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X-ray 63 Program System for X-ray Crystallography (1965). The Univ. of Maryland.

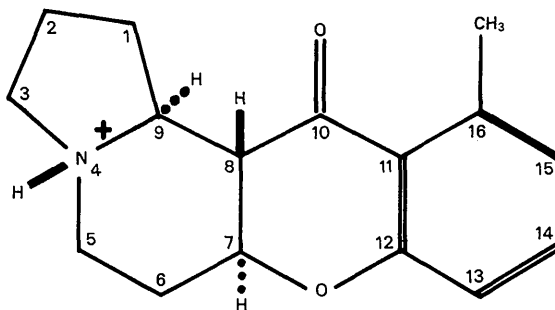# The Crystal Structure of (±)-Elaeocarpine Hydrobromide

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The structure of elaeocarpine ($C_{16}H_{19}NO_2$), the first member of a new class of indolizidine alkaloids, has been determined as its hydrobromide salt. The crystals are triclinic with $a=12\cdot46$, $b=7\cdot38$, $c=8\cdot05$ Å; $\alpha=96\cdot1$, $\beta=92\cdot8$, $\gamma=94\cdot0°$. Since the space group, determined by the $N(z)$ *versus z* test, is $P\bar{1}$ the base is a racemate. The bromine, carbon, nitrogen and oxygen and fifteen hydrogen atom sites were determined from the Patterson, electron density and difference maps respectively and refinement was carried out by full-matrix least-squares methods to a final R value of 0·131.

The structure and relative stereochemistry are shown below:

The two *trans* ring junctions result in a roughly flat molecule. Steric interaction between the carbonyl and methyl groups results in an out-of-plane distortion of the carbonyl group as well as an in-plane angular distortion of the bond between the methyl group and the aromatic ring.

Introduction

Several *Elaeocarpus* species, large trees of the rain forests of New Guinea, have been found to contain as many as five different alkaloids (Johns, Lamberton & Sioumis, 1968*a*). Preliminary chemical studies indicated that these alkaloids were closely related structurally and represented the first members of a new class of indolizidine alkaloids. It was therefore decided to determine the structure of one base by X-ray crystallography in the hope that the structures of the other bases could be established from their relationship to the known alkaloid, with the use of standard chemical and spectroscopic, especially nuclear magnetic resonance, techniques. The base chosen for the crystal structure analysis, named elaeocarpine, was extracted from

the species *E.polydactylus* Schl. and was readily separated as its hydrobromide salt* from the co-occurring isomer, isoelaeocarpine.

A preliminary account of the X-ray crystallographic, chemical and spectroscopic studies has been published elsewhere (Johns, Lamberton, Sioumis & Wunderlich, 1968).

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* In view of the continued use of methohalide salts in the structure analysis of alkaloids by the heavy atom method it may not be out of place here to emphasize the disadvantages of this practice while stressing the advantages of the use of hydrohalide salts whenever it is chemically feasible to do so. Firstly, since the free base cannot be regenerated from the methohalide salt, doubts may arise concerning their structural inter-relationship. In certain rare cases, for example, retusamine (Wunderlich, 1967a,b) such problems may also occur when hydrohalide salts are used. Secondly, if a bromide salt is desired to preserve an advantageous ratio of Σf^2 (heavy)/ Σf^2 (light) the metho salt generally has to be made through the iodide followed by ion exchange to the bromide. The hydrobromide is, of course, prepared by simple addition of HBr. Lastly, in hydrohalide salts, the high probability of N–H$\cdots$Br hydrogen bond formation can be of direct assistance in locating the light atoms and identifying the basic nitrogen atom in particular. No such criterion is possible in the case of quaternary alkyl salts.
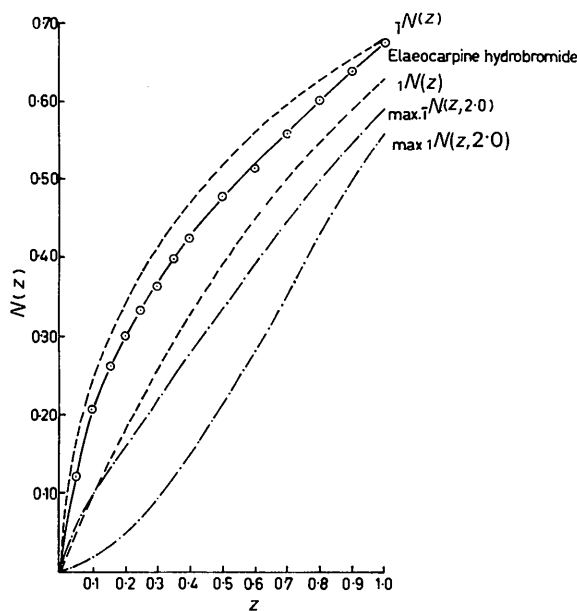
Experimental

