspidospermine-N(b)-methiodide has recently been determined by Craven & Zacharias (1968).



* Present address: Smith Kline and French Laboratories, Philadelphia, Pa. 19101, U.S.A.



deviations
standard
estimated
their
and
parameters
thermal
and
positional
. Atomic
Table 1.

The temperature factor expression used is exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$. Ē

	β_{23}	0-0003 (2)	0-0009 (2)	0.0012(11)	0.004/ (13)	(61) 0000 0	0.0002	-0.0046 (16)	-0.0078 (18)	0.0050 (14)	0.0014 (13)	0.0024 (13)	-0.0019 (13)	0.0021 (15)	-0.0007 (15)	- 0.0014 (1 /)	(cl) cl00-0-	0.0007 (15)	0.0043 (15)	-0.0012 (14)	-0.0007 (17)	-0.0018 (18)	0.0058 (21)	0-0023 (17)	0-0015 (16)	0-0005 (17)	0-0009 (14)	-0.0007 (16)	0-0014 (21)	0-0037 (17)	(11) (200 0 $-$ 0.0009 (14)	-0.0001 (16)	-0.0002 (16)	0-0017 (14)	0.0039 (18)	-0.0012(13)	-0.0000 (13)	-0.0007 (15)	-0.0010 (15)	-0.0052 (21)	-0.0009 (19)	0.0002 (16)	-0.0034 (32)	- 0.0030 (1b) - 0.0015 (73)	(51) (12) (12)	-0.0047 (19)
	β_{13}	0.0000 (0)	0.0006 (0)	-0.0001(2)	0-0005 (3)	(4) 0000	(c) 1100-0	0-0004 (2)	0.0000 (3)	0-0006 (3)	0-0009 (3)	0-0005 (3)	0.0001 (3)	0-0006 (4)	0-0002 (3)	0.0001 (3)	(c) 1000-0	0.0001 (3)		0.0000 (3)	0.0008 (6)	0.0001 (4)	0.0013 (5)	0-0005 (4)	0-0010 (4)	0.0001 (3)	0-0002 (3)	0-0004 (4)	-0.0001 (4)	-0.0002 (4)	0.0001 (3)	0.0009 (4)	0.0001 (4)	0-0000 (3)	0.0010 (3)	0.0000 (5)	0.0000 (J)	-0.0004 (4)	0.0008 (4)	-0.0002(5)	0.0003 (3)	0.0010(4)	0.0011(5)	0-0011 (4) 0-0003 (4)	0.0003 (3)	0.0002 (5)
respective values.	β_{12}	-0.0002 (1)	-0.0006 (1)	0-0010 (8)	0.0023 (9)	-0.001(10)	(a) 0100-0-	0.0000 (8)	0.0000 (10)	0.0025 (10)	0-0006 (8)	-0.0004 (10)	-0.0010 (9)	0.0008 (8)	0-0000 (10)	-0.0005 (12)	- (6) C100 0	0.0012 (7)	(11) 0.00.0	0.0000 (0)	0.0017 (16)	0-0001 (15)	0.0008 (8)	0.0020 (12)	0-0009 (2)	-0-0018 (12)	-0.0005 (9)	0-0007 (13)	0-0011 (12)	0.001 / 100-0	0.0017(10)	0.0009 (13)	0.0007 (13)	0.0002 (12)	0.0020 (14)	0.0004 (11)	-0.0016(11)	0.0001 (11)	0.0008 (12)	-0.0023 (14)	0-0021 (14)	0.0023 (13)	-0.0011 (19)	- 0-0006 (12)	0-0014 (12)	- 0.0019 (14)
cimal digits of the	β_{33}	0.0040 (1)	0.0032 (1)	0.0015 (4)	0-0023 (4)	0-0030 (5)	(c) 10000	0-0066 (8)	0.00066 (7)	0.0025 (6)	0-0034 (6)	0-0026 (6)	0-0016 (5)	0.0033 (7)	0.0031 (7)	0.0028 (6)		0,0000	0-0004 (4)	0.0024 (0)	0.0051 (0)	0.0006 (4)	0-0030 (6)	0-0030 (8)	0-0047 (9)	0-0019 (5)	0.0019 (6)	0.0020(7)	0.0020 (7)	0-0042 (8)	0-0071 (6)	0.0015 (5)	0-0013 (6)	0-0006 (5)	0.0020(6)	(9) / 700.0	0-0010 (5)	0.0015 (6)	0-0028 (6)	0.0033(8)	0.0008 (5)	0-0027 (7)	0-0025 (8)	0-0026 (7)	0.0010 (6)	0.0031 (9)
erer to the last de	β_{22}	0.0182 (5)	0-0216 (6)	0.0267(33)	0-0295 (37)	0-0254 (43)	0-01 / 2 (34)	0.0307(48)	0-0458 (64)	0.0254 (47)	0-0104 (39)	0-0214 (43)	0-0240 (40)	0.0097 (38)	0.0185(51)	0.0132(41)	0.0002 (22)	(15) 5600-0	0.0150 (46)	0.01.02 (38)	0.0178 (60)	0.001 0/ 10-0	0.0320 (65)	0.0169 (49)	0-0116 (41)	0-0188 (48)	0-0125 (46)	0.0171(50)	0.0157(50)	0.0185 (68)	0-01 02 (40)	0-0182 (51)	0-0198 (53)	0.0288 (59)	$0_i 0223 (48)$	0.0100 (47)	0.0079 (38)	0.0120(37)	0.0129 (49)	0-0235 (48)	0-0370 (69)	0.0203(53)	0-0350 (67)	0.0126(48)	0.0186 (53)	0.0206 (46)
s in parentheses r	β_{11}	0.0012 (0)	0.0013 (0)	0-0005 (2)	0.0014(3)	0.0024(3)	(6) 1700-0	0.0003 (2)	(C) 1100 0	0.0009 (3)	0-0006 (2)	0.0010 (3)	0.0003 (2)	0.0007 (3)	0.0002(3)	0-0007 (3)	(5) 5000 0	0-0000 (3)	(c) 6000-0	0.0005 (3)	(c) 0.0010	0-0020 (4)	0 0022 (4)	0-0011 (3)	0-0003 (3)	0-0007 (3)	0.0004 (3)	0.0021 (5)	0.0022(4)	0.0010 (4)	(c) 0100-0	0.0017 (4)	0.0017 (4)	0.0015 (3)	0.0014(3)	0-0010 (3)	0.0010 (4)	(2) (100 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	0.0013 (3)	0.0012(4)	0.0014 (3)	0.0017 (4)	0-0020 (5)	0.0012(4)	(c) c000.0	0.0014 (5)
tandard deviation	И	0-1546 (1)	0-1161 (1)	0.3902(5)	0.4331 (7)	0.0048 (7)	(1) 0.000	0.2770 (0)	0-3635 (9)	0.3633 (8)	0-2017 (8)	0.1092(8)	0-2709 (7)	0.3148 (10)	0.2862(10)	0-2670 (8)	0.2346 (8)	(6) 6702 (6)	(0) 787 (0) 0.2481 ((6) 1040-0 0.2078 (8)	0.4773(13)	0.4603 (9)	0-4314 (11)	0.2570(10)	0-1836 (11)	0.1521 (9)	0-2106 (9)	0-2696 (10)	0.1309(10)	0.0010 (10)	0.1195 (0)	0.0474 (9)	0.3302 (9)	0-1955 (8)	0.1278(8)	0.2603(9)	(8) 0/CI-0 (0) 1/0C-0	0-2395 (9)	0.1380(10)	0-3517 (11)	0-0331 (9)	0.2524 (11)	0.3947 (11)	0.3144(9)	(8) 0.3167 (8)	0.3963 (11)
The estimated s	ý	0.0000 (0)	0-5349 (5)	0.2725 (20)	0.1463 (22)	0.3537 (23)	(07) 1877-0	(0.1) 242 (10)	0.4398 (27)	0.3107 (26)	0.7896(21)	0.3490(23)	0-3033 (24)	0.4217(26)	0-5694 (28)	0-5231 (30)	0.4424 (26)	0.2200 (20)	(20) + (20) + (20)	(07) 70CC-0	0-4/0/ (24)	(12) (12) (12)	(12) 0545 0	0-3131 (29)	0-3428 (27)	0-4922 (32)	0-6204 (25)	0-8962 (30)	0.8823 (29)	0.5028 (20)	0-4741 (76)	0-3358 (30)	0-7544 (31)	0-5978 (30)	0.5068 (36)	0.4803 (29)	(22) 21070	(22) (21)	0.1045 (26)	0.7082(33)	0-2967 (36)	0-1756 (31)	0-7756 (41)	0.5510(26)	(/c) 0050-0 (72) 1051-0	0.6820 (31)
	×	0-2286 (1)	0-4452 (1)	0-3335 (4)	0.2421(5)	0.1569(6)	0.0854 (6)	0.4048 (5)	0.5186 (5)	0-1386 (6)	0.1079 (5)	0-3165 (5)	0.4112(5)	0.0989 (6)	0-1328 (6)	0.2306(6)	0.2804 (6)	0.2832(6)	0,1002 (6)	(0) 5601.0	(0) COOLO	0.2500 (8)	0-1305 (9)	(2) (2) (2) (2) (2) (2) (2) (2) (2) (2) (2)	0.0615 (6)	0.0891 (6)	0.1098 (6)	0.1287(8)	0.0845(8)	0.0707 (8)	0-0409 (7)	0.1263(7)	0.1360(8)	0-3181 (7)	0.2874(6)	0.3301(6)	0.3498(6)	0.3537 (7)	0-3813 (7)	0.3745 (7)	0.3029 (7)	0-4449 (8)	0.4235 (9)	0.3764 (6)	0.4704 (6)	(v) 02642 (8)
		Br(1)	Br(2)	0(1)	0(2)	0(3)	0(4)	(c))			N(2)	N(3)	N(4)	C(1)	C(2)	C(3)	C(4)	(<u>)</u>							C(13)	C(14)	C(15)	C(16)	C(17)	C(18)		C(21)	C(22)	C(23)	C(24)	C(25)	C(26)	C(2))	C(29)	C(30)	C(31)	C(32)	C(33)	C(34)		C(37)

The absolute configuration determination of the dihydrobromide of haplophytine (IV) when combined with the chemical and spectroscopic data from the alkaloid and its dihydrobromide permit the assignment of (V) as the absolute configuration of haplophytine (Rae, Rosenberg, Szabo, Willis, Yates, Zacharias, Jeffrey, Douglas, Kirkpatrick & Weisbach, 1967).

Experimental

Haplophytine dihydrobromide, recrystallized from methanol, was provided by Dr Bryce Douglas of

Smith Kline and French Laboratories, Philadelphia, Pennsylvania.

Crystal data:

$C_{37}H_{42}Br_2N_4O_7$	M.W. 814·5
Monoclinic, space group	C2 (No. 5)
$a = 25.535 \pm 0.005 \text{ Å}$	$V = 3537.2 \text{ Å}^3$
$b = 7.490 \pm 0.005$	Z = 4
$c = 18.861 \pm 0.005$	$D_x = 1.530 \text{ g.cm}^{-3}$
$\beta = 101^{\circ}19 \pm 5'$	D_m (flotation) = 1.528 g.cm ⁻³
Prismatic, elongated alon	ng b.

Table 2. Observed and calculated structure factors

The columns listed are l, $10|F_o|$, $10F_c$.

2202212552525646175227146600000000000000000000000000000000000
6441231454 E746543216487454321612334547876121233454787612121212121212121212121212121212121212
1010071310030 242424204714712649714712649714712649714214872204642732212012731210111011101142144204424424432244324400474326424414411444114444444444444444444444
12 0 12 12 12 12 12 12 12 12 12 12 12 12 12
14,967 #7654321C967654321C9274567840123456 #87654321C92745674701234567890112114 #7654321C987454321C987
31053300445151175500745745740745725700041275780074262739074262739232323222245464935668460526578521224832714020464442224120-3228232227734051304
······································
12-12/2004/3/2/24/4-19410011-2/22/3/24/3/40110774052/2003/3/2012/2003/3/2014/0014/014/11007/012/22/22/22/22/22/1001007502/75/2/102/104/004/2002/22/22/22/22/2004/22/22/22/2004/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/22/2004/22/2004/22/22/22/22/2004/22/2004/22/22/22/22/22/2004/22/2004/22/22/22/22/22/2004/22/2004/22/22/22/22/22/2004/22/22/22/22/22/22/22/22/22/22/22/22/22
1.12111558785437151735587858111111558 1115411211558785854574587851111111
122221122222784744472721231411111111111111111111111111
7 47 46 414114 47 45 47 47 47 47 47 47 47 47 47 47 47 47 47
× + L L 2 88 - 19 4 × 6 + L L 2 19 × 7 1 × 1 × 0 9 + 4 + 19 × 0 5 + 2 + 1 × 6 × 1 × 6 × 1 × 6 × 1 × 6 × 7 × 6 × 1 × 6 × 7 × 6 × 6 × 6 × 7 × 6 × 6 × 6 × 7 × 6 × 6
CLACK CLA

