III. From the reflexions with the largest values for the product of the normalized structure factor with the number of $\sum_2$ relations for a reflexion, code Nos. 9 and 21 are respectively assigned symbols *A* and *B*. The interdependence of the $\sum_2$ relations is shown by the graph in Fig. 3, verifying many times over that $\mathrm{III}=-\mathrm{I}\times\mathrm{II}$. Fourteen phases are obtained through the two symbols *A* and *B*. The best of four possible maps clearly showed the molecule in projection (Fig. 4). The projection refined easily to $R=0{\cdot}150$ with individual isotropic temperature factors on the thirteen (non-hydrogen) atoms.

Both structures will be published in greater detail.

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References

SWAMINATHAN, S. & LESSINGER, L. (1973). *Acta Cryst.* **A29**, 717–720.

SWAMINATHAN, S. & LESSINGER, L. (1974). *Acta Cryst.* **A30**, 458.

SWAMINATHAN, S., VIMALA, T. M. & LESSINGER, L. (1975). *Acta Cryst.* **A31**, S119.

Acta Cryst. (1976). **B32**, 1900

(*R*)-7-Ethyl-1,4,5,6,7,8,9,10-octahydro-2*H*-3,7-methanoazacycloundecan[5,4-*b*]indole, (Quebrachamine)

BY C. PUGLISI*
Departamento de Físico-Química, Facultad de Ciencias Exactas y Naturales, Buenos Aires, Argentina

R. F. BAGGIO
División Cristalografía, Comisión Nacional de Energía Atómica, Av. del Libertador 8250, *Buenos Aires, Argentina*

AND S. BAGGIO†
Departamento de Físico-Química, Facultad de Farmacia y Bioquímica, Buenos Aires, Argentina

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Abstract. $C_{19}H_{26}N_2$, monoclinic, $P2_1$; $a=15{\cdot}01$ (3), $b=7{\cdot}10$ (2), $c=8{\cdot}25$ (2) Å, $\beta=105{\cdot}8$ (3)°, $V=846{\cdot}2$ Å^3; $Z=2$, $D_m=1{\cdot}114$, $D_x=1{\cdot}108$ g cm^{-3}; $\mu(\mathrm{Cu}\ K\alpha)=4{\cdot}9$ cm^{-1}, $\lambda(\mathrm{Cu}\ K\alpha)=1{\cdot}5418$ Å, filtered with Ni. The conformation of the eleven-membered ring and the geometry around its N atom are discussed and compared with those of a related alkaloid (cleavamine). A correlation between the slow rate of methylation observed, and the expected positions of the lone pair of N electrons according to the structure obtained, is made.

Introduction. The crude material, extracted from *Aspidosperma* (*Quebracho blanco*), was recrystallized from a saturated methanol solution. On standing, well-developed colourless needles were obtained. They were mounted with the needle axis (*b*) parallel to the goniometer spindle. Preliminary precession photographs taken with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å) gave the cell dimensions with an accuracy of about 3/1000.

From systematic extinctions ($0k0$: $k=2n+1$) as well as from the well known optical activity of the compound, $P2_1$ was inferred to be the correct space group.

Integrated intensity data were gathered by photographic methods. Levels $h0l$ to $h5l$ were taken with Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) using equi-inclination Weissenberg techniques, while levels $0kl$ and $hk0$ were recorded with a precession camera, and Mo $K\alpha$ radiation. A total of 1244 reflexions (about 65% of the Cu sphere) were measured with a manual densitometer. Of these, 128 were considered unobserved and given $F_o=0$.

After the usual geometrical corrections were performed, data were cross correlated by the least-squares method of Hamilton, Rollett & Sparks (1965). Absorption corrections were neglected (maximum $\mu R=0{\cdot}5$). A Wilson plot was used to reduce structure amplitudes to an absolute scale and normalized structure factors $|E|$ were calculated.

To solve the phase problem, the multi-solution method described by Germain, Main & Woolfson (1970) and implemented in their program *MULTAN*, was attempted. The origin-defining phases were chosen to be 203, $11,0,\bar{3}$ and 615 and assigned the value 0. The starting set was completed with three well connected phases: $a=10,4,2$, $b=21\bar{2}$ and $c=13,0,0$.

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[*] Present address: INTI, Av. Gral Paz y Constituyentes, San Martin, Pcia de Buenos Aires, Argentina.

[†] Present address: ALUAR, Cangallo 525, Buenos Aires, Argentina.

