The SiN_2C_2 ring described here is a structural unit in five other crystal structures [(3)–(7)] (Clegg, Noltemeyer & Sheldrick, 1979; Clegg, Haase, Hesse, Klingebiel & Sheldrick, 1982; Clegg, Graalmann, Haase, Klingebiel, Sheldrick, Werner, Henkel & Krebs, 1983; Clegg, Hesse, Klingebiel & Sheldrick, 1983). In each case (ten crystallographically independent rings in seven crystal structures) the N and C atoms of the ring are virtually coplanar as a consequence of the N=C double bond (Table 5). The deviation of the Si atom from this plane varies from 0·060 (1) to 0·701 (1) Å. Conjugation of the trigonally coordinated N atom adjacent to Si with the N=C bond tends to impose coplanarity on the Si atom [(2), (3) and (7)], and this effect is enhanced when the conjugation is extended, as in (4) and (5), both of which are strongly coloured.
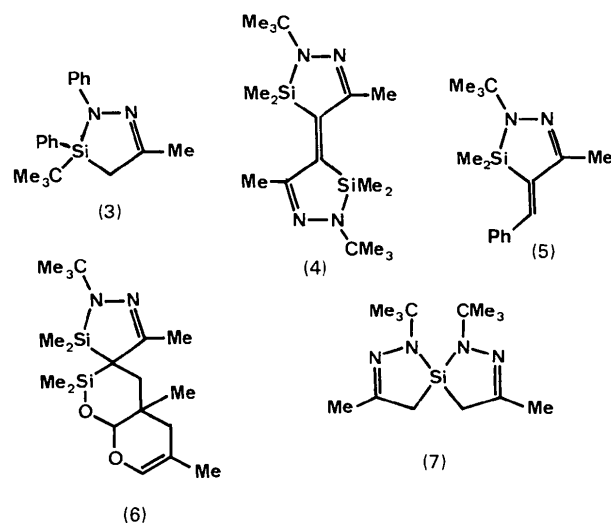
Table 5. *Deviations* (Å) *of atoms from* N_2C_2 *mean planes*

Structure	R.m.s.$\Delta(N_2C_2)$	$\Delta(Si)$
(1) {	0·001 (3)	0·628 (1)
	0·012 (3)	0·519 (1)
(2) {	0·004 (3)	0·060 (1)
	0·001 (3)	0·065 (1)
(3)	0·002 (2)	0·263 (1)
(4) {	0·007 (2)	0·071 (1)
	0·008 (2)	0·071 (1)
(5)	0·006 (2)	0·132 (1)
(6)	0·011 (3)	0·701 (1)
(7)	0·008 (2)	0·172 (1)

Without such extended conjugation, however, steric interaction of substituents on the Si atom and the neighbouring C atom may cause greater deviations from coplanarity [(1) and (6)].

(3)

(4)

(5)

(6)

(7)

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Structure of Crogyroidine Dihydrate, $C_{20}H_{34}Br_2N_2.2H_2O$

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Abstract. $M_r = 498·4$, monoclinic, $P2_1/n$, $a = 10·965$ (3), $b = 12·129$ (3), $c = 8·602$ (3) Å, $\beta = 93·78$ (2)°, $V = 1141·5$ Å^3 at 138 (2) K and $a = 11·090$ (5), $b = 12·146$ (2), $c = 8·659$ (2) Å, $\beta = 93·15$ (3)°, $V = 1164·6$ Å^3 at 293 K, $Z = 2$, $D_x = 1·421$, $D_m = 1·425$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1·89$ mm^{-1}, $F(000) = 516$. Final $R = 0·046$ for 1705 observed reflections ($T = 138$ K). The

crogyroidine molecule possesses a center of symmetry. The overall conformation of the pyrrolizidine nucleus is folded and twisted about the bridging bond. Both the rings are in the *exo*-puckered form and exist in an envelope conformation.