17 e 5 4 12 12 9 e 7 e 5 4 3 2 1 0 1 2 3 4 5 .	• -3 - 27 20 -7 20 -7 -27 -27 -27 -27 -27 -27 -27		85C112 =	260 12 • + • - 234 525 4 5 11 6 3 • C C C S 5 5 4 2 4 5 6 3 • C C C S 5 5 5 5 4 6 5 6 3 • C C C S 5 5 5 5 6 4 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 6 6 7 2 6 7 2 6 6 7 2 7 2	21 35- 53 15 27 91 15 27 91 15 27 91 15 27 91 15 27 91 15 27 91 15 27 91 15 27 91 15 15 27 91 15 15 15 15 15 15 15 15 15 1		3835511EC3356636892776233 1CC6157851389452859146482	222 41 5244 5583 550104 65760		24422212734536722C5878518724	17	- 3 - 2 - 2 - 2 - 12 - 12 - 12 - 12 - 12 -	×3,233-362226627545265423	1	-F -7 -5 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	257252280 57252280 25725280 25725280 25725280 25725280 25725280 25725280 25725280 25725280 25725280 25725280 2572572580 2572572580 2575570 25755000 257550000000000	5754854451245081400184114 12248445124508140018414	456789C × 1098765432101236.	57 J50 54 20 54 20 12 20 17 32 57 42 55 12 12 12 12 12 12 12 12 12 12	4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	5 6 K 6 5 4 3 2 1 0 1 2 3 4 5 K 5 4 3 2 1 C 1 2 3	51 LC7 + 22 35 - 35 22 22 31 9 22 22 15 - 15 - 15 - 15 - 15 - 15 - 15 - 15 -	5 11 2047 e 42 e 4 C 5 5 C 5 2 2 8 e 2 7 +	
7 8 90 112345 K 1543211098745321	70 337 24 22 48 15 15 38 40 53 40 543 300 74 57 74 57 74 57	72-7 26 18 32 0 9 417- 853- 4822- 854- 870- 870- 114 870- 114	456785C 3211C587654321C1234	36500 2520 3384 - 2520 3264 2520 3264 2520 3264 2550 8651 2578 8653 2578 8653	2 22 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	15432110587854321012345678	22 -45 +* 23 -45 +* 23 -45	1 201 317-4 35 0 1 - 7 - 9 - 6 4 - 9 - 7 - 9 - 1 - 7 - 9 - 6 4 - 9 - 7 - 9 - 1 - 7 - 9 - 1 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7 - 7	12 ** -143 -143 -143 -143 -143 -143 -143 -143	2-233657479405556408602483	31275 J EC J 7	1121 1121	5457 ***********************************	/ J 1	-7 65 4321C123456789 -11	5177955364246051442-222444529 6632862951460514605146229	5479793676469176153866083553	6765 CS67654321G123456789 K	24 200 200 200 200 200 200 200 2	2C 52 11 11 11 11 11 11 11 11 12 12	4 K. 4 3 2 2 1 C 1 2 2 1 2 1 2 2 1 1 2 1 1 2 1 1 2 1 1 2 1 1 2 1 1 2 1 1 2 1	15****	4 7 16 8 32- 22- 8 6	-
C 2 3 4 5 6 7 8 9 10 12 13 4 16 5 6 7 8 9 10 12 13 14 16 5 4 7 8 9 10 12 13 14 16 5 4 17 9 17 9 17 9 17 9 17 9 17 9 17 9 17	7242787635651482368327573666 **********************************	31 142- 142- 14- 67 57 14- 67 57 37 37 11- 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 37 55 27 57 27 57 27 57 27 57 27 57 27 57 27 57 27 27 27 27 27 27 27 27 27 2	-12 -12 -12 -12 -12 -12 -12 -12 -12 -12	446 420 46 46 46 46 46 46 46 46 46 46	4 2585-4 28893413C7 64553814	VC 11 12 13 14 -15 -14 -15 -14 -15 -14 -15 -15 -15 -15 -15 -15 -15 -15	50 43 34 34 34 34 34 34 34 34 34	42 L5 e C e L 27-0 24 2 2 5 e C e L 27-0 24 3 2 4 5 6 L 2 1 4 5 6 L 9 5	10 11 -13 -11 -15 -8 -7 -8 -7 -8 -7 -1 -1 -1 -8 -7 -7 -8 -7 -7 -8 -7 -7 -7 -7 -7 -7 -7 -7 -7 -7	372 - 208 -	2957 45 15 16 15 16 16 16 16 16 16 16 16 16 16	3 4 5 6 7 5 9 9 1 C 1 1 2 1 3 K 1 - 1 2 1 1 0 9 9 - 2 7 - 2 5 4 - 3 2 - 1 0 1	44762202321-375715641703513966128428554081874886362177	764864 667		35556527245426570 4252322455424553253736263342	1009305-100733581442-431434477325	-1	100 402 200 432 200 44 200 40 200 40 200 40 200 40 200 40 200 40 200 40 200 40 200 40 200 40 200 40 200 20	6 6 1228 1460 1556 1001- 1176 1001- 1176 1001- 1176				
	46 145 170 123 135 135 135 135 135 135 135 13	4C 142 142 117-128- 128- 7C 23 23 41- 7C 23 27- 11- 13- 16- 21- 21- 21- 13- 13- 13- 13- 13- 13- 13- 13- 13- 1	-e76-54321C	26 42 41 31 57 52 34 42 22 34 42 22 25 24 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 42 15 15 15 15 15 15 15 15 15 15 15 15 15	13 C 42 33- 52- 462 18 623 38- 14 53- 14 53- 14 13 54- 34- 34- 34- 34- 34- 34- 34- 3	5 67 8 5 C 1 1 2 3 4 5 4 3 2 1 C 5 8 7 6 5 4 3 2 1 C 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 5 8 7 6 5 4 3 2 1 C 1 5 8 7 6 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7 7	27 600 8124 3524 207 40 40 40 40 40 40 40 40 40 40	11 +2	-12 -11 -9 -9 -7 -5 -4 -12 -12 -12 -12 -12 -12 -12 -12 -12 -12	31 26 72 33 36 72 33 61 45 25 25 26 20 20 20 20 20 20 20 20 20 20 20 20 20	1 × 5 × 4 = 1 × 5 × 4 = 4 × 5 × 5 × 4 = 4 × 5 × 5 × 5 × 5 × 5 × 5 × 5 × 5 × 5 ×	2 3 5 6 7 9 -11 12 -13 -12 -12 -12 -12 -12 -12 -13 -2 -2 -3 -3 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2	LC #2264 57 #25 # ##############################	1 21806 12806 12906 12906	5 6 87 65 4 3 2 1 C 1 2 3 K 	26.00	2 07 5-9- 121 7 5-9- 1 20 2 1 15 2 4 2 5 2 4 - 2 1 2 2 1 2 2 2 2 3 2 4 - 2 1 2 2 1 2 4 2 4 2 4 1 2 4 2 4 1 2 4 5 2 5 2 4 1 2 4 5 2 4 1 2 4 5 2 5 2 4 1 1 2 4 5 2 5 2 4 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1		55 342 202 220 220 220 220 220 220 220 220 2	48 72- 172- 172- 175 18 14 175 17 17 18 12 12 14 14 14 14 14 14 14 14 14 14 14 14 14				
	20 29 19 39 53 41 42 42 71 42 42 71 42 65 65	13- 13- 157 170 343 270- 57- 37 51 56	-7 -7 -5 -3 -2 -1 C -15 -15 -14 -15 -14 -15 -14 -15 -14 -15 -14 -15 -14 -15 -14 -15 -14 -15 -14 -16 -16 -16 -16 -16 -16 -16 -16 -16 -16	-1 61 46 17 122 63 39 76 108 -4 H 34 22 53 33 35	17 51 17- 110- 52- 141 22 141 23- 33- 24- 24-	234 5 e 7 e 5 1C 112 13 -15 -14		40 23 27- 31 47 31 47 31 47 31 4 5 21 5 0 21 5 0 21 5 21 5 21 5 21 5 21	- 2 (- 2) - 2) - 4 , ki - 7 & 5 / - 4	-465 -405 -244 -36 -36 -36 -36 -36 -36 -36 -36 -36 -36	20 20 10 10 10 10 10 10 10 10 10 1	3 6 7 8 1C 11 11 -13 -11 -9		775 . Souto 5 . 5 . 5 . 5	-11 -15 -6 -7 -3 -12 -12 -12 -12 -12 -12 -12 -12 -12 -12	32 35 26 20 20 32 22 42 22 42 22 42 30 22 42 30	8-11287 Let CO 203	- 6 - 6 - 3 - 2 - 0 - 4 - 3 - 2 - 1 0 - 4 - 3 - 2 - 0 - 4 - 3 - 2 - 0 - 4 - 3 - 4 - 3 - 4 - 3 - 4 - 3 - 4 - 3 - 4 - 10 - 4 - 10 - 4 - 4 - 10 - 4 - 4 - 4 - 4 - 4 - 4 - 4 - 4 - 4 - 4	50 20* 18 23 32 32 32 32 32 20* 43 22 43 23 20* 47 47	23 20- 25- 21- 20- 25- 20- 20- 20- 20- 20- 20- 20- 20				

Table 2 (cont.)

* Indicates unobserved reflections.

A crystal, $0.05 \times 0.3 \times 0.03$ mm, was mounted with the **b** direction parallel to the φ axis of a Picker automated four-circle diffractometer. Diffraction data for 2001 independent reflections (sin $\theta \le 0.765$, $2\theta \le 100^{\circ}$) were measured using Cu K α radiation ($\lambda = 1.5418$ Å) and a scintillation counter detector. Integrated intensities were obtained using $\theta/2\theta$ scans of 2° in 2θ at a scanning rate of 2° min⁻¹ with background counts of 20 sec at the limits of each scan. There were 334 reflections for which the integrated intensity, *I*, was less than $3\sigma(I)$. These were given values of *I* equal to $0.5\sigma(I)$. There was no evidence of decomposition of the crystal during X-irradiation. The initial and final integrated intensities

of three standard reflections varied less than 1 % from the average of the integrated intensities of the standards recorded during the course of data collection. No absorption correction was made. For the determination of absolute configuration, the integrated intensities of thirteen reflections of the type hkl were measured and compared with the corresponding reflections recorded in the main body of the data which were $h\bar{k}l$.

The structure determination and refinement

The positions of the bromine atoms were found by identification of the bromine-bromine vectors in the threedimensional Patterson function. The space group origin was fixed by arbitrarily setting the y coordinate of one bromine atom equal to zero. Using the phases of only the two heavy atoms, all of the light atoms excepting hydrogen were located after three cycles of structure factor calculations and three-dimensional electron density syntheses.

The structure was refined by a full-matrix leastsquares procedure using isotropic temperature factors until convergence at R=0.103. The atomic scattering factors and the dispersion corrections for the bromine atoms ($\Delta f' = -0.95$, $\Delta f'' = 1.6$ for Cu Ka radiation) were those in International Tables for X-ray Crystallography, (1962). The estimated standard deviation in an observed structure amplitude |F| was taken as $\sigma(F) =$ $|F_{\min}| + 0.07|F|$, where $|F_{\min}|$ is the average value for the structure amplitude assigned to the unobservable reflections. The structure factors were then calculated reversing the sign of the imaginary contribution $\Delta f''$, for the bromine atoms. The resulting R = 0.108 gave an initial indication that the assumed absolute configuration was correct. Three further refinement cycles of all positional parameters and anisotropic temperature factors for bromine converged with R = 0.084. The correctness of the assumed absolute configuration was again tested by a structure factor calculation using these refined positional parameters with the sign of the y coordinate reversed for all atoms. The higher disagreement index of 0.094 again supported the assumed model. Finally, all atoms were refined anisotropically until the shift-to-error ratio was less than 0.1 for all parameters refined. Owing to the limitation of computer memory, it was necessary to refine the atoms of the molecule in four groups, as follows:

Atomic groups for full-matrix anisotropic refinement:

- (1) O: 5, 6, 7; N: 3, 4; C: 3, 4, 5, 23 through 32, 34, 36.
 (2) Br: 1, 2; O: 1, 2; N: 4;
 - C: 3, 4, 6 through 10, 25, 28, 30, 33 through 37.
- (3) N: 1, 2; C: 1 through 8, 11 through 16, 20, 22, 25.
- (4) O: 3, 4; N: 1, 2; C: 1, 2, 12 through 22.

The final disagreement factors are as follows:

U	nweighted R	Weighted	R
All data	0.086	0.096	
Omitting unobserved reflection	ons 0.071	0.083	

where

$$R = \sum |\Delta| / \sum |F_o| \text{ Weighted } R = \sqrt{\sum (W\Delta^2)} / \sqrt{\sum (W|F_o|^2)}$$
$$W = [1/\sigma(F)]^2 \qquad \Delta = |F_o| - |F_c|$$

The final atomic parameters with e.s.d.'s are given in Table 1. The corresponding observed and calculated structure factors are listed in Table 2. The comparison of the observed and calculated values using these positional parameters referred to a right-handed crystal axial system for the intensities I(hkl) and I(hkl) is made in Table 3. The hydrogen atom positions were not determined.

Table 3.	Determination	of a	bsolute	configurat	ion

			$(I_{hkl} - I_{\overline{hkl}})/$	$(I_{hkl} + I_{\overline{hkl}})$
h	k	1	Calc.*	Obs.
1	1	13	+0.05	+0.04
1	1	-13	+0.06	+0.21
5	1	7	+0.04	+0.05
5	1	-7	+0.06	+0.04
5	1	14	-0.50	-0.18
5	1	-14	+0.02	-0.01
9	1	6	-0.02	-0.05
9	1	-6	-0.12	-0·11
13	1	6	+0.05	+0.03
13	1	-6	-0.05	0.00



Fig. 1. The absolute configuration of haplophytine dihydrobromide. The positive sense of y is towards the viewer.

Table 3 (cont.)

9	1	-11	+0.12	+0.11
6	2	15	-0.20	-0.30
6	2	-15	+0.08	0.00

* These values are calculated with the atomic parameters listed in Table 1, referred to a right-handed crystal axial system.

Description and discussion of the structure

The absolute atomic configuration of the molecular ion is shown in Fig. 1. It consists of two structural units: part A, on the left, has the framework and absolute configuration of (-)-aspidospermine as confirmed by Craven & Zacharias (1968); part B, on the right, possesses the β -carboline skeleton and resembles eburnamine. The bond lengths are shown in Fig. 2(a) and (b)and are listed in Table 4. The bond angles are given in Table 5. Conformation data are presented in Table 6. In part A, the carboxyl group and C(20) to which it is attached are nearly coplanar. O(2) lies in the same plane as that formed by the benzene ring but the other atoms attached to the ring, C(2), C(25), O(1) and N(1) are considerably out of the plane. Both the six-membered rings, C(1), C(2), C(15), C(14), C(13), C(12) and N(2), C(15), C(14), C(19), C(18), C(17) have the boat conformation but are distorted owing to the rigidity imposed by the quaternary N(2) atom and adjacent double bond to C(15). The planarity of the least-squares plane through N(2), C(15) and their associated atoms C(2), C(14), C(16) and C(17) is comparable with that of the benzene ring.