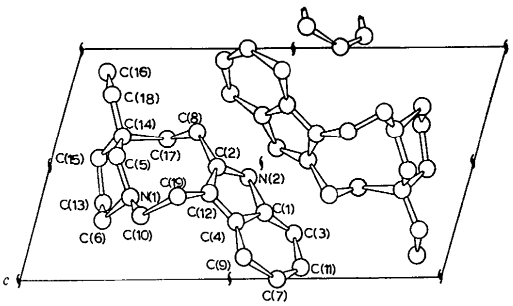
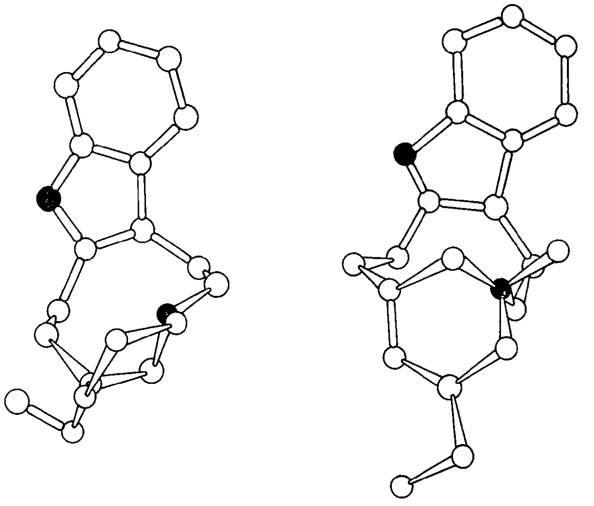


Fig. 1. Projection of the unit cell down the *b* axis.



(*a*) (*b*)

Fig. 2. Projection of the molecule of (*a*) quebrachamine and (*b*) cleavamine methiodide onto the least-squares plane through the indolic group.

After ordering the eight sets generated according to their decreasing value of ABSFOM, the third ($a=\frac{3}{4}\pi$, $b=\frac{1}{4}\pi$, $c=0$, ABSFOM$=1{\cdot}12$) gave the whole solution in a Fourier synthesis with the 200 highest $|E|$ reflexions.

Scale factors, atomic positions and isotropic temperature factors were refined by full-matrix least squares with the program *SFLS*-5. The process converged to a conventional R of 0·108. At this stage, the 23 hydrogen atoms with positions completely determined by the molecular geometry were added in their expected positions, with isotropic temperature factors equal to those of the atoms to which they were attached; their parameters were kept constant throughout the rest of the refinement. In the last four cycles, thermal parameters of non-H atoms were allowed to vary anisotropically. The function minimized was $w\Delta^2=\sum w_i(|F_o|-|F_c|)^2$, where the weights $w_i=[(0{\cdot}46+0{\cdot}38F_o-0{\cdot}03F_o^2)(0{\cdot}84-0{\cdot}95r^2)/\{1{\cdot}05-\exp(-1{\cdot}5r^2)\}]^{-1/2}$ were chosen so as to make the average value of $w\Delta^2$ as constant as possible in the ranges of F_o and $r=(\sin\theta/\lambda)$.

Refinement was considered complete when shifts of atom parameters were less than $\frac{1}{3}$ of their e.s.d.'s. The final R was 0·095.

At this stage a ΔF synthesis was computed to look for any solvent molecule, but no peak significantly above background could be detected.

Final atomic coordinates and temperature factors for non-H atoms are quoted in Table 1. Calculated positions for H atoms are listed in Table 2.*

Table 1. *Final parameters* ($\times 10^4$)