Introduction. The pyrrolizidine alkaloids (PA's) represent a group of compounds present in a variety of plants throughout the world. In general, these alkaloids are classified into three categories: (i) macrocyclic diesters, *e.g.* monocrotaline, (ii) non-cyclic mono- or diesters, *e.g.* heliotrine, lasiocarpine and (iii) non-ester, *e.g.* 1-methylenepyrrolizidine. The PA's are well documented for their mutagenic, antineoplastic, carcinogenic, hepatotoxic and many interesting pharmacological activities. The toxicity of these alkaloids has been attributed to the presence of the following features:

(*a*) The presence of a double bond at C_1–C_2 in the pyrrolizidine ring system.

(*b*) The presence of an allylic ester linkage.

(*c*) The branching of the acid moiety.

We have isolated an alkaloid, 1-methylenepyrrolizidine from *Crotalaria anagyroides* and transformed this base into 4,4'-tetramethylenebis(1,1'-dimethylenepyrrolizidine) dibromide, now called crogyroidine, by treating 1-methylenepyrrolizidine with 1,4-dibromobutane. Crogyroidine has been found to exhibit a significant neuromuscular-blocking activity which both resembles and differs from the activity of curare and depolarizing types of neuromuscular-blocking agents (Suri, Sawhney, Gupta & Atal, 1976).
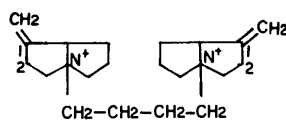
A thorough comparison of the three-dimensional structure of different biologically active PA's is needed to elucidate the structure–function relationship. Of special interest would be a study of those biologically potent PA's which lack structural features believed to be responsible for their toxicity. In this communication we present the structural details of crogyroidine.

Experimental. Crogyroidine was prepared by adding dibromobutane (1·1 mmol) to a solution of 1-methylenepyrrolizidine (2mmol) in methanol. The solution was stirred at room temperature for 40 h and subsequently refluxed for 10 h. As revealed by paper chromatography the product was a mixture of the mono and bis quaternary compounds. The reaction mixture, on concentration under reduced pressure, yielded a syrup which was resolved into the mono and bis derivatives by preparative paper chromatography. The bis derivative (crogyroidine) was crystallized from acetone–methanol (m.p. 526 K).

D_m measured by flotation. Well formed colorless prismatic crystal, 0·20 × 0·20 × 0·19 mm. Enraf–Nonius CAD-4 automatic diffractometer fitted with a low-temperature (liquid N_2) device. Cell parameters obtained from a least-squares fit to the $+2\theta$ and -2θ values of 48 reflections, Mo $K\alpha_1$ radiation. Space group determined from systematic absences 0*k*0 for $k = 2n+1$ and *h*0*l* for $h + l = 2n + 1$. 2350 unique reflections, $2\theta < 53°$, Mo $K\bar{\alpha}$ radiation (graphite monochromator), θ–2θ scan technique, variable scan width (0·80 + 0·20tanθ)°, a receiving aperture with a variable width of (3·50 + 0·86tanθ)mm and a constant height of 6mm located at a distance of 173mm from the crystal, maximum scan time 60s, $\frac{2}{3}$ of total scan time spent scanning the peak and $\frac{1}{6}$ each of the two backgrounds. Intensities of three reflections monitored every 3600 s showed no significant variations (3%) during course of data collection. 1720 reflections considered observed with $I > 2\sigma(I)$; intensities corrected for Lorentz and polarization; a Gaussian method (Coppens, Leiserowitz & Rabinovich, 1965) employed to make an absorption correction by using 216 sampling points. Each structure amplitude assigned an experimental weight, $w_F = (\sigma_F^2)^{-1}$, where σ_F was obtained from counting statistics (Ealick & van der Helm, 1975). Position of Br$^-$ ion determined from a three-dimensional sharpened Patterson map; a difference Fourier map, phased with the Br$^-$ ion revealed positions of all non-H atoms in asymmetric unit and also indicated presence of a water molecule. Positional and thermal parameters (initially isotropic and later anisotropic) of atoms refined in stages using a block-diagonal least-squares program (Ahmed, 1966). A difference Fourier map revealed positions of the 17 H atoms, those belonging to the water molecule could not be located. H atoms refined isotropically. Final $R = 0·046$ for 1705 reflections included in least-squares calculations and 0·078 for all 2350 reflections, $S = 1·44$; a structure-factor analysis did not show a significant variation for $\langle w\Delta^2 \rangle$ as a function of either F_o or index *k*. Final difference map contained peaks in range $-0·4$ to $+0·6$e Å^{-3}. Refinement discontinued when maximum parameter shifts $< \frac{1}{4}$ of their corresponding standard deviations. Scattering factors for Br$^-$, C, O, and N taken from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); anomalous-dispersion values for Br$^-$ from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional parameters for all non-H atoms are listed in Table 1.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters for non-*H *atoms with e.s.d.'s in parentheses*