Table 4. Intramolecular bond lengths and distances and their estimated standard deviations

The e.s.d.'s are in parentheses and refer to the last decimal digits of the respective values.

Bond	Length	Bond	Length
O(1)-C(10)	1·41 (2) Å	C(4) - C(5)	1.42 (2) Å
O(1) - C(5)	1.39 (2)	C(4) - C(25)	1.56 (2)
O(2) - C(9)	1.47 (3)	C(5) - C(6)	1.35 (2)
O(2) - C(6)	1.39 (2)	C(6) - C(7)	1.42 (2)
O(3) - C(21)	1.23(2)	C(7) - C(8)	1.34 (2)
O(4) - C(21)	1.30 (2)	C(12) - C(13)	1.38 (2)
O(5)-C(28)	1.41 (2)	C(13) - C(14)	1.51 (2)
O(6) - C(32)	1.27(3)	C(14) - C(15)	1.48 (3)
O(7)-C(35)	1.39 (3)	C(14)-C(19)	1.60 (2)
N(1)-C(1)	1.48 (2)	C(14) - C(20)	1.60 (3)
N(1)-C(7)	1.41 (2)	C(16) - C(22)	1.54 (3)
N(1)-C(11)	1.42 (2)	C(17) - C(18)	1.44 (3)
N(2)-C(15)	1.28 (2)	C(18) - C(19)	1.48 (2)
N(2)-C(16)	1.51 (2)	C(20) - C(21)	1.49 (3)
N(2)-C(17)	1.52 (3)	C(23) - C(24)	1.52 (3)
N(3)-C(24)	1.48 (2)	C(23) - C(25)	1.49 (2)
N(3)-C(26)	1.29 (2)	C(25)-C(28)	1.60(2)
N(3)-C(31)	1.46 (3)	C(25) - C(34)	1.50 (3)
N(4) - C(28)	1.47 (2)	C(26) - C(28)	1.56 (2)
N(4)-C(32)	1.38 (2)	C(26) - C(29)	1.51 (3)
N(4) - C(36)	1.44 (2)	C(27) - C(29)	1.49 (3)
C(1) - C(2)	1.56 (2)	C(27) - C(32)	1.45 (3)
C(1)-C(12)	1.48 (2)	C(30) - C(33)	1.44 (2)
$C(2) - C(\xi)$	1.56 (2)	C(30) - C(34)	1.38(2)
C(2) - C(15)	1.48 (2)	C(33) - C(37)	1.34 (2)
C(2) - C(22)	1.61 (2)	C(34)-C(36)	1.38 (2)
C(3) - C(4)	1.41 (2)	C(35)-C(36)	1.41 (2)
C(3) - C(8)	1.36 (2)	C(35) - C(37)	1.34(3)

Table 4 (cont.)

Distances less than the sum of the van der Waals radii

	Distance		Distance
O(1) $O(5)$	2.64 (2) \$	$D_{r}(1) = O(5)$	2 17 (1)
O(1) = O(3)	2.04 (2) A	Br(1) = O(3)	3·17 (1) A
O(6) - O(7)	2.32 (2)	Br(2) - C(26)	3-39 (2)
	Close approach	es less than 4 Å	
	Distance		Distance
Br(1)-C(26)	3·65 (2) Å	Br(2)-N(3)	3·55 (2) Å
-N(3)	3.66 (2)	–N(4)	3.64 (2)
-C(20)	3.90 (2)	-C(29)	3.67 (2)
-C(21)	3.90 (2)	-C(32)	3.72 (2)
-C(31)	3.94 (2)	-C(23)	3.86 (2)
-C(28)	3.95 (2)	-C(36)	3.96 (2)

Bond lengths averaged according to bond type Trigonally and tetrahedrally bonded atoms are denoted by 'trig' and 'tetr' respectively.

Туре	No. of bonds	Average bond length	R.m.s. deviation
C(tetr)-C(tetr)	11	1·54 Å	0·017 Å
C(tetr)-C(trig)	11	1.51	0.011



(b)

Fig.2. Intramolecular distances in haplophytine dihydrobromide.

Table 4 (cont.)

C(tetr)–N(tetr)	3	1.46	0.030
C(tetr)-N(trig)	4	1.49	0.028
C(trig)-C(trig)	13	1.38	0.010
C(trig)-N(tetr)	3	1.41	0.027
C(trig)-N(trig)	2	1.29	0.003

In the *B* part of the molecular ion, the benzene ring is more nearly planar and the adjacent atoms N(4) and O(7) lie within this plane (*cf.* planes 4 and 5 in Table 6). Both the aliphatic six-membered rings also have the boat conformation, again somewhat distorted by the double bond between N(3) and C(26). The junctions

Table 5. Molecular bond angles and their estimated standard deviations

The e.s.d.'s are in parentheses and refer to the corresponding decimal digits of the respective values.