B_{ij}'s define anisotropic temperature factors as $\exp[-(\sum_i \sum_j B_{ij}h_ih_j)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	2080 (4)	7011 (0)	1481 (7)	34 (4)	70 (27)	113 (8)	12 (11)	26 (5)	13 (10)
N(2)	4752 (4)	5887 (13)	675 (8)	35 (5)	131 (33)	137 (10)	3 (17)	38 (6)	−14 (13)
C(1)	5312 (6)	6700 (13)	2133 (9)	36 (5)	30 (38)	130 (11)	11 (14)	30 (6)	9 (15)
C(2)	3917 (5)	6849 (14)	177 (9)	34 (5)	30 (36)	142 (11)	17 (14)	40 (7)	8 (15)
C(3)	6199 (6)	6261 (16)	3083 (12)	37 (5)	154 (46)	184 (14)	−2 (16)	35 (8)	12 (20)
C(4)	4801 (5)	8121 (14)	2599 (9)	37 (5)	84 (36)	134 (11)	0 (14)	37 (7)	3 (14)
C(5)	1532 (5)	7121 (16)	−267 (10)	35 (5)	220 (42)	161 (12)	−29 (15)	36 (7)	−37 (17)
C(6)	1590 (6)	5889 (16)	2439 (10)	35 (5)	79 (40)	160 (13)	41 (15)	55 (7)	13 (16)
C(7)	6078 (6)	8785 (16)	4959 (10)	42 (5)	189 (49)	118 (11)	6 (18)	20 (7)	20 (16)
C(8)	3211 (6)	6189 (16)	−1343 (10)	46 (6)	168 (43)	145 (12)	−10 (16)	55 (8)	−47 (17)
C(9)	5183 (6)	9236 (16)	4025 (9)	50 (6)	148 (42)	122 (11)	−5 (18)	37 (7)	16 (17)
C(10)	2454 (6)	8780 (14)	2244 (11)	45 (6)	23 (39)	200 (13)	23 (16)	46 (8)	−4 (17)
C(11)	6576 (5)	7301 (15)	4493 (9)	34 (5)	166 (38)	140 (11)	8 (15)	22 (6)	17 (15)
C(12)	3924 (5)	8260 (12)	1340 (8)	37 (5)	42 (34)	119 (9)	7 (14)	36 (6)	−14 (12)
C(13)	1480 (6)	3875 (16)	1687 (10)	45 (5)	172 (47)	162 (13)	6 (17)	29 (7)	23 (18)
C(14)	1544 (5)	5265 (14)	−1144 (9)	34 (4)	156 (39)	118 (10)	9 (14)	18 (6)	17 (15)
C(15)	1077 (5)	3824 (17)	−202 (11)	35 (5)	192 (47)	176 (13)	10 (16)	34 (7)	0 (19)
C(16)	749 (9)	3715 (24)	−4011 (12)	87 (9)	416 (75)	146 (13)	−26 (29)	21 (9)	6 (24)
C(17)	2551 (5)	4607 (13)	−1007 (9)	33 (4)	109 (36)	128 (10)	16 (14)	19 (6)	12 (14)
C(18)	982 (7)	5473 (19)	−2978 (9)	52 (6)	334 (53)	108 (11)	5 (20)	4 (8)	−3 (18)
C(19)	3157 (5)	9596 (12)	1384 (10)	41 (5)	26 (35)	159 (11)	8 (15)	35 (6)	−27 (14)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31701 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Calculated positions* (× 10^4) *for some hydrogen atoms*

Only those H atoms whose atomic parameters are fixed by non-H atom positions are included. The atoms to which they are attached are in parentheses.

	x	*y*	*z*
H(1) (C9)	4857	404	4428
H(2) (C7)	6356	9571	6093
H(3) (C11)	7208	7072	5181
H(4) (C3)	6514	5119	2656
H(5) (N2)	4901	4737	49
H(6) (C8)	3492	5655	−2284
H(7) (C8)	2869	7451	−1863
H(8) (C17)	2794	4018	222
H(9) (C17)	2517	3490	−1916
H(10) (C19)	3415	10853	2065
H(11) (C19)	2866	10007	107
H(12) (C10)	1977	9834	2093
H(13) (C10)	2725	8560	3557
H(14) (C5)	1760	8210	−957
H(15) (C5)	914	7451	−235
H(16) (C6)	979	6500	2262
H(17) (C6)	1891	5803	3740
H(18) (C13)	2075	3232	1930
H(19) (C13)	1103	3075	2325
H(20) (C15)	1120	2414	−675
H(21) (C15)	437	422	−450
H(22) (C18)	1281	6377	−3676
H(23) (C18)	415	6144	−2906

Discussion. Kinetic studies performed on some alkaloids closely related to quebrachamine [vincaminorine and vincaminoreine: Mokry, Kompis, Shamma & Shine (1964)] showed that rates of methiodide formation are very slow. Although no such studies seem to have been made on quebrachamine, it is a well known fact that its methiodide derivative is not easily obtained. This seems to indicate that, in this family of alkaloids with a common N-containing eleven-membered ring, the N atom must be highly hindered. Accordingly, conformations where the non-bonded electrons on N are sterically shielded by the indolic bridge must predominate at room temperature. The crystal structure determination of quebrachamine confirms these assumptions. Fig. 1 shows a projection of the unit cell down the *b* axis, where, besides the numbering system used throughout this paper, the conformation of the eleven-membered ring can be observed. As suggested by the kinetic studies performed on vincaminorine and vincaminoreine, the N atom in the ring has the lone pair pointing towards a region 'protected' by neighbouring atoms, thus keeping them away from chemical reactions unless a drastic change in conformation takes place.