	x	y	z	$U_{eq}{}^*(\text{Å}^2)$
Br	2410·5 (3)	1846·7 (3)	1292·6 (5)	0·0334 (2)
O	3299 (5)	4547 (4)	1548 (5)	0·080 (3)
C(1)	1786 (4)	3254 (4)	5992 (4)	0·027 (2)
C(2)	1456 (4)	2255 (4)	6916 (5)	0·031 (2)
C(3)	2357 (4)	1384 (4)	6453 (5)	0·027 (2)
N(4)	3501 (3)	2028 (3)	6184 (4)	0·020 (2)
C(5)	4237 (4)	2343 (4)	7731 (5)	0·027 (2)
C(6)	4178 (4)	3598 (4)	7849 (5)	0·034 (3)
C(7)	3966 (4)	3963 (4)	6164 (5)	0·031 (2)
C(8)	3065 (4)	3133 (4)	5475 (4)	0·024 (2)
C(9)	1081 (4)	4117 (4)	5628 (5)	0·036 (3)
C(1')	4289 (4)	1430 (4)	5084 (4)	0·023 (2)
C(2')	4651 (4)	281 (4)	5623 (5)	0·028 (2)

$$* U_{eq} = (\tfrac{1}{6}\pi^2) \sum_i \sum_j b_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

Table 2. *Molecular geometry, with e.s.d.'s for the last digit in parentheses*

(*a*) Bond distances (Å)

C(1)—C(2)	1·506 (6)	N(4)—C(8)	1·536 (5)
C(1)—C(8)	1·506 (6)	C(5)—C(6)	1·527 (7)
C(1)—C(9)	1·327 (6)	C(6)—C(7)	1·518 (6)
C(2)—C(3)	1·518 (6)	C(7)—C(8)	1·505 (6)
C(3)—N(4)	1·508 (5)	C(1')—C(2')	1·513 (6)
N(4)—C(5)	1·558 (5)	C(2')—C(2'')	1·516 (6)
N(4)—C(1')	1·508 (5)		

(*b*) Bond angles (°)

C(2)—C(1)—C(8)	109·8 (3)	C(5)—N(4)—C(8)	104·8 (3)
C(2)—C(1)—C(9)	127·1 (4)	N(4)—C(5)—C(6)	106·3 (3)
C(8)—C(1)—C(9)	123·2 (4)	C(5)—C(6)—C(7)	103·4 (4)
C(1)—C(2)—C(3)	103·8 (4)	C(6)—C(7)—C(8)	103·7 (4)
C(2)—C(3)—N(4)	104·0 (3)	C(7)—C(8)—N(4)	104·4 (3)
C(3)—N(4)—C(1')	111·3 (3)	C(7)—C(8)—C(1)	114·7 (3)
C(3)—N(4)—C(5)	112·7 (3)	C(1)—C(8)—N(4)	103·9 (3)
C(3)—N(4)—C(8)	105·8 (3)	N(4)—C(1')—C(2')	113·6 (3)
C(1')—N(4)—C(5)	111·6 (3)	C(1')—C(2')'—C(2'')	109·4 (3)
C(1')—N(4)—C(8)	110·3 (3)		

(*c*) Endocyclic torsion angles (°)