$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Angle		Angle
$\begin{array}{ccccc} C(3) = C(3) = C(3) & 1174 (1.5) & C(3) = C(3) = C(7) & 1076 (1.5) \\ C(1) = N(1) = C(7) & 1076 (1.5) & C(3) = C(8) = C(7) & 1253 (1.6) \\ C(1) = N(1) = C(11) & 1225 (1-7) & C(1) = C(12) = C(13) & 1249 (1-7) \\ C(7) = N(1) = C(11) & 1225 (1-7) & C(12) = C(13) = C(14) & 1249 (1-7) \\ C(15) = N(2) = C(16) & 1144 (1-5) & C(13) = C(14) = C(19) & 1094 (1-5) \\ C(16) = N(2) = C(17) & 1245 (1-5) & C(13) = C(14) = C(19) & 1094 (1-5) \\ C(24) = N(3) = C(31) & 1234 (1-5) & C(15) = C(14) = C(20) & 1107 (1-4) \\ C(26) = N(3) = C(31) & 1234 (1-5) & C(15) = C(14) = C(20) & 1107 (1-4) \\ C(28) = N(4) = C(36) & 1295 (1-6) & C(2) = C(14) = C(20) & 1107 (1-4) \\ C(28) = N(4) = C(36) & 1295 (1-6) & C(2) = C(15) = C(14) & 1234 (1-5) \\ C(23) = N(4) = C(36) & 1295 (1-6) & C(2) = C(15) = C(14) & 1234 (1-5) \\ C(2) = C(1) = N(1) & 11045 (1-4) & N(2) = C(15) = C(14) & 1234 (1-5) \\ C(12) = C(1) = N(1) & 11045 (1-4) & N(2) = C(16) = C(22) & 1034 (1-5) \\ C(12) = C(1) = N(1) & 11045 (1-4) & N(2) = C(16) = C(22) & 1034 (1-5) \\ C(12) = C(1) = N(1) & 11045 (1-4) & N(2) = C(16) = C(22) & 1034 (1-5) \\ C(12) = C(1) = N(1) & 11045 (1-5) & N(2) = C(17) = C(18) & 1100 (1-7) \\ C(1) = C(2) = C(15) & 11178 (1-5) & C(14) = C(20) = C(15) & 11175 (1-7) \\ C(1) = C(2) = C(22) & 1114 (1-5) & O(3) = C(21) = C(10) & 1107 (1-7) \\ C(8) = C(2) = C(22) & 1114 (1-5) & O(3) = C(21) = C(20) & 1197 (1-7) \\ C(8) = C(2) = C(22) & 1114 (1-6) & O(3) = C(21) = C(20) & 1197 (1-7) \\ C(8) = C(2) = C(22) & 1117 (1-5) & O(3) = C(21) = C(20) & 1197 (1-7) \\ C(3) = C(4) = C(25) & 1215 (1-5) & C(4) = C(25) = C(23) & 11039 (1-5) \\ C(3) = C(4) = C(25) & 1217 (1-5) & C(4) = C(25) = C(23) & 11039 (1-5) \\ C(3) = C(4) = C(25) & 1217 (1-5) & C(4) = C(25) = C(23) & 11039 (1-5) \\ C(3) = C(4) = C(25) & 11187 (1-6) & N(3) = C(26) = C(23) & 11079 (1-5) \\ C(3) = C(4) = C(25) & 11187 (1-6) & N(3) = C(26) = C(23) & 1105 (1-6) \\ C(3) = C(3) = C(3) & 1187 (1-6) & C(23) = C(23) & 11079 (1-5) \\ C(3) = C(3) = C(3) & 1187 (1-6) & C(33) = C(33) = C(33) & 11079 (1-5) \\ C(3) = C(3) = C(26) & 1157 (1-4) &$	C(5) - O(1) - C(10)	115·5 (1·4)°	C(2) - C(8) - C(3)	126.9 (1.5)
$ \begin{array}{c} C(1) - N(1) - C(7) & 107 \cdot 6 (1 \cdot 5) & C(3) - C(8) - C(7) & 125 \cdot 3 (1 \cdot 6) \\ C(1) - N(1) - C(11) & 122 \cdot 5 (1 \cdot 7) & C(1) - C(12) - C(13) & 124 \cdot 9 (1 \cdot 7) \\ C(15) - N(2) - C(16) & 114 \cdot 4 (1 \cdot 5) & C(13) - C(14) - C(15) & 108 \cdot 3 (1 \cdot 5) \\ C(15) - N(2) - C(17) & 124 \cdot 5 (1 \cdot 5) & C(13) - C(14) - C(19) & 109 \cdot 4 (1 \cdot 5) \\ C(16) - N(2) - C(17) & 120 \cdot 9 (1 \cdot 5) & C(13) - C(14) - C(120) & 112 \cdot 6 (1 \cdot 5) \\ C(24) - N(3) - C(26) & 122 \cdot 4 (1 \cdot 5) & C(15) - C(14) - C(20) & 107 \cdot 4 (1 \cdot 4) \\ C(26) - N(3) - C(31) & 123 \cdot 1 (1 \cdot 5) & N(2) - C(15) - C(14) - C(20) & 107 \cdot 4 (1 \cdot 4) \\ C(28) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) + 123 \cdot 1 (1 \cdot 6) \\ C(23) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 1 (1 \cdot 6) \\ C(23) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 1 (1 \cdot 6) \\ C(23) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 1 (1 \cdot 6) \\ C(22) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & N(2) - C(17) - C(18) & 113 \cdot 5 (1 \cdot 7) \\ C(2) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & N(2) - C(17) - C(18) & 113 \cdot 5 (1 \cdot 7) \\ C(2) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & C(17) - C(18) - C(19) & 111 \cdot 6 (1 \cdot 9) \\ C(1) - C(2) - C(18) & 100 \cdot 8 (1 \cdot 4) & C(14) - C(19) - C(18) & 110 \cdot 0 (1 \cdot 7) \\ C(1) - C(2) - C(15) & 115 \cdot 3 (1 \cdot 5) & O(3) - C(21) - O(4) & 122 \cdot 5 (1 \cdot 8) \\ C(3) - C(4) - C(22) & 104 \cdot 4 (1 \cdot 5) & C(14) - C(20) - C(21) & 116 \cdot 7 (1 \cdot 5) \\ C(1) - C(2) - C(22) & 104 \cdot 2 (1 \cdot 5) & C(14) - C(20) - C(21) & 116 \cdot 7 (1 \cdot 5) \\ C(1) - C(2) - C(22) & 104 \cdot 2 (1 \cdot 5) & C(2) - C(22) & 117 \cdot 4 (1 \cdot 6) \\ C(15) - C(2) - C(22) & 104 \cdot 2 (1 \cdot 5) & C(2) - C(22) & 117 \cdot 4 (1 \cdot 6) \\ C(15) - C(2) - C(22) & 104 \cdot 2 (1 \cdot 5) & C(2) - C(23) & 1102 \cdot 9 (1 \cdot 5) \\ C(4) - C(3) - C(8) & 117 \cdot 5 (1 \cdot 6) & C(23) - C(23) & 1102 \cdot 9 (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 (1 \cdot 5) & C(4) - C(25) - C(23) & 1102 \cdot 9 (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 (1 \cdot 5) & C(4) - C(25) - C(23) & 113 \cdot 3 (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 4 (1 \cdot 6) & C(23) - C(23) & 113 \cdot 5 (1 \cdot 6) \\ O(5) - C(23) - C(24) & 113 $	C(6) = O(2) = C(9)	117.4 (1.5)	C(2) - C(8) - C(7)	107.6 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1) - N(1) - C(7)	107.6 (1.5)	C(3) - C(8) - C(7)	125.3 (1.6)
$\begin{array}{c} C(7) = N(1) - C(11) & 123 + 6 (1 - 7) & C(12) - C(13) - C(14) & 124 + 0 (1 - 7) \\ C(13) - N(2) - C(16) & 114 + 4 (1 - 5) & C(13) - C(14) - C(19) & 108 + 3 (1 - 5) \\ C(15) - N(2) - C(17) & 124 + 5 (1 - 5) & C(13) - C(14) - C(19) & 108 + 3 (1 - 5) \\ C(24) - N(3) - C(26) & 122 + 4 (1 - 5) & C(15) - C(14) - C(20) & 110 + 7 (1 + 4) \\ C(26) - N(3) - C(31) & 114 + 4 (1 - 5) & C(15) - C(14) - C(20) & 110 + 7 (1 + 4) \\ C(26) - N(3) - C(31) & 112 + 3 (1 - 5) & N(2) - C(15) - C(14) - C(20) & 110 + 7 (1 + 4) \\ C(28) - N(4) - C(36) & 111 + 1 (1 + 4) & N(2) - C(15) - C(14) & 123 + 1 (1 - 6) \\ C(23) - N(4) - C(36) & 111 + 1 (1 + 4) & N(2) - C(15) - C(14) & 124 + 5 (1 - 5) \\ C(21) - C(1) - N(1) & 104 + 5 (1 + 4) & N(2) - C(15) - C(14) & 124 + 5 (1 - 5) \\ C(22) - C(1) - N(1) & 111 + 5 (1 - 5) & N(2) - C(17) - C(18) & 113 + 5 (1 - 7) \\ C(2) - C(1) - C(12) & 114 + 0 (1 + 5) & C(17) - C(18) & 113 + 5 (1 - 7) \\ C(1) - C(2) - C(15) & 111 + 8 (1 + 5) & C(14) - C(20) - C(18) & 111 + 6 (1 - 9) \\ C(1) - C(2) - C(15) & 115 + 3 (1 + 5) & O(3) - C(21) - O(4) & 122 + 5 (1 + 8) \\ C(8) - C(2) - C(15) & 115 + 3 (1 + 5) & O(3) - C(21) - O(4) & 122 + 5 (1 + 8) \\ C(8) - C(2) - C(22) & 104 + 0 (1 + 5) & C(14) - C(20) - C(20) & 117 + 1 (1 - 6) \\ C(15) - C(2) - C(22) & 104 + 2 (1 + 5) & C(14) - C(20) - C(21) & 116 + 7 (1 - 5) \\ C(3) - C(4) - C(25) & 121 + 1 (1 + 4) & O(4) - C(21) - C(20) & 117 + 1 (1 - 6) \\ C(3) - C(4) - C(25) & 121 + 0 (1 + 5) & C(4) - C(25) - C(23) & 110 + 9 (1 + 5) \\ C(3) - C(4) - C(25) & 121 + 0 (1 + 5) & C(4) - C(25) - C(23) & 110 + 9 (1 + 5) \\ C(3) - C(4) - C(25) & 121 + 8 (1 + 5) & C(4) - C(25) - C(23) & 110 + 9 (1 + 5) \\ C(3) - C(4) - C(25) - C(4) & 117 + 3 (1 + 5) & C(4) - C(25) - C(23) & 110 + 9 (1 + 5) \\ C(3) - C(4) - C(25) & 121 + 8 (1 + 5) & C(4) - C(25) - C(23) & 113 + 3 (1 + 4) \\ O(1) - C(5) - C(4) & 117 + 3 (1 + 5) & C(4) - C(25) - C(23) & 113 + 3 (1 + 5) \\ C(3) - C(4) - C(25) & 121 + 8 (1 + 5) & C(23) - C(23) - C(23) & 113 + 3 (1 + 5) \\ C(3) - C(3) - C(3) & 113 + 9 (1 + 6) & C(33) - C(33) - C(33) - (33) + 115$	C(1) = N(1) = C(11)	122.5 (1.7)	C(1) - C(12) - C(13)	123.9(1.0) 124.9(1.7)
$\begin{array}{c} C(15) - N(2) - C(16) & 114 + 4 (1 + 5) \\ C(13) - N(2) - C(17) & 124 + 5 (1 + 5) \\ C(13) - N(2) - C(17) & 122 + 5 (1 + 5) \\ C(13) - C(14) - C(19) & 109 + 4 (1 + 5) \\ C(13) - C(14) - C(20) & 112 + 6 (1 + 5) \\ C(24) - N(3) - C(26) & 122 + 4 (1 + 5) \\ C(24) - N(3) - C(31) & 114 + 4 (1 + 5) \\ C(24) - N(3) - C(31) & 112 + 1 (1 + 5) \\ C(24) - N(3) - C(31) & 112 + 1 (1 + 5) \\ C(26) - N(4) - C(32) & 119 + 3 (1 + 5) \\ C(28) - N(4) - C(36) & 119 + 3 (1 + 5) \\ C(28) - N(4) - C(36) & 129 + 5 (1 + 6) \\ C(32) - N(4) - C(36) & 129 + 5 (1 + 6) \\ C(32) - N(4) - C(36) & 129 + 5 (1 + 6) \\ C(12) - C(1) - N(1) & 104 + 5 (1 + 4) \\ C(2) - C(1) - N(1) & 111 + 5 (1 + 5) \\ C(12) - C(1) - N(1) & 111 + 5 (1 + 5) \\ C(12) - C(1) - N(1) & 111 + 5 (1 + 5) \\ C(12) - C(1) - N(1) & 111 + 5 (1 + 5) \\ C(11) - C(2) - C(22) & 114 + 0 (1 + 5) \\ C(11) - C(2) - C(15) & 111 + 8 (1 + 5) \\ C(14) - C(19) - C(18) & 110 + 0 (1 + 7) \\ C(1) - C(2) - C(22) & 114 + 0 (1 + 5) \\ C(1) - C(2) - C(22) & 114 + 0 (1 + 5) \\ C(1) - C(2) - C(22) & 114 + 0 (1 + 5) \\ C(1) - C(2) - C(22) & 111 + 3 (1 + 5) \\ C(1) - C(2) - C(22) & 111 + 1 (1 + 4) \\ O(4) - C(21) - C(20) & 119 + 7 (1 + 7) \\ C(3) - C(4) - C(3) & 117 + 1 (1 + 5) \\ C(4) - C(3) - C(22) & 111 + 1 (1 + 4) \\ O(4) - C(21) - C(20) & 119 + 7 (1 + 7) \\ C(3) - C(4) - C(25) & 121 + 8 (1 + 5) \\ C(4) - C(23) - C(22) & 111 + 1 (1 + 4) \\ O(4) - C(23) - C(22) & 111 + 1 (1 + 5) \\ O(2) - C(4) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(23) - C(23) & 112 + 1 (1 + 5) \\ C(4) - C(5) - C(4) & 112 + 2 (1 + 6) \\ C(23) - C(24) - C(23) & 113 + 1 (1 + 6) \\ O(3) - C(28) - C(28) & 113 + 1 (1 + 6) \\ O(3) - C(28) - C(28) & 113 + 1 (1 + 6) \\ O(3) - C(28) - C(28) & 113 + 1 (1 + 6) \\ O(3) - C(28) - C(28) & 113 + 1 (1 + 6) \\ O(3) - C(28) - C(28) & 113 + 1 (1 + 6) \\ O(3$	C(7) = N(1) = C(11)	123.6 (1.7)	C(12) = C(13) = C(14)	1249(17) 1240(1.7)