Elaeocarpine hydrobromide crystallizes in the triclinic system as colourless flat prisms. A few needle-shaped crystals were found in which the elongation was along the c axis. The unit-cell parameters were measured at room temperature from the Weissenberg patterns of crystals mounted about the b,c and $(b-c)$ axes. The powder pattern of silicon ($a=5\cdot4305$ Å at 25 °C) was used to calibrate all the films. The density of the crystals was determined by flotation in a mixture of CCl_4 and $CHCl_3$, the density of which was measured using a relative density bottle.

Crystal data

Elaeocarpine hydrobromide, $C_{16}H_{19}NO_2$. HBr, M.W. 338·26.

Triclinic, $a=12\cdot46\pm0\cdot02$, $b=7\cdot38\pm0\cdot02$, $c=8\cdot05\pm 0\cdot02$ Å, $\alpha=96\cdot1\pm0\cdot4°$, $\beta=92\cdot8\pm0\cdot6°$, $\gamma=94\cdot0\pm0\cdot2°$, $V=735\pm6$ Å^3, $D_m=1\cdot54$, $Z=2$, $D_x=1\cdot53\pm0\cdot01$, $F(000)=348$, $\mu=42$ cm^{-1} for Cu $K\alpha$ radiation. $\Sigma f^2(Br)/\Sigma f^2(C,H,N,O)=1\cdot62$ at $\sin\theta/\lambda=0$.

The experimental plot of $N(z)$ *versus* z (Howells, Phillips & Rogers, 1950) is shown in Fig. 1 along with the theoretical curves for centric and acentric structures containing, on the one hand atoms all of one kind, and on the other, one 'heavy' atom and a number of light atoms in a triclinic cell (Sim, 1958). For the latter case, $r=f(Br)/[\Sigma f^2(C.N.O)]^{1/2}=2\cdot0$ at $\sin\theta/\lambda= 0\cdot35$. These curves clearly show the crystals to be centrosymmetric and, therefore, the space group is $P\bar{1}$ and the material racemic. Confirmation of this assignment was obtained after this work was completed by the identification of the alkaloid (+)-elaeocarpiline as (+)-15,16-dihydroelaeocarpine (Johns, Lamberton & Sioumis, 1968b). This base was converted by catalytic dehydrogenation to (+)-elaeocarpine, $[\alpha]_D=+206°$ (CHCl$_3$) which was identical in its infrared nuclear magnetic resonance and mass spectra with the material used for the X-ray analysis. Despite repeated recrystallizations, solutions of natural elaeocarpine possessed very small optical activity ($[\alpha]_D=0\cdot1°$ in CHCl$_3$) which must, therefore, be a result of the slight excess of one enantiomorph over the other or the result of other impurities. The virtually complete racemization could have occurred during the extraction and isolation proce-

Fig. 1. Plots of $N(z)$ *versus* z for elaeocarpine hydrobromide, compared with theory for centric and acentric distributions with atoms of one kind only (– – –) and for one Br and nineteen C, N and O atoms in a triclinic cell (–·–·–).

Table 1. *Analysis of* $R=\Sigma\,||F_o|-|F_c||/\,\Sigma\,|F_o|$

	R	Range of $\sin\theta$	R	Number of reflexions
All planes	0·131	0·00–0·40	0·157	213
All 0kl	0·130	0·40–0·50	0·109	198
All h0l	0·141	0·50–0·60	0·110	296
All hk0	0·119	0·60–0·70	0·118	356
		0·70–0·80	0·146	185
		0·80–0·85	0·152	229
		0·85–0·90	0·163	226
		0·90–0·95	0·185	242
		0·95–1·00	0·216	248

Table 2. *List of observed and calculated structure factors*

Unobserved reflexions are starred.

Table 2 (cont.)

H	K	10|F_o|	10F_c

The table consists of multiple repeated column groups each headed **H K 10|F_o| 10F_c**, listing crystallographic structure-factor data arranged in successive blocks labelled L = 4, L = 5, L = 6, L = 7.

dures, but it is more probable that elaeocarpine already existed in the plant cells as a racemate.