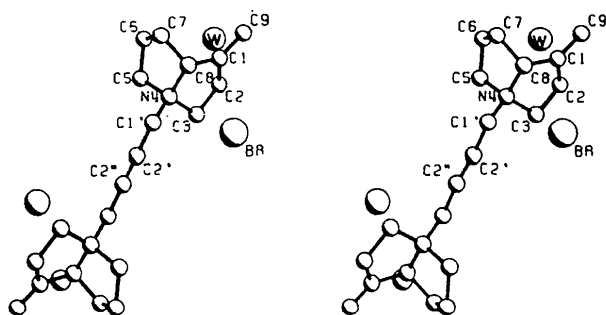|			
C(1)—C(2)—C(3)—N(4)	33·4 (3)	N(4)—C(5)—C(6)—C(7)	−25·0 (4)
C(2)—C(3)—N(4)—C(8)	−35·4 (3)	C(5)—C(6)—C(7)—C(8)	40·5 (4)
C(3)—N(4)—C(8)—C(1)	23·0 (3)	C(6)—C(7)—C(8)—N(4)	−40·5 (4)
N(4)—C(8)—C(1)—C(2)	−1·8 (3)	C(7)—C(8)—N(4)—C(5)	24·3 (3)
C(8)—C(1)—C(2)—C(3)	−19·6 (3)	C(8)—N(4)—C(5)—C(6)	0·6 (4)

Fig. 1. Stereoview of the single molecule of crogyroidine dihydrate. Water O atoms are designated by *W*.

A stereoscopic view of the single molecule of crogyrodine is shown in Fig. 1. The bond lengths, bond

angles and endocyclic torsion angles are listed in Table 2. The molecule of crogyroidine possesses a center of symmetry which coincides with the crystallographic center at ($\tfrac{1}{2}$, 0, $\tfrac{1}{2}$). The unique half of the molecule is composed of two saturated five-membered rings, ring *A* [atoms C(1), C(2), C(3), N(4) and C(8)] and ring *B* [atoms N(4), C(5), C(6), C(7) and C(8)]. There is *exo*-methylene substitution at C(1) and exocyclic substitution at N(4). Both the rings in the pyrrolizidine nucleus exist in an *exo*-puckered envelope form (Bull, Culvenor & Dick, 1968). The puckering parameters for the two rings are: $q = 0.35$ Å, $\varphi = 32.3°$ for ring *A*; $q = 0.40$ Å, $\varphi = -107.3°$ for ring *B* (Cremer & Pople, 1975). The conformation of ring *B* is a near-perfect envelope (deviation of 0·7°), while the slight deviation (3·7°) from a perfect envelope in the case of ring *A* may have been caused by the *exo*-methylene substitution at C(1).

The overall conformation of the pyrrolizidine nucleus is folded and twisted about the bridgehead bond, N(4)—C(8). This conformation is consistent with the observation that the *cis*-substituted fused-ring system shows a twist about the bridging bond in such a way that the bridgehead substituents tend to stagger (Phillips & Trotter, 1976). The degree of twist about the N(4)—C(8) bond is given by the torsion angles C(1)—C(8)—N(4)—C(5) −96·3 (3) and C(1')—N(4)—C(8)—H(8) 29 (3)°.

The bond angles and C—C bond distances are normal and compare quite well with those observed in other related structures. The angles at N(4) range between 104·8 (3) and 112·7 (3)° with a mean value of 109·4 (3)°. The four N—C distances differ from each other significantly. The pyrrolizidine ring-fusion distance [N(4)—C(8) = 1·536 (4) Å] is considerably larger than that observed in other PA's. The corresponding N—C distance is 1·485 (8) in lasiocarpine (Hay, Mackay & Culvenor, 1982), 1·487 (3) in fulvine (Sussman & Wodak, 1973), 1·494 (3) in heliotrine (Wodak, 1975), 1·486 (5) in jacobine (Pérez-Salazar, Cano & Garcia-Blanco, 1978) and 1·51 (2) Å in monocrotaline (Stoeckli-Evans, 1979).