$\begin{array}{c} C(13) - V(2) - C(17) & 124 + (1-5) & C(13) - C(14) - C(19) & 109 + (1-5) \\ C(16) - N(2) - C(17) & 120 + 9 (1-5) & C(13) - C(14) - C(20) & 112 - 6 (1-5) \\ C(24) - N(3) - C(26) & 122 + (1-5) & C(15) - C(14) - C(20) & 110 - 7 (1+4) \\ C(26) - N(3) - C(31) & 114 + 4 (1-5) & C(15) - C(14) - C(20) & 110 - 7 (1+4) \\ C(26) - N(3) - C(31) & 123 + 1 (1-5) & N(2) - C(15) - C(2) & 110 - 7 (1+4) \\ C(28) - N(4) - C(36) & 111 + 1 (1+4) & N(2) - C(15) - C(14) & 123 + 1 (1-6) \\ C(32) - N(4) - C(36) & 111 + 1 (1+4) & N(2) - C(15) - C(14) & 124 + 5 (1-5) \\ C(2) - C(1) - N(1) & 104 + 5 (1+4) & N(2) - C(16) - C(22) & 103 + (1-5) \\ C(12) - C(1) - N(1) & 111 + 5 (1-5) & N(2) - C(17) - C(18) & 113 + 5 (1-7) \\ C(12) - C(1) - N(1) & 111 + 5 (1-5) & N(2) - C(17) - C(18) & 113 + 5 (1-7) \\ C(1) - C(2) - C(28) & 100 + 8 (1+4) & C(14) - C(19) - C(18) & 113 + 5 (1-7) \\ C(1) - C(2) - C(15) & 115 + 3 (1-5) & O(3) - C(21) - O(4) & 122 + 5 (1+8) \\ C(3) - C(2) - C(15) & 115 + 3 (1-5) & O(3) - C(21) - O(4) & 122 + 5 (1+8) \\ C(3) - C(2) - C(15) & 115 + 3 (1-5) & O(3) - C(21) - C(20) & 119 + 7 (1-7) \\ C(8) - C(2) - C(12) & 111 + 1 (1+4) & O(4) - C(21) - C(20) & 119 + 7 (1-7) \\ C(8) - C(2) - C(12) & 111 + 1 (1+4) & O(4) - C(21) - C(20) & 119 + 7 (1-7) \\ C(8) - C(2) - C(22) & 111 + 1 (1+4) & O(4) - C(21) - C(20) & 119 + 7 (1-7) \\ C(8) - C(2) - C(22) & 111 + 1 (1+4) & O(4) - C(21) - C(20) & 119 + 7 (1-7) \\ C(8) - C(2) - C(22) & 111 + 1 (1-5) & N(3) - C(24) - C(23) & 110 + 9 (1-5) \\ C(3) - C(4) - C(25) & 121 + 6 (1-5) & C(24) - C(23) - C(23) & 110 + 9 (1-5) \\ C(3) - C(4) - C(25) & 121 + 6 (1-5) & C(4) - C(23) - C(23) & 110 + 9 (1-5) \\ C(3) - C(4) - C(25) & 121 + 6 (1-5) & C(23) - C(23) & 113 + 3 (1-5) \\ C(5) - C(6) - C(7) & 118 + 7 (1-6) & N(3) - C(26) - C(28) & 113 + 3 (1-5) \\ C(5) - C(6) - C(7) & 118 + 7 (1-6) & N(3) - C(26) - C(28) & 113 + 3 (1-5) \\ C(5) - C(6) - C(7) & 118 + 7 (1-6) & N(3) - C(26) - C(28) & 113 + 3 (1-5) \\ C(5) - C(6) - C(7) & 118 + 7 (1-6) & N(3) - C(26) - C(28) & 113 + 3 (1-5) \\ C(5) - C(6) - C(7) & 118 + 7 (1-6) & N(3) - C(2$	C(15) = N(2) = C(16)	114.4(1.5)	C(12) = C(13) = C(14)	108.3(1.5)
$\begin{array}{c} C(15) - V(2) - C(17) & 120 \cdot 9 (1 \cdot 5) & C(13) - C(14) - C(20) & 112 \cdot 6 (1 \cdot 5) \\ C(24) - N(3) - C(26) & 122 \cdot 4 (1 \cdot 5) & C(15) - C(14) - C(20) & 107 \cdot 4 (1 \cdot 4) \\ C(26) - N(3) - C(31) & 112 \cdot 4 (1 \cdot 5) & C(15) - C(14) - C(20) & 107 \cdot 4 (1 \cdot 4) \\ C(26) - N(3) - C(31) & 123 \cdot 1 (1 \cdot 5) & C(19) - C(14) - C(20) & 110 \cdot 7 (1 \cdot 4) \\ C(28) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 1 (1 \cdot 6) \\ C(28) - N(4) - C(36) & 111 \cdot 1 (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 4 (1 \cdot 5) \\ C(2) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & N(2) - C(15) - C(14) & 123 \cdot 4 (1 \cdot 5) \\ C(2) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & N(2) - C(17) - C(18) & 113 \cdot 5 (1 \cdot 7) \\ C(2) - C(1) - N(1) & 111 \cdot 5 (1 \cdot 5) & C(17) - C(18) - C(19) & 111 \cdot 6 (1 \cdot 9) \\ C(1) - C(2) - C(12) & 110 \cdot 40 \cdot 15) & C(17) - C(18) - C(19) & 111 \cdot 6 (1 \cdot 9) \\ C(1) - C(2) - C(28) & 100 \cdot 8 (1 \cdot 4) & C(14) - C(19) - C(18) & 110 \cdot 0 \cdot (1 \cdot 7) \\ C(1) - C(2) - C(22) & 111 \cdot 3 (1 \cdot 5) & O(3) - C(21) - O(4) & 122 \cdot 5 (1 \cdot 8) \\ C(8) - C(2) - C(22) & 111 \cdot 3 (1 \cdot 5) & O(3) - C(21) - O(4) & 122 \cdot 5 (1 \cdot 8) \\ C(8) - C(2) - C(22) & 111 \cdot 1 (1 \cdot 4) & O(4) - C(21) - C(20) & 117 \cdot 4 (1 \cdot 6) \\ C(15) - C(2) - C(22) & 111 \cdot 1 (1 \cdot 5) & O(3) - C(21) - C(20) & 117 \cdot 4 (1 \cdot 6) \\ C(15) - C(2) - C(22) & 111 \cdot 1 (1 \cdot 5) & C(2) - C(22) & 114 \cdot 4 (1 \cdot 5) \\ C(3) - C(4) - C(5) & 117 \cdot 1 (1 \cdot 5) & C(4) - C(23) - C(23) & 110 \cdot 9 (1 \cdot 5) \\ C(3) - C(4) - C(5) & 117 \cdot 1 (1 \cdot 5) & C(4) - C(23) - C(23) & 110 \cdot 9 (1 \cdot 5) \\ C(3) - C(4) - C(5) & 121 \cdot 5 (1 \cdot 6) & C(23) - C(23) & 103 \cdot 6 (1 \cdot 4) \\ O(1) - C(5) - C(4) & 117 \cdot 3 (1 \cdot 5) & C(4) - C(25) - C(34) & 110 \cdot 9 (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 (1 - 6) & C(23) - C(23) - C(23) & 113 \cdot 3 (1 \cdot 4) \\ O(1) - C(5) - C(4) & 122 \cdot 4 (1 - 6) & C(23) - C(23) - C(34) & 110 \cdot 9 (1 \cdot 5) \\ O(1) - C(5) - C(4) & 122 \cdot 4 (1 - 6) & C(23) - C(23) - C(34) & 110 \cdot 9 (1 \cdot 5) \\ O(1) - C(5) - C(4) & 122 \cdot 4 (1 - 6) & C(23) - C(23) - C(34) & 110 \cdot 9 (1 \cdot 5) \\ O(1) - C(5) - C(4) & 117 \cdot 3 (1 \cdot 6) & C(23) - C(34) & 100 \cdot 9 (1 \cdot 4) \\ O(2) - C(6) - C(77) & 118 \cdot 8$	C(15) = N(2) = C(17)	124.5(1.5)	C(13) - C(14) - C(19)	100.4(1.5)
$\begin{array}{c} C(24) - N(3) - C(26) & 122 \cdot 4 \ (1 \cdot 5) & C(15) - C(14) - C(19) & 108 \cdot 3 \ (1 \cdot 5) \\ C(24) - N(3) - C(31) & 114 \cdot 4 \ (1 \cdot 5) & C(15) - C(14) - C(20) & 110 \cdot 7 \ (1 \cdot 4) \\ C(26) - N(3) - C(31) & 123 \cdot 1 \ (1 \cdot 5) & C(19) - C(14) - C(20) & 110 \cdot 7 \ (1 \cdot 4) \\ C(28) - N(4) - C(32) & 119 \cdot 3 \ (1 \cdot 5) & N(2) - C(15) - C(14) & 123 \cdot 1 \ (1 \cdot 6) \\ C(32) - N(4) - C(36) & 111 \cdot 1 \ (1 \cdot 4) & N(2) - C(15) - C(14) & 123 \cdot 1 \ (1 \cdot 6) \\ C(32) - N(4) - C(36) & 129 \cdot 5 \ (1 \cdot 6) & C(2) - C(15) - C(14) & 124 \cdot 5 \ (1 \cdot 5) \\ C(12) - C(1) - N(1) & 104 \cdot 5 \ (1 \cdot 4) & N(2) - C(16) - C(22) & 103 \cdot 4 \ (1 \cdot 5) \\ C(12) - C(1) - N(1) & 111 \cdot 5 \ (1 \cdot 5) & N(2) - C(17) - C(18) & 111 \cdot 6 \ (1 \cdot 9) \\ C(1) - C(2) - C(28) & 100 \cdot 8 \ (1 \cdot 4) & C(14) - C(19) - C(18) & 1110 \cdot 6 \ (1 \cdot 7) \\ C(1) - C(2) - C(22) & 114 \cdot 0 \ (1 \cdot 5) & C(17) - C(18) - C(19) & 111 \cdot 6 \ (1 \cdot 9) \\ C(1) - C(2) - C(22) & 114 \cdot 0 \ (1 \cdot 5) & O(3) - C(21) - C(20) & 119 \cdot 7 \ (1 \cdot 7) \\ C(1) - C(2) - C(22) & 114 \cdot 0 \ (1 \cdot 5) & O(3) - C(21) - C(20) & 119 \cdot 7 \ (1 \cdot 7) \\ C(1) - C(2) - C(22) & 104 \cdot 2 \ (1 \cdot 5) & C(2) - C(22) & 114 \cdot 4 \ (1 \cdot 5) \\ C(3) - C(4) - C(25) & 117 \cdot 1 \ (1 \cdot 5) & N(3) - C(24) - C(23) & 113 \cdot 3 \ (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 6 \ (1 \cdot 5) & C(4) - C(25) - C(23) & 113 \cdot 3 \ (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 \ (1 \cdot 5) & C(4) - C(25) - C(23) & 113 \cdot 3 \ (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 \ (1 \cdot 5) & C(4) - C(25) - C(23) & 113 \cdot 3 \ (1 \cdot 5) \\ C(3) - C(4) - C(25) & 121 \cdot 8 \ (1 \cdot 5) & C(4) - C(25) - C(23) & 113 \cdot 3 \ (1 \cdot 5) \\ C(5) - C(4) - C(25) & 121 \cdot 8 \ (1 \cdot 6) & N(3) - C(26) - C(28) & 102 \cdot 9 \ (1 \cdot 5) \\ C(4) - C(5) - C(6) & 122 \cdot 2 \ (1 \cdot 6) & C(23) - C(25) - C(34) & 111 \cdot 0 \ (1 \cdot 5) \\ O(1) - C(5) - C(4) & 122 \cdot 4 \ (1 \cdot 6) & C(23) - C(25) - C(34) & 111 \cdot 0 \ (1 \cdot 5) \\ O(1) - C(5) - C(6) & 122 \cdot 2 \ (1 \cdot 6) & C(23) - C(25) - C(34) & 111 \cdot 0 \ (1 \cdot 5) \\ O(1) - C(5) - C(6) & 123 \cdot 2 \ (1 \cdot 6) & C(23) - C(23) - C(36) & 114 \cdot 1 \ (1 \cdot 5) \\ O(1) - C(5) - C(6) & 113 \cdot 7 \ (1 \cdot 6) & N(3) - C(26) - C(29) & 122 \cdot 6 \ (1 \cdot 5$	C(16) = N(2) = C(17)	120.9(1.5)	C(13) = C(14) = C(19)	112.6 (1.5)
$\begin{array}{c} C(24)-N(3)-C(13) & 112+4 (1-5) & C(15)-C(14)-C(19) & 100-3 (1-3) \\ C(26)-N(3)-C(31) & 123+1 (1-5) & C(15)-C(14)-C(20) & 110-7 (1-4) \\ C(28)-N(4)-C(32) & 119-3 (1-5) & N(2)-C(15)-C(2) & 112-3 (1-5) \\ C(28)-N(4)-C(36) & 111+1 (1-4) & N(2)-C(15)-C(14) & 123+1 (1-6) \\ C(32)-N(4)-C(36) & 129-5 (1-6) & C(2)-C(15)-C(14) & 123+1 (1-6) \\ C(32)-N(4)-C(36) & 129-5 (1-6) & C(2)-C(15)-C(14) & 123+1 (1-6) \\ C(12)-C(1)-N(1) & 104+5 (1-4) & N(2)-C(16)-C(22) & 103-4 (1-5) \\ C(12)-C(1)-N(1) & 111+5 (1-5) & N(2)-C(17)-C(18) & 113-5 (1-7) \\ C(2)-C(1)-N(1) & 111+5 (1-5) & C(17)-C(18)-C(19) & 111-6 (1-9) \\ C(1)-C(2)-C(15) & 111+8 (1-5) & C(14)-C(20)-C(18) & 113-5 (1-7) \\ C(1)-C(2)-C(15) & 111+8 (1-5) & C(14)-C(20)-C(18) & 110-0 (1-7) \\ C(1)-C(2)-C(15) & 111+8 (1-5) & C(14)-C(20)-C(21) & 116-7 (1-5) \\ C(1)-C(2)-C(22) & 114-0 (1-5) & O(3)-C(21)-O(4) & 122-5 (1-8) \\ C(8)-C(2)-C(22) & 111+1 (1-4) & O(4)-C(21)-C(20) & 117-4 (1-6) \\ C(15)-C(2)-C(22) & 110+2 (1-5) & C(2)-C(22) & 110-9 (1-5) \\ C(4)-C(3)-C(8) & 117-5 (1-6) & C(24)-C(23) & 110-9 (1-5) \\ C(3)-C(4)-C(5) & 127-1 (1-5) & N(3)-C(24)-C(23) & 110-9 (1-5) \\ C(4)-C(5)-C(6) & 120-2 (1-5) & C(4)-C(25)-C(23) & 113-3 (1-5) \\ C(4)-C(5)-C(6) & 120-2 (1-5) & C(4)-C(25)-C(23) & 113-3 (1-5) \\ C(5)-C(4)-C(5) & 121-6 (1-6) & C(23)-C(25)-C(34) & 112-3 (1-4) \\ C(4)-C(5)-C(6) & 120-2 (1-5) & C(23)-C(25)-C(34) & 112-3 (1-4) \\ C(4)-C(5)-C(6) & 120-2 (1-5) & C(23)-C(25)-C(34) & 112-3 (1-4) \\ C(4)-C(5)-C(6) & 120-2 (1-5) & C(23)-C(25)-C(34) & 110-9 (1-5) \\ O(1)-C(5)-C(6) & 120-2 (1-5) & C(23)-C(25)-C(34) & 110-9 (1-5) \\ O(1)-C(5)-C(6) & 120-2 (1-5) & C(23)-C(25)-C(34) & 112-3 (1-4) \\ O(2)-C(6)-C(7) & 118-7 (1-6) & N(3)-C(26)-C(28) & 121-3 (1-5) \\ C(5)-C(6)-C(7) & 118-7 (1-6) & N(3)-C(26)-C(28) & 121-3 (1-5) \\ C(5)-C(6)-C(7) & 118-9 (1-6) & C(23)-C(35) & 113-5 (1-6) \\ O(5)-C(28)-C(26) & 105-7 (1-4) & O(7)-C(35)-C(36) & 119+1 (1-5) \\ N(4)-C(28)-C(26) & 105-7 (1-4) & O(7)-C(35)-C(36) & 119+1 (1-5) \\ N(4)-C(28)-C(26) & 105-7 (1-4) & O(7)-C(35)-C(35) & 115-5 (1-4) \\ O(6)-C(32)-N(4) & 120-8 (1-9) & N($	C(24) = N(3) = C(26)	120 9 (1 3) 122.4 (1.5)	C(15) = C(14) = C(20)	108.2(1.5)