The intensity data were collected by the equi-inclination multiple film Weissenberg method. From 6 c axis levels and 4 (011) zone axis levels, a total of 2429 reflexions were measured, 410 (17·3%) of which were too weak to be observed. The intensities were corrected for Lorentz and polarization factors and for splitting of the $\alpha_1\alpha_2$ doublet (Rae & Barker, 1961).

Since the small cross-sections of the crystals (0·07 × 0·03 mm² and 0·12 × 0·08 mm² for the c axis and diagonal axis settings respectively) would have resulted in an average absorption correction factor of about 0·05, these were not applied.

Approximate correlation factors between sets of photographs were determined and used to place the data on the absolute scale. The overall temperature factor derived from a least-squares fit of Wilson's plot (Wilson, 1942) was 3·67 Å² which compares satisfactorily with the final individual atomic temperature factors given in Table 2.

Structure determination

The position of the bromide ion was readily determined from the three-dimensional sharpened Patterson map, by the use of structure amplitudes modified by the expression $(1/f^2)\cosh(2a\sin\theta/\lambda)$ $\exp[-(4\pi^2/p)\sin^2\theta/\lambda^2]$ (Wunderlich, 1965) in which the constants a and p were set equal to 4·0 Å and 3·3 Å⁻² in this case.

An unweighted electron density map based only on the bromide ion parameters revealed the location of all 19 non-hydrogen atom sites. Stereochemical interpretation of the resultant ball and rod model allowed the identification of the C, N and O atoms, leading directly to the molecular structure of the alkaloid. At this stage, the discrepancy index $R = \Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ was 0·236 for observed reflexions only.

Refinement of the structure was carried out by the least-squares method with the use of the full-matrix computer program of Busing, Martin & Levy (1962) the weighting scheme of Hughes (1941) being used throughout. It was evident from an electron density difference map that the thermal vibrations of the bromide ion were markedly anisotropic, whereas it was not considered meaningful to treat the lighter atoms similarly. Consequently, the least-squares program was modified so that refinement of both isotropic and anisotropic temperature parameters could be carried out simultaneously. Minimization of $\Sigma w(F_o^2-F_c^2)^2$ led to a discrepancy index value of 0·165 after several cycles. Different values of the weighting scheme constants F_o(optimum) and its standard deviation) were then tried but no further improvement in the structure factor agreement could be made. It was then decided to minimize $\Sigma w(|F_o|-|F_c|)^2$ with F_o(opt) and $\sigma_{F_o\text{(opt)}}$ equal to 14·0 and 1·0 respectively. This change had its principal effects on the temperature factors and on the 14 scale factors, the positional parameters remaining constant to within 0·02 Å. The overall R value reduced to 0·142 in three cycles. A difference map calculated at this stage revealed the possible sites of 15 of the 20 hydrogen atoms and their coordinates are given in Table 3(b). Their inclusion in the structure factor seg-

Table 3(a). *Atomic positional and temperature parameters*

Numbers in brackets are the standard deviations × 10⁴ for x, y and z parameters of C, N and O atoms, × 10⁵ for those of Br and 10² for the B parameters.

	x	y	z	B
C(1)	0·3695 (9)	0·7585 (16)	0·4422 (18)	3·80 (22) Å²
C(2)	0·4831 (11)	0·7443 (19)	0·3859 (20)	4·67 (27)
C(3)	0·4747 (9)	0·6800 (15)	0·1949 (16)	3·35 (20)
N(4)	0·3644 (7)	0·7280 (12)	0·1466 (13)	2·81 (16)
C(5)	0·3189 (9)	0·6419 (15)	−0·0228 (17)	3·38 (20)
C(6)	0·2063 (9)	0·7057 (15)	−0·0513 (17)	3·51 (21)
C(7)	0·1349 (8)	0·6771 (13)	0·0941 (15)	2·89 (19)
C(8)	0·1873 (8)	0·7598 (13)	0·2617 (15)	2·81 (18)
C(9)	0·2958 (8)	0·6850 (13)	0·2878 (15)	2·69 (18)
C(10)	0·1103 (8)	0·7278 (13)	0·3938 (16)	2·76 (18)
C(11)	−0·0041 (7)	0·7534 (12)	0·3532 (14)	2·29 (16)
C(12)	−0·0331 (8)	0·7700 (12)	0·1891 (15)	2·59 (17)
C(13)	−0·1390 (9)	0·8029 (15)	0·1366 (17)	3·54 (21)
C(14)	−0·2138 (9)	0·8188 (15)	0·2607 (17)	3·54 (21)
C(15)	−0·1876 (8)	0·7983 (14)	0·4256 (16)	3·20 (20)
C(16)	−0·0813 (7)	0·7657 (12)	0·4763 (15)	2·55 (17)
C(17)	−0·0594 (10)	0·7529 (16)	0·6590 (18)	3·93 (23)
O(18)	0·0366 (6)	0·7577 (10)	0·0606 (11)	3·36 (15)
O(19)	0·1440 (7)	0·6843 (12)	0·5317 (13)	4·35 (18)
Br	0·37932 (10)	1·17156 (15)	0·17289 (17)	