The N(4)—C(3) and N(4)—C(5) distances differ from each other by about 0·05 Å while the latter distance of 1·558 (5) Å is significantly longer than the normally observed value of 1·51 Å for an N^+—C bond (Speck, 1976; Singh & Ahmed, 1969). In general, the N—C distances in crogyroidine differ from those in the other PA structures. In the present structure the folding of the pyrrolizidine nucleus, given by the dihedral angle [96·9 (1)°] between the planes defined by C(1), C(2), N(4), C(8) and C(5), C(6), C(8) N(4), is significantly different from that in other related structures. The analogous dihedral angle is 120·6 (3) in lasiocarpine, 125·7 (2) in fulvine, 121·7 (1) in heliotrine, 127·4 (1) in jacobine and 124·6 (5)° in monocrotaline. This angle in crogyroidine is not directly comparable with that in other structures, because the pyrrolizidine nucleus in crogyroidine does not contain an unsaturated ring.
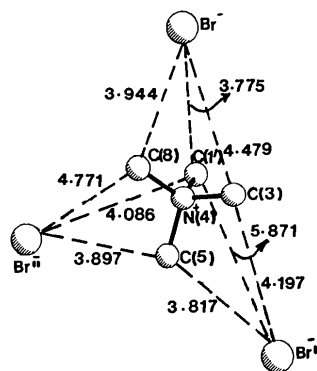
Fig. 2. Spatial distribution of Br^- ions with respect to N^+R_4. Br' and Br'' are related to Br by $(x, y, z + 1)$ and $(\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z)$ respectively. Distances are in Å, e.s.d.'s are 0·003 Å.

Crogyroidine is an example of a non-ester type PA. It lacks the structural features common to most diester and monoester alkaloids, such as the double bond between atoms C(1) and C(2), the ester linkages and associated macrocycles. The present structure also differs from other known PA's in having exocyclic substitution at N(4). In most PA molecules referred to above, the N atom is unsubstituted and invariably forms a hydrogen bond with a neighboring hydroxyl group.

Fig. 2 shows the association of the N^+R_4 system with the Br ions. It is seen that the positively charged N is associated with three Br^- ions. Association of more than one halide ion to tetracovalent N^+R_4 ions has been reported in the case of thelepogine methiodide (Fridrichsons & Mathieson, 1963). In the present structure, the closest approach of the negative ion $[Br-N(4) = 4·303 (3) Å]$ is through the approximate center of a triad formed by the atoms C(3), C(8) and C(1'). The other two approach distances are somewhat longer, $Br'-N(4) = 4·494 (3)$ and $Br''-N(4) = 4·635 (3)$ Å. Compared to Br, both Br' and Br'' assume less symmetric positions with respect to the N^+R_4 system (see Fig. 2). Such orientations of the Br^- ions with respect to the N^+R_4 ions are likely to cause uneven charge distribution among the four C atoms attached to the N atoms, and may very well explain the asymmetry in the four N—C bonds.

The nearest neighbors of the Br^- ion are two water molecules. The Br—O(1) distance of 3·420 (4) Å and $Br-O(1)(\frac{1}{4}-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ distance of 3·468 (4) Å are somewhat longer than the normally accepted distance (3·28 Å) for a Br···O hydrogen bond (Kuleshova & Zorkii, 1981).

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Structure of 2-Furoic Acid, $C_5H_4O_3$: a Redetermination

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Abstract. $M_r = 112·1$, triclinic, $P\bar{1}$, $a = 10·221 (2)$, $b = 6·762 (1)$, $c = 3·781 (2)$ Å, $\alpha = 83·59 (2)$, $\beta = 96·75 (2)$, $\gamma = 106·76 (2)°$, $V = 247·6$ Å^3, $Z = 2$, $D_m = 1·483$ [Goodwin & Thomson (1954). *Acta Cryst.* 7, 166–173], $D_x = 1·503$ Mg m^{-3}, $\lambda(Mo K\alpha) = 0·71069$ Å, $\mu = 0·137$ mm^{-1}, $F(000) = 116$, $T = 293$ K. Final $R = 0·035$ based on 901 independent observed reflections. The structure determined from