$\begin{array}{c} C(26) - N(3) - C(31) & 11 + 1 (1-2) & C(13) - C(14) - C(20) & 110.^4 (1-4) \\ C(28) - N(4) - C(32) & 119.3 (1-5) & N(2) - C(14) - C(20) & 110.^2 (1-4) \\ C(28) - N(4) - C(32) & 119.3 (1-5) & N(2) - C(15) - C(14) & 123.1 (1-6) \\ C(28) - N(4) - C(36) & 119.^5 (1-6) & C(2) - C(15) - C(14) & 124.5 (1-5) \\ C(12) - C(1) - N(1) & 110.^5 (1-4) & N(2) - C(16) - C(12) & 113.5 (1-7) \\ C(12) - C(1) - N(1) & 111.5 (1-5) & N(2) - C(17) - C(18) & 111.5 (1-7) \\ C(1) - C(2) - C(15) & 111.8 (1-5) & C(14) - C(20) - C(12) & 110.6 (1-7) \\ C(1) - C(2) - C(22) & 110.4 0 (1-5) & C(14) - C(20) - C(12) & 110.6 (1-7) \\ C(1) - C(2) - C(15) & 111.8 (1-5) & C(14) - C(20) - C(12) & 110.6 (1-7) \\ C(1) - C(2) - C(22) & 110.4 0 (1-5) & O(3) - C(21) - O(14) & 122.5 (1-8) \\ C(8) - C(2) - C(22) & 110.4 0 (1-5) & O(3) - C(21) - C(20) & 117.4 (1-6) \\ C(15) - C(2) - C(22) & 110.4 (1-5) & C(2) - C(22) & 117.4 (1-6) \\ C(15) - C(2) - C(22) & 110.4 (1-5) & C(2) - C(22) & 110.7 (1-7) \\ C(3) - C(4) - C(5) & 117.5 (1-6) & C(24) - C(23) - C(25) & 113.3 (1-5) \\ C(4) - C(3) - C(4) & 117.3 (1-5) & C(4) - C(25) - C(23) & 110.9 (1-5) \\ C(4) - C(5) - C(4) & 117.3 (1-5) & C(4) - C(25) - C(23) & 110.3 (1-5) \\ C(4) - C(5) - C(4) & 117.4 (1-6) & N(3) - C(24) - C(23) & 110.9 (1-5) \\ O(1) - C(5) - C(4) & 117.4 (1-6) & C(23) - C(25) - C(34) & 110.4 (1-6) \\ O(1) - C(5) - C(4) & 117.3 (1-5) & C(4) - C(25) - C(34) & 110.9 (1-5) \\ O(2) - C(6) - C(7) & 119.8 (1-6) & N(3) - C(26) - C(28) & 102.9 (1-5) \\ O(1) - C(5) - C(4) & 122.4 (1-6) & C(23) - C(25) - C(34) & 110.9 (1-4) \\ O(2) - C(6) - C(7) & 118.7 (1-6) & N(3) - C(26) - C(28) & 121.3 (1-5) \\ C(5) - C(6) - C(7) & 118.7 (1-6) & N(3) - C(26) - C(28) & 112.3 (1-5) \\ C(5) - C(6) - C(7) & 118.7 (1-6) & C(28) - C(26) - C(28) & 115.5 (1-6) \\ C(6) - C(7) - C(8) & 113.9 (1-6) & C(28) - C(30) - C(34) & 113.4 (1-5) \\ N(1) - C(7) - C(8) & 113.9 (1-6) & C(28) - C(34) - C(36) & 112.4 (1-5) \\ N(4) - C(28) - C(25) & 109.4 (1-4) & C(25) - C(34) & 110.4 (1-5) \\ N(4) - C(28) - C(25) & 109.4 (1-4) & C(30) - C(34) & 113.4 (1-5) \\ N(4) - C($	C(24) = N(3) = C(20)	1224(15) 114.4(1.5)	C(15) = C(14) = C(19)	$103^{-3}(1^{-3})$ 107.4(1.4)
$\begin{array}{c} C(28) - N(4) - C(31) & 123 + (12) & C(12) - C(12) - C(22) & 1123 + (14) \\ C(28) - N(4) - C(36) & 111 + (14) & N(2) - C(15) - C(14) & 123 + (16) \\ C(32) - N(4) - C(36) & 129 + 5 + (16) & C(2) - C(15) - C(14) & 123 + (16) \\ C(32) - N(4) - C(36) & 129 + 5 + (16) & C(2) - C(15) - C(14) & 124 + 5 + (15) \\ C(12) - C(1) - N(1) & 111 + 5 + (15) & N(2) - C(16) - C(22) & 103 + (15) \\ C(12) - C(1) - N(1) & 111 + 5 + (15) & N(2) - C(17) - C(18) & 113 + 5 + (17) \\ C(1) - C(2) - C(8) & 100 + 8 + (14) & C(14) - C(19) - C(18) & 110 + 0 + (17) \\ C(1) - C(2) - C(22) & 114 + 0 + (15) & C(14) - C(20) - C(21) & 116 + 7 + (15) \\ C(1) - C(2) - C(22) & 114 + 0 + (15) & O(3) - C(21) - O(4) & 122 + 5 + (18) \\ C(8) - C(2) - C(22) & 115 + 3 + (15) & C(24) - C(23) - C(20) & 119 + 7 + (17) \\ C(8) - C(2) - C(22) & 114 + 0 + (15) & C(24) - C(23) - C(25) & 114 + 4 + (15) \\ C(15) - C(2) - C(22) & 104 + 2 + (15) & C(24) - C(23) - C(23) & 110 + 9 + (15) \\ C(3) - C(4) - C(5) & 117 + 1 + (15) & N(3) - C(24) - C(23) & 110 + 9 + (15) \\ C(3) - C(4) - C(25) & 121 + 0 + (15) & C(4) - C(25) - C(23) & 110 + 9 + (15) \\ C(3) - C(4) - C(25) & 121 + 0 + (15) & C(4) - C(25) - C(23) & 110 + 9 + (15) \\ C(3) - C(4) - C(25) & 121 + 8 + (15) & C(4) - C(25) - C(23) & 110 + 9 + (15) \\ C(3) - C(4) - C(25) & 121 + 8 + (15) & C(4) - C(25) - C(23) & 110 + 9 + (15) \\ C(4) - C(5) - C(4) & 122 + 4 + (16) & C(23) - C(25) - C(34) & 111 + 0 + (15) \\ O(1) - C(5) - C(4) & 122 + 4 + (16) & C(23) - C(25) - C(34) & 111 + 0 + (15) \\ O(1) - C(5) - C(4) & 122 + 4 + (16) & C(23) - C(25) - C(34) & 110 + 9 + (16) \\ O(2) - C(6) - C(7) & 118 + 7 + (16) & N(3) - C(26) - C(28) & 121 + 3 + (15) \\ C(4) - C(28) - C(25) & 104 + 9 + (14) & C(25) - C(34) - C(36) & 112 + 1 + 5) \\ N(4) - C(28) - C(25) & 104 + 9 + (14) & C(25) - C(34) - C(36) & 112 + 1 + 15) \\ N(4) - C(28) - C(26) & 105 + 7 + (14) & O(7) - C(35) - C(37) & 120 + 3 + (14) \\ O(5) - C(28) - C(26) & 105 + 7 + (14) & O(7) - C(35) - C(37) & 120 + 3 + (14) \\ O(5) - C(28) - C(26) & 105 + 7 + (14) & O(7) - C(35) - C(35) & 113 + 5 + (16)$	C(24) = N(3) = C(31)	123.1(1.5)	C(19) - C(14) - C(20)	1074(14) 1107(14)
$\begin{array}{c} C(28) - N(4) - C(32) & 119^{-3} (1^{-3}) & N(2) - C(1^{-3}) - C(2^{-3}) & 112^{-3} (1^{-5}) \\ C(28) - N(4) - C(36) & 129^{-5} (1^{-6}) & C(2) - C(1^{-3}) - C(1^{-3}) & 12^{-5} (1^{-5}) \\ C(2) - C(1) - N(1) & 104^{-5} (1^{-4}) & N(2) - C(1^{-5}) - C(1^{-4}) & 12^{-5} (1^{-5}) \\ C(12) - C(1) - N(1) & 111^{-5} (1^{-5}) & N(2) - C(1^{-5}) - C(1^{-3}) & 113^{-5} (1^{-7}) \\ C(1) - C(2) - C(1) - N(1) & 111^{-5} (1^{-5}) & N(2) - C(1^{-5}) - C(1^{-3}) & 113^{-5} (1^{-7}) \\ C(1) - C(2) - C(1^{-5}) & 111^{-6} (1^{-5}) & C(1^{-1}) - C(1^{-5}) - C(1^{-5}) & 113^{-5} (1^{-7}) \\ C(1) - C(2) - C(2) & 114^{-0} (1^{-5}) & C(1^{-1}) - C(2^{-1}) - C(1^{-5}) & 111^{-5} (1^{-5}) \\ C(1) - C(2) - C(2) & 111^{-1} (1^{-5}) & O(3) - C(2^{-1}) - C(2^{-2}) & 111^{-2} (1^{-7}) \\ C(8) - C(2) - C(2^{-2}) & 111^{-1} (1^{-4}) & O(4) - C(2^{-1}) - C(2^{-2}) & 111^{-2} (1^{-7}) \\ C(8) - C(2) - C(2^{-2}) & 111^{-1} (1^{-5}) & C(2) - C(2^{-2}) & 111^{-2} (1^{-7}) \\ C(8) - C(2) - C(2^{-2}) & 111^{-1} (1^{-5}) & C(2) - C(2^{-2}) & 111^{-2} (1^{-6}) \\ C(1^{-5}) - C(4) - C(2^{-5}) & 117^{-1} (1^{-5}) & C(2) - C(2^{-2}) & 111^{-4} (1^{-5}) \\ C(3) - C(4) - C(2^{-5}) & 117^{-1} (1^{-5}) & C(4) - C(2^{-5}) - C(2^{-2}) & 114^{-4} (1^{-5}) \\ C(3) - C(4) - C(2^{-5}) & 121^{-6} (1^{-5}) & C(4) - C(2^{-5}) - C(2^{-2}) & 113^{-3} (1^{-5}) \\ C(5) - C(4) - C(2^{-5}) & 121^{-6} (1^{-5}) & C(2^{-3}) - C(2^{-5}) - C(2^{-3}) & 113^{-3} (1^{-5}) \\ O(1) - C(5) - C(4) & 127^{-4} (1^{-6}) & N(3) - C(2^{-5}) - C(2^{-3}) & 110^{-6} (1^{-5}) \\ O(1) - C(5) - C(4) & 128^{-2} (1^{-6}) & C(2^{-3}) - C(2^{-5}) - C(2^{-3}) & 111^{-2} (1^{-5}) \\ O(1) - C(5) - C(4) & 113^{-9} (1^{-6}) & N(3) - C(2^{-5}) - C(2^{-3}) & 113^{-3} (1^{-5}) \\ O(2) - C(6) - C(7) & 118^{-7} (1^{-6}) & N(3) - C(2^{-5}) - C(2^{-3}) & 113^{-5} (1^{-6}) \\ N(4) - C(2^{-5}) - C(2^{-5}) & 113^{-5} (1^{-6}) & N(3) - C(2^{-5}) - C(3^{-5}) & 113^{-5} (1^{-6}) \\ O(5) - C(2^{-2}) - C(2^{-5}) & 113^{-7} (1^{-6}) & C(2^{-5}) - C(3^{-5}) & 113^{-5} (1^{-7}) \\ N(4) - C(2^{-5}) - C(2^{-5}) & 118^{-7} (1^{-6}) & C(2^$	C(28) = N(3) = C(31)	$125^{1}(15)$	N(2) = C(15) = C(20)	110.7(1.4) 112.2(1.5)
$\begin{array}{c} C(32) - N(4) - C(30) & 1111 (14) & N(2) - C(13) - C(14) & 1231 (170) \\ C(32) - N(4) - C(36) & 1295 (1:6) & C(2) - C(15) - C(14) & 1245 (1:5) \\ C(2) - C(1) - N(1) & 1045 (1:4) & N(2) - C(16) - C(22) & 1034 (1:5) \\ C(12) - C(1) - N(1) & 1115 (1:5) & N(2) - C(18) - C(19) & 1115 (1:7) \\ C(2) - C(2) - C(12) & 114 0 (1:5) & C(17) - C(18) - C(19) & 1115 (1:7) \\ C(1) - C(2) - C(28) & 100*8 (1:4) & C(14) - C(19) - C(18) & 110*0 (1:7) \\ C(1) - C(2) - C(22) & 114*0 (1:5) & C(14) - C(20) - C(21) & 116*7 (1:5) \\ C(1) - C(2) - C(22) & 114*0 (1:5) & O(3) - C(21) - C(20) & 117*4 (1:6) \\ C(15) - C(2) - C(22) & 104*2 (1:5) & C(2) - C(22) - (16) & 102*9 (1:5) \\ C(4) - C(3) - C(8) & 117*5 (1:6) & C(24) - C(23) - C(25) & 114*4 (1:5) \\ C(3) - C(4) - C(25) & 121*0 (1:5) & C(4) - C(25) - C(23) & 110*9 (1:5) \\ C(3) - C(4) - C(25) & 121*0 (1:5) & C(4) - C(25) - C(23) & 110*3 (1:5) \\ C(5) - C(4) - C(25) & 121*0 (1:5) & C(4) - C(25) - C(23) & 110*3 (1:5) \\ C(5) - C(4) - C(25) & 121*0 (1:5) & C(4) - C(25) - C(23) & 110*6 (1:4) \\ O(1) - C(5) - C(4) & 117*3 (1:5) & C(4) - C(25) - C(23) & 110*3 (1:5) \\ O(2) - C(6) - C(7) & 118*7 (1:6) & N(3) - C(26) - C(28) & 108*6 (1*4) \\ O(1) - C(5) - C(4) & 122*4 (1:6) & C(23) - C(25) - C(34) & 111*0 (1:5) \\ O(2) - C(6) - C(7) & 118*7 (1:6) & N(3) - C(26) - C(28) & 121*3 (1:5) \\ C(5) - C(6) - C(7) & 118*7 (1:6) & N(3) - C(26) - C(28) & 121*3 (1:5) \\ C(5) - C(6) - C(7) & 118*7 (1:6) & N(3) - C(26) - C(28) & 121*3 (1:5) \\ C(5) - C(6) - C(7) & 118*7 (1:6) & N(3) - C(26) - C(28) & 121*3 (1:5) \\ C(5) - C(28) - C(25) & 101*9 (1:6) & C(23) - C(32) - C(33) & 111*1 (1:5) \\ N(4) - C(28) - C(25) & 101*9 (1:6) & C(23) - C(34) - C(30) & 123*2 (1:6) \\ O(5) - C(28) - C(25) & 101*9 (1:4) & C(25) - C(34) & 101*4 (1:5) \\ N(4) - C(28) - C(25) & 101*9 (1:4) & C(25) - C(34) & 101*4 (1:5) \\ N(4) - C(28) - C(25) & 101*9 (1:4) & C(35) - C(35) & 115*5 (1:4) \\ O(7) - C(35) - C(37) & 112*1 (1:5) & C(36) - C(35) & 115*5 (1:4) \\ O(7) - C(35) - C(37) & 112*1 (1:5) & C(36) - C(35) & 115*5 (1:6) \\ O(6) - C(32) - N(4) & 122*8 (1:9)$	C(28) = N(4) = C(32)	$113^{1}3^{1}(13)$	N(2) = C(15) = C(2)	112.3(1.3) 122.1(1.6)
$\begin{array}{c} C(2) = C(1) = N(1) & 12+3 (1+0) & C(2) = C(1) = C(14) & 12+3 (1+3) \\ C(2) = C(1) = N(1) & 111+5 (1+3) & N(2) = C(16) = C(22) & 103+4 (1+5) \\ C(12) = C(1) = N(1) & 111+5 (1+5) & N(2) = C(17) = C(18) & 111+6 (1+9) \\ C(1) = C(2) = C(12) & 114+0 (1+5) & C(17) = C(18) = C(19) & 111+6 (1+9) \\ C(1) = C(2) = C(15) & 111+8 (1+5) & C(14) = C(19) = C(18) & 110+0 (1+7) \\ C(1) = C(2) = C(15) & 111+8 (1+5) & O(3) = C(21) = C(20) & 119+7 (1+7) \\ C(1) = C(2) = C(15) & 115+3 (1+5) & O(3) = C(21) = C(20) & 119+7 (1+7) \\ C(8) = C(2) = C(22) & 114+0 (1+5) & O(3) = C(21) = C(20) & 119+7 (1+7) \\ C(8) = C(2) = C(22) & 104+2 (1+5) & C(2) = C(22) = C(20) & 119+7 (1+6) \\ C(15) = C(2) = C(22) & 104+2 (1+5) & C(2) = C(22) = C(23) & 110+9 (1+5) \\ C(3) = C(4) = C(25) & 121+0 (1+5) & C(4) = C(25) = C(23) & 110+9 (1+5) \\ C(3) = C(4) = C(25) & 121+8 (1+5) & C(4) = C(25) = C(23) & 110+9 (1+5) \\ C(4) = C(5) = C(4) & 117+3 (1+5) & C(4) = C(25) = C(24) & 112+3 (1+4) \\ O(1) = C(5) = C(4) & 122+4 (1+6) & C(23) = C(25) = C(24) & 112+3 (1+4) \\ O(1) = C(5) = C(4) & 122+4 (1+6) & C(23) = C(25) = C(34) & 110+9 (1+5) \\ O(2) = C(6) = C(7) & 119+8 (1+6) & N(3) = C(26) = C(29) & 115+5 (1+4) \\ O(1) = C(7) = C(6) & 128+2 (1+6) & C(28) = C(25) = C(34) & 100+9 (1+4) \\ O(2) = C(6) = C(7) & 119+8 (1+6) & N(3) = C(26) = C(29) & 115+5 (1+4) \\ O(1) = C(7) = C(8) & 113+9 (1+6) & C(28) = C(26) = C(29) & 115+5 (1+4) \\ O(1) = C(7) = C(8) & 113+9 (1+6) & C(28) = C(26) = C(29) & 115+5 (1+4) \\ O(5) = C(28) = C(25) & 104+9 (1+4) & C(25) = C(34) = C(36) & 112+1 (1+5) \\ N(4) = C(28) = C(26) & 101+7 (1+3) & C(25) = C(34) = C(36) & 112+1 (1+5) \\ N(4) = C(28) = C(25) & 104+9 (1+4) & C(25) = C(34) = C(36) & 112+1 (1+5) \\ N(4) = C(28) = C(26) & 101+7 (1+3) & C(25) = C(34) = C(36) & 112+1 (1+5) \\ N(4) = C(28) = C(26) & 101+7 (1+3) & C(36) = C(35) = C(37) & 120+5 (1+9) \\ O(3) = C(34) = C(34) & 118+2 (1+9) & N(4) = C(36) = C(35) & 135+2 (1+6) \\ O(6) = C(32) = N(4) & 120+8 (1+9) & N(4) = C(36) = C(35) & 135+2 (1+6) \\ O(6) = C(32) = C(27) & 112+1 (1+5) & C(34) = C(35) = C(35) & 1$	C(23) = N(4) = C(30)	170.5(1.6)	C(2) = C(15) = C(14)	123.1(1.0) 124.5(1.5)