Br	$\beta_{11} =$	0·00667	$U_{11} =$	0·0522 ± 0·0008 Å²
	$\beta_{22} =$	0·01317	$U_{22} =$	0·0356 ± 0·0007
	$\beta_{33} =$	0·01597	$U_{33} =$	0·0516 ± 0·0031
	$\beta_{12} =$	−0·00036	$U_{12} =$	−0·0016 ± 0·0004
	$\beta_{13} =$	0·00033	$U_{13} =$	0·0017 ± 0·0007
	$\beta_{23} =$	0·00107	$U_{23} =$	0·0032 ± 0·0006

Table 3(b). *Coordinates of those hydrogen atoms which were located from the difference map*

	x	y	z
H(1)–C(1)	0·37	0·89	0·44
H(2)–C(1)	0·38	0·67	0·53
H(1)–C(2)	0·50	0·85	0·33
H(2)–C(2)	0·55	0·67	0·47
H(1)–C(3)	0·47	0·53	0·20
H(2)–C(3)	0·48	0·75	0·10
H––N(4)	0·40	0·86	0·16
H––C(5)	0·32	0·53	0·05
H(1)–C(6)	0·21	0·83	−0·06
H(2)–C(6)	0·15	0·66	−0·19
H––C(7)	0·13	0·54	0·11
H––C(8)	0·19	0·88	0·23
H––C(9)	0·28	0·56	0·27
H––C(15)	−0·24	0·72	0·52
H––C(17)	0·03	0·58	0·65

ment only of two further least-squares calculations reduced the R value to 0·131. A final difference map contained most features of the previous map and failed to indicate any new hydrogen atom positions. An analysis of the discrepancy index for different classes of reflexions and as a function of $\sin\theta$ is given in Table 1 and a complete listing of observed and calculated structure factors in Table 2.

The final atomic positional and temperature parameters of non-hydrogen atoms are given along with their standard deviations in Table 3(a). The temperature parameters of Br⁻ are given in terms of both the usual β_{ij} parameters in the expression $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$ and in terms of the vibration tensor elements of the type $U_{12}=\beta_{12}/2\pi^2a^*b^*$ along with the standard deviations as obtained for the latter. The exceptionally large value of σ_{U33} is also reflected in the elements $a_{ij}/a_{ii}\times a_{jj}$ of the correlation matrix relating β_{33} to the fourteen scale factors, especially the eleven corresponding to the hkL data. This effect is no doubt a result of the incompleteness of the data in the c^* direction.

The atomic scattering factor curves used for C and O were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal(1955). Values for N^+ were obtained by extrapolation, with the use of data given by Freeman (1959) and *International Tables for X-ray Crystallography* (1962). Data for Br⁻ were corrected for anomalous scattering.

Discussion of the structure

Molecular packing

The cation molecules are roughly planar and are aligned almost parallel to the (130) plane. The pairs of molecules related by the centers of symmetry at $(0,0,0)$ and $(0,\frac{1}{2},\frac{1}{2})$ have their mean planes spaced by 3·5 and 3·7 Å respectively. In the former pair, the quaternary nitrogen atom of one molecule is hydrogen
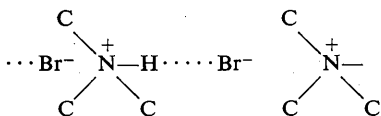
Table 4. *Interatomic distances*

C_{te}–C_{te}*
(Characteristic value = 1·537 ± 0·005 Å)†

C(1)–C(2)	1·51 Å
C(1)–C(9)	1·54
C(2)–C(3)	1·56
C(5)–C(6)	1·53
C(6)–C(7)	1·53
C(7)–C(8)	1·52
C(8)–C(9)	1·51

C_{te}–C_{arom}*
(Characteristic value = 1·505 ± 0·005 Å)