It is interesting to compare the geometry of quebrachamine with that of cleavamine, a related alkaloid whose methiodide crystal structure was determined several years ago (Camerman & Trotter, 1964). In Fig. 2 the differences in conformation between both structures are depicted, showing the projections onto the least-squares planes through the indolic group. The different geometry around the N atom is apparent: the lone pair of N electrons is shielded by the indolic bridge in quebrachamine, while the methyl group points outwards in cleavamine methiodide.

The facility with which cleavamine reacts with methyl iodide suggests that either the conformation of the eleven-membered ring in the free base is similar to that in the heavy-atom derivative, or that the alkaloid has a much greater facility for changing its conformation than has quebrachamine. Whatever the answer, the double bond in the tetrahydropyridine group must play an outstanding role.

The indolic group in quebrachamine is perfectly planar, and the equation of the least-squares plane, together with individual deviations from it, are reported in Table 3. The piperidine ring has a normal chair conformation. Bond distances and angles are listed in Table 4. No departures from the commonly accepted values for these structures were found.

Table 3. *Equation of the least-squares plane and deviations* (Å) *from this plane*

E.s.d.'s for these deviations are given in parentheses.

Plane determined by N(2), C(1), C(2), C(3), C(4), C(7), C(8), C(9), C(11), C(12), C(19):

$$0{\cdot}5412x+0{\cdot}6401y-0{\cdot}5453z-6{\cdot}1736=0{\cdot}0$$

N(2)	−0·012 (8)	C(1)	0·004 (8)
C(2)	0·023 (9)	C(3)	−0·001 (10)
C(4)	−0·023 (9)	C(7)	0·008 (10)
C(8)	−0·008 (10)	C(9)	0·003 (9)
C(11)	−0·004 (9)	C(12)	0·025 (8)
C(19)	−0·015 (8)		

Table 4. *Interatomic distances and angles*

(*a*) Distances (in Å; e.s.d.'s in brackets, in units of last decimal figure)

N(1)—C(5)	1·455 (10)	N(1)—C(10)	1·448 (10)
N(2)—C(1)	1·392 (10)	C(1)—C(3)	1·384 (13)
C(1)—C(4)	1·383 (13)	C(2)—C(12)	1·385 (12)
C(3)—C(11)	1·364 (13)	C(4)—C(12)	1·442 (11)
C(5)—C(14)	1·505 (14)	C(7)—C(9)	1·393 (12)
C(7)—C(11)	1·404 (14)	C(10)–C(19)	1·536 (12)
C(12)–C(19)	1·500 (12)	C(14)–C(15)	1·560 (13)
C(14)–C(17)	1·557 (12)	C(16)–C(18)	1·498 (19)
N(1)—C(6)	1·455 (11)	C(6)—C(13)	1·550 (16)
N(2)—C(2)	1·388 (12)	C(8)—C(17)	1·571 (14)
C(2)—C(8)	1·481 (12)	C(13)–C(15)	1·511 (12)
C(4)—C(9)	1·405 (12)	C(14)–C(18)	1·526 (11)

(*b*) Angles (in degrees; e.s.d.'s in brackets, in units of last decimal figure)

C(5)—N(1)—C(6)	109·6 (6)	C(5)—N(1)—C(10)	115·6 (6)
C(6)—N(1)—C(10)	115·6 (6)	C(1)—N(2)—C(2)	109·7 (7)
N(2)—C(1)—C(3)	131·2 (8)	N(2)—C(1)—C(4)	107·0 (7)
C(3)—C(1)—C(4)	121·8 (8)	N(2)—C(2)—C(8)	118·4 (8)
N(2)—C(2)—C(12)	108·3 (7)	C(8)—C(2)—C(12)	133·2 (8)
C(1)—C(3)—C(11)	118·3 (9)	C(1)—C(4)—C(9)	120·9 (8)
C(1)—C(4)—C(12)	108·4 (7)	C(9)—C(4)—C(12)	130·5 (8)
N(1)—C(5)—C(14)	110·6 (7)	N(1)—C(6)—C(13)	107·6 (7)
C(9)—C(7)—C(11)	121·7 (9)	C(2)—C(8)—C(17)	114·7 (8)
C(4)—C(9)—C(7)	116·5 (8)	N(1)—C(10)–C(19)	111·1 (7)
C(3)—C(11)–C(7)	120·8 (9)	C(2)—C(12)–C(4)	106·5 (7)
C(2)—C(12)–C(19)	127·8 (7)	C(4)—C(12)–C(19)	125·6 (7)
C(6)—C(13)–C(15)	113·9 (8)	C(5)—C(14)–C(15)	105·6 (7)
C(5)—C(14)–C(17)	111·4 (7)	C(5)—C(14)–C(18)	108·5 (7)
C(15)–C(14)–C(17)	109·0 (7)	C(15)–C(14)–C(18)	110·8 (7)
C(17)–C(14)–C(18)	111·4 (7)	C(13)–C(15)–C(14)	112·9 (8)
C(8)—C(17)–C(14)	114·8 (7)	C(14)–C(18)–C(16)	117·7 (9)
C(10)–C(19)–C(12)	113·7 (7)		