$\begin{array}{c} C(2) = C(1) - N(1) & 104-3 & (14) & N(2) - C(10) - C(22) & 103-4 & (1-3) \\ C(12) - C(1) - C(12) & 114-0 & (1-5) & N(2) - C(17) - C(18) & 113-5 & (1-7) \\ C(2) - C(3) - C(3) & 100+8 & (1-4) & C(14) - C(19) - C(18) & 110-0 & (1-7) \\ C(1) - C(2) - C(22) & 111+8 & (1-5) & C(14) - C(20) - C(21) & 116-7 & (1-5) \\ C(1) - C(2) - C(22) & 114+0 & (1-5) & O(3) - C(21) - O(4) & 122-5 & (1-8) \\ C(8) - C(2) - C(15) & 115-3 & (1-5) & O(3) - C(21) - O(4) & 122-5 & (1-8) \\ C(8) - C(2) - C(22) & 104+2 & (1-5) & C(2) - C(22) - C(16) & 102-9 & (1-5) \\ C(4) - C(3) - C(8) & 117-5 & (1-6) & C(24) - C(23) - C(23) & 113-3 & (1-5) \\ C(3) - C(4) - C(25) & 117-1 & (1-5) & N(3) - C(24) - C(23) & 110-9 & (1-5) \\ C(3) - C(4) - C(25) & 121-0 & (1-5) & C(4) - C(25) - C(28) & 108+6 & (1-4) \\ O(1) - C(5) - C(4) & 117-3 & (1-5) & C(4) - C(25) - C(28) & 108+6 & (1-4) \\ O(1) - C(5) - C(4) & 122-4 & (1-6) & C(23) - C(25) - C(34) & 111-0 & (1-5) \\ O(2) - C(6) - C(7) & 119+8 & (1-6) & N(3) - C(26) - C(28) & 109-9 & (1-5) \\ O(2) - C(6) - C(7) & 119+8 & (1-6) & N(3) - C(26) - C(28) & 110-9 & (1-5) \\ O(2) - C(6) - C(7) & 119+8 & (1-6) & N(3) - C(26) - C(28) & 121-3 & (1-5) \\ C(5) - C(6) - C(7) & 119+7 & (1-6) & N(3) - C(26) - C(28) & 112-3 & (1-5) \\ O(2) - C(6) - C(7) & 119+7 & (1-6) & N(3) - C(26) - C(28) & 121-3 & (1-5) \\ O(2) - C(6) - C(7) & 119+7 & (1-6) & C(28) - C(23) - C(32) & 115-5 & (1-6) \\ O(5) - C(28) - C(25) & 101-7 & (1-3) & C(25) - C(34) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 101-7 & (1-3) & C(25) - C(34) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(36) & 119+1 & (1-7) \\ C(25) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(36) & 114+1 & (1-5) \\ O(5) - C(28) - C(25) & 105-7 & (1-4) & O(7) - C(35) - C(35) & 135-2 & (1-6) \\ O(5) - C(28) - C(27) & 112-1 & (1-$	C(32) = N(4) = C(30)	104.5 (1.4)	N(2) = C(15) - C(14)	124.3(1.3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2) = C(1) = N(1)	$104^{\circ}5(1^{\circ}4)$	N(2) = C(10) - C(22) N(2) = C(17) - C(18)	103.4(1.3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(12) = C(1) = N(1)	111.5(1.5) 114.0(1.5)	R(2) = C(17) = C(18)	113.5 (1.7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(2) = C(1) = C(12)	100.8 (1.4)	C(17) - C(18) - C(19)	111.6 (1.9)
$\begin{array}{c} C(1) - C(2) - C(13) & 111*6 (1*5) & C(14) - C(20) - C(21) & 116*7 (1*5) \\ C(1) - C(2) - C(22) & 114*0 (1*5) & O(3) - C(21) - O(4) & 122*5 (1*8) \\ C(8) - C(2) - C(15) & 115*3 (1*5) & O(3) - C(21) - C(20) & 119*7 (1*7) \\ C(8) - C(2) - C(22) & 104*2 (1*5) & C(2) - C(22) - C(16) & 102*9 (1*5) \\ C(4) - C(3) - C(8) & 117*5 (1*6) & C(24) - C(23) - C(25) & 114*4 (1*5) \\ C(3) - C(4) - C(25) & 121*0 (1*5) & C(4) - C(25) - C(28) & 110*9 (1*5) \\ C(3) - C(4) - C(25) & 121*0 (1*5) & C(4) - C(25) - C(28) & 109*6 (1*4) \\ O(1) - C(5) - C(4) & 117*3 (1*5) & C(4) - C(25) - C(28) & 109*9 (1*5) \\ O(1) - C(5) - C(4) & 117*3 (1*5) & C(4) - C(25) - C(28) & 109*9 (1*5) \\ O(1) - C(5) - C(4) & 122*4 (1*6) & C(23) - C(25) - C(28) & 109*9 (1*5) \\ O(1) - C(5) - C(4) & 122*4 (1*6) & C(23) - C(25) - C(28) & 109*9 (1*5) \\ O(1) - C(5) - C(4) & 122*4 (1*6) & C(23) - C(25) - C(34) & 111*0 (1*5) \\ O(2) - C(6) - C(7) & 119*8 (1*6) & N(3) - C(26) - C(28) & 109*9 (1*5) \\ O(2) - C(6) - C(7) & 119*8 (1*6) & N(3) - C(26) - C(28) & 121*3 (1*5) \\ C(5) - C(6) - C(7) & 119*7 (1*6) & N(3) - C(26) - C(29) & 125*5 (1*4) \\ N(1) - C(7) - C(8) & 113*9 (1*6) & C(29) - C(27) - C(32) & 115*5 (1*6) \\ C(6) - C(7) - C(8) & 113*9 (1*6) & C(29) - C(24) - C(30) & 123*2 (1*6) \\ O(5) - C(28) - C(25) & 109*4 (1*4) & C(25) - C(34) - C(36) & 112*1 (1*5) \\ N(4) - C(28) - C(25) & 109*4 (1*4) & C(25) - C(34) - C(36) & 112*1 (1*7) \\ N(4) - C(28) - C(25) & 109*4 (1*4) & C(25) - C(34) - C(36) & 112*1 (1*7) \\ N(4) - C(28) - C(25) & 109*4 (1*4) & C(25) - C(34) - C(36) & 112*1 (1*7) \\ N(4) - C(28) - C(25) & 109*4 (1*4) & C(30) - C(34) - C(36) & 112*1 (1*7) \\ N(4) - C(28) - C(25) & 109*4 (1*4) & C(30) - C(34) - C(36) & 112*1 (1*7) \\ N(4) - C(28) - C(25) & 109*7 (1*4) & O(7)C(35) - C(37) & 120*5 (1*9) \\ C(26) - C(29) - C(27) & 112*1 (1*5) & C(36) - C(35) & 135*2 (1*6) \\ O(6) - C(32) - N(4) & 120*8 (1*9) & N(4) - C(36) - C(35) & 135*2 (1*6) \\ O(6) - C(32) - C(27) & 117*3 (1*7) & C(33) - C(37) - C(35) & 123*5 (2*1) \\ C(30) - C(33) - C(37) & 118*3 (2*2) \\ \end{array}$	C(1) = C(2) = C(8)	100.8 (1.4)	C(14) - C(19) - C(18)	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1) = C(2) = C(13)	111.8 (1.5)	C(14) - C(20) - C(21)	116.7 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(1) = C(2) = C(22)	114.0 (1.5)	O(3) = O(21) = O(4)	122.5 (1.8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(8) = C(2) = C(15)	115.3 (1.5)	O(3) = C(21) - C(20)	119.7 (1.7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(8) = C(2) = C(22)	111.1(1.4)	O(4) - C(21) - C(20)	117.4 (1.6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(15) - C(2) - C(22)	104-2 (1-5)	C(2) = C(22) = C(16)	102.9 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(4) - C(3) - C(8)	117-5 (1-6)	C(24) - C(23) - C(25)	114.4 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3) - C(4) - C(5)	117.1(1.5)	N(3) - C(24) - C(23)	110.9 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(3) - C(4) - C(25)	121.0 (1.5)	C(4) - C(25) - C(23)	113.3 (1.5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(5) - C(4) - C(25)	121.8 (1.5)	C(4) - C(25) - C(28)	108.6 (1.4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(1) - C(5) - C(4)	117.3 (1.5)	C(4) - C(25) - C(34)	112.3 (1.4)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	C(4) - C(5) - C(6)	120.2 (1.5)	C(23) - C(25) - C(28)	109.9 (1.5)
$\begin{array}{cccccc} O(2)C(6)C(5) & 121\cdot5 (1\cdot6) & C(28)-C(25)-C(34) & 100\cdot9 (1\cdot4) \\ O(2)C(6)C(7) & 119\cdot8 (1\cdot6) & N(3)C(26)-C(28) & 121\cdot3 (1\cdot5) \\ C(5)C(6)C(7) & 118\cdot7 (1\cdot6) & N(3)C(26)-C(29) & 122\cdot6 (1\cdot5) \\ N(1)C(7)C(6) & 128\cdot2 (1\cdot6) & C(28)C(26)-C(29) & 115\cdot5 (1\cdot4) \\ N(1)C(7)C(8) & 113\cdot9 (1\cdot6) & C(29)C(27)-C(32) & 115\cdot5 (1\cdot6) \\ C(6)C(7)C(8) & 118\cdot0 (1\cdot6) & O(5)C(28)-N(4) & 108\cdot8 (1\cdot4) \\ O(5)C(28)-C(25) & 119\cdot4 (1\cdot4) & C(25)-C(34)-C(30) & 123\cdot2 (1\cdot6) \\ O(5)C(28)-C(25) & 104\cdot9 (1\cdot4) & C(25)-C(34)-C(36) & 114\cdot1 (1\cdot5) \\ N(4)C(28)-C(26) & 105\cdot7 (1\cdot4) & O(7)C(35)-C(36) & 119\cdot1 (1\cdot7) \\ C(25)-C(28)-C(26) & 115\cdot5 (1\cdot4) & O(7)C(35)-C(37) & 120\cdot5 (1\cdot9) \\ C(26)-C(29)-C(27) & 112\cdot1 (1\cdot5) & C(36)-C(35)-C(37) & 120\cdot3 (1\cdot8) \\ C(33)-C(30)-C(34) & 118\cdot2 (1\cdot9) & N(4)C(36)-C(35) & 135\cdot2 (1\cdot6) \\ O(6)C(32)-N(4) & 120\cdot8 (1\cdot9) & N(4)C(36)-C(35) & 117\cdot5 (1\cdot6) \\ O(6)C(32)-C(27) & 112\cdot1 (1\cdot7) & C(33)-C(37)-C(35) & 123\cdot5 (2\cdot1) \\ C(30)-C(33)-C(37) & 118\cdot3 (2\cdot2) \end{array}$	O(1) - C(5) - C(4)	122.4 (1.6)	C(23)-C(25)-C(34)	111.0 (1.5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(2) - C(6) - C(5)	121.5 (1.6)	C(28) - C(25) - C(34)	100.9 (1.4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(2) - C(6) - C(7)	119.8 (1.6)	N(3) - C(26) - C(28)	121-3 (1-5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(5) - C(6) - C(7)	118.7 (1.6)	N(3) - C(26) - C(29)	122.6 (1.5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(1)-C(7)-C(6)	128.2 (1.6)	C(28) - C(26) - C(29)	115.5 (1.4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	N(1) - C(7) - C(8)	113.9 (1.6)	C(29)-C(27)-C(32)	115.5 (1.6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(6) - C(7) - C(8)	118.0 (1.6)	O(5) - C(28) - N(4)	108.8 (1.4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(5) - C(28) - C(25)	119.4 (1.4)	C(25)-C(34)-C(30)	123.2 (1.6)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	O(5) - C(28) - C(26)	101.7 (1.3)	C(25)-C(34)-C(36)	114.1 (1.5)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	N(4) - C(28) - C(25)	104.9 (1.4)	C(30)-C(34)-C(36)	122.1 (1.7)
$\begin{array}{ccccccc} C(25)-C(28)-C(26) & 115 \cdot 5 & (1 \cdot 4) & O(7)C(35)-C(37) & 120 \cdot 5 & (1 \cdot 9) \\ C(26)-C(29)-C(27) & 112 \cdot 1 & (1 \cdot 5) & C(36)-C(35)-C(37) & 120 \cdot 3 & (1 \cdot 8) \\ C(33)-C(30)-C(34) & 118 \cdot 2 & (1 \cdot 9) & N(4)C(36)-C(34) & 107 \cdot 4 & (1 \cdot 4) \\ O(6)C(32)-N(4) & 120 \cdot 8 & (1 \cdot 9) & N(4)C(36)-C(35) & 135 \cdot 2 & (1 \cdot 6) \\ O(6)C(32)-C(27) & 121 \cdot 8 & (1 \cdot 9) & C(34)-C(36)-C(35) & 117 \cdot 5 & (1 \cdot 6) \\ N(4)C(32)-C(27) & 117 \cdot 3 & (1 \cdot 7) & C(33)-C(37)-C(35) & 123 \cdot 5 & (2 \cdot 1) \\ C(30)-C(33)-C(37) & 118 \cdot 3 & (2 \cdot 2) \end{array}$	N(4) - C(28) - C(26)	105.7 (1.4)	O(7)C(35)-C(36)	119.1 (1.7)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(25)-C(28)-C(26)	115.5 (1.4)	O(7) - C(35) - C(37)	120.5 (1.9)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(26) - C(29) - C(27)	112.1 (1.5)	C(36) - C(35) - C(37)	120.3 (1.8)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	C(33) - C(30) - C(34)	118.2 (1.9)	N(4) - C(36) - C(34)	107.4 (1.4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O(6) - C(32) - N(4)	120.8 (1.9)	N(4) - C(36) - C(35)	135.2 (1.6)
$\begin{array}{cccc} N(4)C(32) -C(27) & 117 \cdot 3 & (1 \cdot 7) \\ C(30) -C(33) -C(37) & 118 \cdot 3 & (2 \cdot 2) \end{array} \qquad C(33) -C(37) -C(35) & 123 \cdot 5 & (2 \cdot 1) \\ \end{array}$	O(6) - C(32) - C(27)	121.8 (1.9)	C(34) - C(36) - C(35)	117.5 (1.6)
C(30) - C(33) - C(37) 118.3 (2.2)	N(4) - C(32) - C(27)	117.3 (1.7)	C(33) - C(37) - C(35)	123·5 (2·1)
	C(30) - C(33) - C(37)	118.3 (2.2)		. ,