C(16)–C(17)	1·50

C_{te}–C_{tr}*
(Characteristic value = 1·506 ± 0·005 Å)

C(8)–C10	1·49

C_{tr}–C_{arom}
(Characteristic value = 1·47 ± 0·02 Å)

C(10)–C(11)	1·48

C_{arom}–C_{arom}
(Characteristic value = 1·394 ± 0·005 Å)

C(11)–C(12)	1·37 Å
C(11)–C(16)	1·41
C(12)–C(13)	1·41
C(13)–C(14)	1·40
C(14)–C(15)	1·38
C(15)–C(16)	1·41

C_{te}–O
(Characteristic value = 1·426 ± 0·005 Å)

C(7)–O(18)	1·43 Å

C_{tr}–O
(Characteristic value = 1·215 ± 0·05 Å)

C(10)–O(19)	1·25

C_{arom}–O
(Characteristic value = 1·36 ± 0·01 Å)

C(12)–O(18)	1·38

C_{te}–N⁺
(Characteristic value = 1·52 ± 0·03 Å)

C(3)–N(4)	1·49
C(5)–N(4)	1·51
C(9)–N(4)	1·50
⁺NH···Br⁻	3·25

* te = tetrahedral and tr = trigonal corresponding to sp^3 and sp^2 hydridization respectively and $arom$ = aromatic.

† The characteristic values quoted are those given by Hamilton, Hamor, Robertson & Sim (1962) for C_{te}–N⁺ and by Sutton (1965) for all other cases.

A C 25B – 2*

bonded to a bromide ion lying in the plane of the other molecule as shown in Fig. 2(b). This results in a sheet at right angles to b sinα, held to sheets on either side only by van der Waals forces and what must be weak electrostatic interactions between the bromide ions of one sheet and the nitrogen atoms of the neighbouring sheets, as shown below.

Despite this lamellar structure, no evidence of cleavage planes was found in any of the crystals. The N–H...Br hydrogen bond length of 3·25 Å is similar to those found in the hydrobromides of alkaloids, N-heterocycles and aliphatic amines, which vary from 3·18 Å in chimonanthine dihydrobromide (Grant, Hamor, Robertson & Sim, 1965) to 3·54 Å in the ethanol addition product of 2-aminopteridinehydrobromide (Batterham & Wunderlich, 1968) and average about 3·4 ± 0·1 Å.

Intermolecular contacts which are not more than 0·3 Å longer than the sum of van der Waals radii are shown in Fig. 2.

Molecular dimensions

The bond distances and angles are listed in Tables 4 and 5, the averaged standard deviations being about 0·015 Å and 0·9° respectively.

The equation of the least-squares plane (Schomaker, Waser, Marsh & Bergman, 1959; Norment, 1963) through the molecule is given by $1·048x + 7·294y - 0·274z = 5·437$ and the average deviation of atoms from this mean plane is 0·27 Å. The aromatic ring and its three substituent atoms C(10), C(17) and O(18) are planar within experimental error, about 0·02 Å, as is the plane containing the carbonyl group and C(8) and C(11). Steric hindrance between the methyl group and the carbonyl oxygen atom forces these planes out of co-planarity, resulting in a dihedral angle of 167·3° as shown in Fig. 2(b). Further measure of this steric interaction is given both by the angle of 15·5° between the carbonyl and the methyl–aromatic ring bonds and by the C(11)–C(16)–C(17) angle of 125·5° which is 6 standard deviations greater than the normal value of 120° [see Fig. 2(a)]. Despite these angular distortions, the C(17)–O(19) intramolecular distance of 3·08 Å is still considerably shorter than the sum of van der Waals radii (3·4 Å). These measurements should help to provide a basis for the quantitative understanding of the relationship in this series of compounds (Johns, Lamberton & Sioumis, 1968a) between the decrease in ultraviolet absorption intensity, ε resulting from the loss of conjugation and the extent of out-of-plane distortion of the carbonyl oxygen atom.