Table 6. Conformation data

(a) Equations of the best least-squares planes

The equations of these planes are in the form Ax + By + Cz = D and are referred to the crystallographic axes with x, y, z in Å. Planes 1-3 are in part A of the molecule, 4 and 5 in part B and 6-9 are those used to calculate the conformation of the atoms about the C(4)-C(25) bond.

- 1 Atoms of the benzene ring (A part)
- 2 Atoms of the carboxyl group and C(20)
- 3 Atoms N(2), C(2), C(14), C(16), C(15), C(17)
- 4 Atoms of the benzene ring (B part)
- 5 Atoms of the benzene ring (B part), O(7) and N(4)

		Table 6 (a	cont.)	
	6 C(3), C(4 7 C(4), C(4 8 C(4), C(4 9 C(4), C(4))	4), C(5) 25), C(23) 25), C(28) 25), C(34)		
Plane	A	В	С	D
1	0.05834	0.74034	0.64524	6.49951
2	-0.49093	0.77544	-0.29305	0.07274
3	0.97185	-0.01598	-0.42118	0.95860
4	0.33300	0.52156	-0.78542	0.40942
5	0.33473	0.52201	-0.83494	0.43100
6	0.12933	0.77405	0.58236	6.72694
7	0.10227	0.80471	0.55337	6.47363
8	0.42136	-0.04447	0.80552	7.34597
9	-0.28686	0.93420	-0.15170	0.19845

(b) Distances of atoms from the planes

For each plane, column (i) lists the distances in Å from the plane of atoms forming the plane and column (ii) lists the distances in Å above or below (-) the plane for atoms not forming the plane. With reference to Fig.1, the positive side of each plane (above) is that side which is furthest from the coordinate origin (*i.e.* closest to the viewer).

(i)	(ii)	(i)	(ii)
Plane 1		Plane 4	
$\begin{array}{rrrr} C(3) & -0.006 \\ C(4) & -0.043 \\ C(5) & 0.053 \\ C(6) & -0.013 \\ C(7) & -0.039 \\ C(8) & 0.049 \end{array}$	$\begin{array}{rrrr} O(1) & 0.257 \\ O(2) & -0.056 \\ N(1) & -0.150 \\ C(2) & 0.339 \\ C(25) & -0.177 \end{array}$	$\begin{array}{ccc} C(30) & 0.002 \\ C(33) & 0.005 \\ C(34) & -0.007 \\ C(35) & -0.001 \\ C(36) & 0.007 \\ C(37) & -0.005 \end{array}$	$\begin{array}{ccc} O(6) & 0.148 \\ O(7) & -0.006 \\ N(4) & 0.005 \\ C(25) & 0.174 \\ C(28) & 0.024 \\ C(32) & 0.086 \end{array}$
Plane 2 O(3) -0.012 O(4) -0.011 C(20) -0.010 C(21) 0.033		Plane 5 O(7) -0.003 N(4) 0.003 C(30) 0.000 C(33) 0.006 C(34) -0.010	O(6) 0·149 C(25) 0·169 C(28) - 0·029 C(32) 0·084
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{ccc} C(18) & 0.143 \\ C(22) & -0.298 \end{array}$	$\begin{array}{c} C(35) & 0.000 \\ C(36) & 0.006 \\ C(37) & -0.002 \end{array}$	

(c) Dihedral angles between planes

Planes	Angle
1, 4	97.0°
3, 2	65.6
3, 1	82.3

(d) Conformation of atoms about the C(4)-C(25) bond



•

between all the aliphatic rings in the structure are *cis*. The dihedral angle between the planes of the benzene rings of parts A and B is 97°. There is a short distance of 2.52 Å between the phenolic O(7) atom and the carbonyl O(6) atom of the cyclic amide which is presump-

tive evidence of an intramolecular hydrogen bond. A second intramolecular hydrogen bond is indicated by the distance 2.64 Å between the tertiary alcoholic O(5) atom in part B and the methoxyl O(1) atom in part A.

Table 7. Intermolecular distances less than 4 Å

Space group: C2

General equivalent positions: (A) x, y, z; (B) -x, y, -z; (D) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (E) $\frac{1}{2} + x, \frac{1}{2} + y, z$

In this Table, the numerical subscripts of the symmetry type designator indicate the relationship of the atom not in the unit cell to the indicated atom of the reference molecule in the unit cell and refer, respectively, to the x, y and z coordinates.

The reference molecule is designated $(A)_{555}$ and its atoms are listed first in each pair. To derive the coordinates of an atom designated $(D)_{546}$, the symmetry operation (D) is first applied to the coordinates of the corresponding reference atom listed in Table 1. The resulting x, y, z are then added to the whole number difference between the subscript of the transformed atom and the reference atom; in this case (5-5)+x, (4-5)+y, (6-5)+z or x, -1+y, 1+z. 't' denotes distance less than the sum of the van der Waals radii of the two atoms.

	Distance		Distance		Distance
Br(2) - O(4)(D)	3·15, v Å	$O(5)-C(30) (A)_{545}$	3·67 Å	$C(7) - C(16) (A)_{545}$	3·91 Å
$Br(1) - N(2) (A)_{545}$	3.72	$O(6)-N(2)(E)_{545}$	3.55	$C(9) - C(11) (D)_{546}$	3.80
$-C(16)(A)_{545}$	3.74	$-C(2)(E)_{545}$	3.26	$-C(22)(A)_{545}$	3.83
$-C(17)(A)_{545}$	3.72	$-C(3)(E)_{545}$	3.59	$-C(30)(A)_{545}$	3.83
$-C(23)(A)_{545}$	3.77	$-C(12)(E)_{545}$	3.37	$C(10)-C(11) (D)_{556}$	3.64
$-C(31)(D)_{535}$	3.79	$-C(13)(E)_{545}$	3.69	$-C(22) (D)_{546}$	3.96
Br(2) - O(3)(D)	3.92	$-C(14)(E)_{545}$	3.44	$C(11)-C(33) (D)_{546}$	3.81
-C(13)(E)	3.78	$-C(16)(E)_{545}$	3.80	$C(12)-C(16)(A)_{545}$	3.49
$-C(17)(E)_{545}$	3.69	$-C(22)(E)_{545}$	3.59	$C(13)-C(16)(A)_{545}$	3.96
-C(21)(D)	3.96	O(7)-C(11)(E)	3.71	$-C(17)(A)_{545}$	3.67
$O(2) - C(9) (D)_{556}$	3.72	-C(12)(E)	3.78	$-C(27)(E)_{455}$	3.94
O(3) - C(29)(D)	3.27	$-C(16)(E)_{545}$	3.62	$C(17)-C(21)(A)_{565}$	3.98
-C(31)(D)	3.59	$-C(22)(E)_{545}$	3.47	C(19)-C(19)(B)	3.81
$O(4) - C(17) (A)_{545}$	3.16	$N(1)-C(16)(A)_{545}$	3.56	$C(37)-C(37)(B)_{656}$	3.93
$-C(18)(A)_{545}$	3.59				



Fig. 3. Molecular packing in haplophytine dihydrobromide.

While parts A and B consist mainly of rigid fusedring systems, different conformers of comparable energy are possible by rotation about the linking bond C(4)-C(25). The conformation about this bond observed in the crystal structure is shown in the Newman diagram in Table 6. This is most likely determined by the intramolecular hydrogen bond $O(1) \cdots H - O(5)$, the interactions $Br(1) \cdots O(5)$, 3.17 Å, and $Br(2) \cdots O(4)$, 3.15 Å, both of which may be hydrogen bonds, and the close approach $Br(2) \cdots C(26)$, 3.39 Å. These Br–O distances and the intramolecular hydrogen bonds are shown in Fig. 3 which is a diagram of the molecular packing in the unit cell. There are no other bromine distances shorter than 3.55 Å, but each bromide ion is within 4.75 Å of 29 C, N and O atoms from three different molecular cations. The intermolecular distances less than 4 Å are listed in Table 7.

It is notable that the bromide ions occupy positions which indicate participation in hydrogen bonding in preference to positions which would imply pure ionic interactions with the formally positively-charged quaternary N(2) and N(3) atoms; the shortest Br–N distance is 3.55 Å. The short Br(2)–C(26) distance may be indicative of some localization of positive charge on the carbon atom adjacent to the quaternary nitrogen atom rather than at the nitrogen atom itself.

I thank Professor G. A. Jeffrey for constructive criticism in the preparation of this report and Professor B. M. Craven for technical advice and assistance during the course of the work described.

References

- CAVA, M. P., TALAPATRA, S. K., NOMURA, K., WEISBACH, J. A., DOUGLAS, B. & SHOOP, E. C. (1963). *Chem. & Ind.* p. 1242.
- CAVA, M. P., TALAPATRA, S. K., YATES, P., ROSENBERGER, M., SZABO, A. G., DOUGLAS, B., RAFFAUF, R. F., SHOOP, E. C. & WEISBACH, J. A. (1963). *Chem. & Ind.* p. 1875.
- CRAVEN, B. M. & ZACHARIAS, D. E. (1968). *Experientia*, 24, 770.
- GILBERT, B. (1965). In *The Alkaloids*, Vol. 8, Ch. 14. Edited by R. H. F. MANSKE. New York: Academic Press.
- GILBERT, B. (1968). In *The Alkaloids*. Vol. 11, Ch. 9. Edited by R. H. F. MANSKE. New York: Academic Press.
- International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
- RAE, I. D., ROSENBERGER, M., SZABO, A. G., WILLIS, C. R., YATES, P., ZACHARIAS, D. E., JEFFREY, G. A., DOUGLAS, B., KIRKPATRICK, J. L. & WEISBACH, J. A. (1967). J. Amer. Chem. Soc. 89, 3061.
- ROGERS, E. F., SNYDER, H. R. & FISCHER, R. F. (1952). J. Amer. Chem. Soc. 74, 1987.
- SAXTON, J. E. (1965). In *The Alkaloids*, Vol. 8, Ch. 18. Edited by R. H. F. MANSKE. New York: Academic Press.
- SCHNOES, H. K., BURLINGAME, A. L. & BIEMANN, K. (1962). Tetrahedron Letters, p. 993.
- SNYDER, H. R., FISCHER, R. F., WALKER, J. F., ELS, H. E. & NUSSBERGER, G. A. (1954a). J. Amer. Chem. Soc. 76 2819.
- SNYDER, H. R., FISCHER, R. F., WALKER, J. F., ELS, H. E. & NUSSBERGER, G. A. (1954b). J. Amer. Chem. Soc. 76, 4601.
- SNYDER, H. R., STROMAYER, H. F. & MOONEY, R. A. (1958). J. Amer. Chem. Soc. 80, 3708.
- TAYLOR, W. I. (1965). In *The Alkaloids*, Vol. 8, Ch. 11. Edited by R. H. F. MANSKE. New York: Academic Press.

Acta Cryst. (1970). B26, 1464

Structures of Ferrimagnetic Fluorides of *AB*F₃ Type. I. RbNiF₃

BY J. E. WEIDENBORNER AND A. L. BEDNOWITZ

IBM Watson Research Center, Yorktown Heights, New York U.S.A.

(Recieved 6 October 1969)

The crystal structure of RbNiF₃ has been determined from a least-squares refinement of three-dimensional X-ray data. Intensity data were acquired with the CCXD, a computer controlled X-ray diffractometer, operating in a time shared environment on an IBM 1800 Controller System. The space group is $P6_3/mmc$. The lattice constants of the unit cell, which contains six formula units of RbNiF₃, are a = $5\cdot840 \pm 0\cdot002$ and $c = 14\cdot308 \pm 0\cdot004$ Å. All of the ions in this structure occupy special positions. The nickel ions occupy two non-equivalent sites, each the center of a fluorine octahedron. Two-thirds of the NiF₆ octahedra occur in face-sharing pairs to form Ni₂F₉ polyhedra. The remaining NiF₆ octahedra are linked to the Ni₂F₉ polyhedra by sharing of corners. The average Ni-F distance is $2\cdot028 \pm 0\cdot008$ Å.

Introduction

A great deal of attention has been directed to studies of the interesting magnetic and optical properties of ABF_3 -type ferrimagnetic fluorides with the hexagonal BaTiO₃ structure. RbNiF₃, an unusually transparent material, has been one of the most extensively studied compounds of this group, at these Laboratories and elsewhere. Rudorff, Kandler & Babel (1962) first synthesized the compound, reported it as a probable ferri-