The author wishes to acknowledge valuable discussions with Dr B. Dawson (Division of Chemical
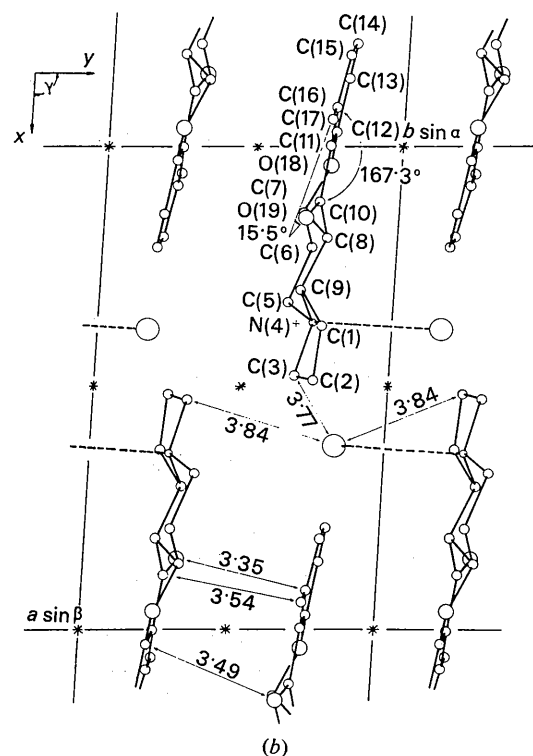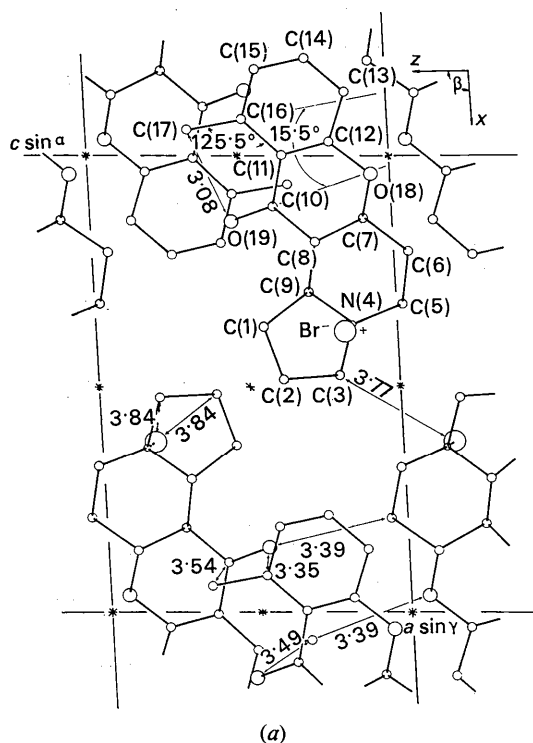

(a)

(b)

Fig. 2. Isometric projections of elaeocarpine hydrobromide viewed (a) down the b axis and (b) down the c axis showing the packing of the molecules and the deformations resulting from steric hindrance between C(17) and O(19).

Table 5. *Bond angles*

C(4)—C(1)—C(9)	105·2		C(10)–C(11)–C(12)	117·0
C(1)—C(2)—C(3)	107·4		C(10)–C(11)–C(16)	122·5
C(2)—C(3)—N(4)	101·6		C(12)–C(11)–C(16)	120·4
C(3)—N(4)—C(5)	115·4		C(11)–C(12)–C(13)	122·2
C(3)—N(4)—C(9)	106·0		C(11)–C(12)–O(18)	124·2
C(5)—N(4)—C(9)	113·0		C(13)–C(12)–O(18)	113·6
N(4)—C(5)—C(6)	108·2		C(12)–C(13)–C(14)	116·7
C(5)—C(6)—C(7)	112·6		C(13)–C(14)–C(15)	122·4
C(6)—C(7)—C(8)	112·6		C(14)–C(15)–C(16)	120·2
C(6)—C(7)—O(18)	107·2		C(11)–C(16)–C(15)	118·1
C(8)—C(7)—O(18)	110·5		C(11)–C(16)–C(17)	125·5
C(7)—C(8)—C(9)	109·6		C(15)–C(16)–C(17)	116·7
C(7)—C(8)—C(10)	108·2			
C(9)—C(8)—C(10)	115·0			
C(1)—C(9)—N(4)	102·1			
C(1)—C(9)—C(8)	120·0			
N(4)—C(9)—C(8)	109·0		Hydrogen bond angles	
C(8)—C(10)—C(11)	116·8		C(3)–N(4)-Br	105·4
C(8)—C(10)—O(19)	120·0		C(5)–N(4)-Br	104·0
C(11)—C(10)—O(19)	123·2		C(9)–N(4)-Br	103·6

Physics, C.S.I.R.O.) and Drs S. R. Johns and J. A. Lamberton of this Division.

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