Mean distances for different types of bonds are: C(sp^3)-C(sp^3) = 1·535; C(sp^2)-C(sp^2) = 1·389; C(sp^2)-N(sp^2) = 1·390; and C(sp^2)-N(sp^3) = 1·453 Å.

Short contacts between non-bonded atoms are typical van der Waals interactions.

We thank Dr E. Rúveda and Lic. E. Tosti for supplying the sample of the alkaloid and for very helpful discussions.

References

Camerman, N. & Trotter, J. (1964). *Acta Cryst.* **17**, 384–391.

Germain, G., Main, P. & Woolfson, M. M. (1970). *Acta Cryst.* **B26**, 274–285.

Hamilton, W. C., Rollett, J. S. & Sparks, R. A. (1965). *Acta Cryst.* **18**, 129–130.

Mokry, J., Kompis, I., Shamma, M. & Shine, R. J. (1964). *Chem. Ind.* **48**, 1988–1989.

Acta Cryst. (1976). B32, 1903

8,8′-Biquinolyl

By Magnus Lenner and Ove Lindgren

Department of Inorganic Chemistry, Chalmers University of Technology and the University of Gothenburg, P.O. Box, S-402 20 Göteborg, Sweden

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Abstract. $C_{18}N_2H_{12}$, monoclinic, $P2_1/a$, $Z=4$, M.W. 256·3; $a=8·668$ (3), $b=19·967$ (10), $c=7·686$ (5) Å, $\beta=103·36$ (4)°; $D_x=1·315$, $D_m=1·30$ g cm^{-3}; final $R=0·034$. The sp^2–sp^2 single bond between the two ring systems has a length of 1·495 (2) Å. The configuration is *trans*, the angle between the two halves of the molecule being 96·8°.

Introduction. The colourless, compact prismatic crystals were supplied by Dr J. Pedersen (Department of Organic Chemistry, Chalmers University of Technology). A specimen, 0·6 × 0·4 × 0·6 mm, was mounted on a Syntex $P2_1$ four-circle diffractometer. A θ–2θ time variable scan technique was used, $2\theta_{\max}$ being 100°, with a scan speed varying between 2·0 and 12·0° min^{-1}. Graphite-monochromatized Cu $K\alpha$ radiation ($\lambda=1·5418$ Å) was used to measure 1448 reflexions, of which 1369 were retained when an observed–unobserved cut-off at $4·0\sigma(I)$ was employed. The systematic absences, $0k0$, $k=2n+1$, and $h0l$, $h=2n+1$, uniquely determined the space group as $P2_1/a$. The intensities were reduced to structure factors by application of Lorentz and polarization factors, but no absorption correction was made.

The structure was solved by direct methods with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1974). With 200 normalized structure factors ($E_{\min}=1·49$) and 1600 $\sum_2$ relationships, sixteen sets of phases were generated. The map computed with the most consistent set showed all twenty non-hydrogen atoms as well as four spurious peaks, the latter at a considerably lower level. Block-diagonal least-squares refinement of the non-hydrogen atoms with isotropic temperature factors gave an R of 0·084. The H atoms, located from geometric considerations, were included in the further refinements. Anisotropic temperature factors were introduced for the N and C atoms, and weights were calculated from $w=(12+|F_o|+0·025\times|F_o|^2)^{-1}$. The final R was 0·034 for 1369 reflexions (0·036 with 79 unobserved reflexions included) when 230 parameters were refined. The scattering factors were those of Doyle & Turner (1968) for C and N, and those of Stewart, Davidson & Simpson (1965) for H. The final atomic positions and thermal parameters are given in Table 1.*

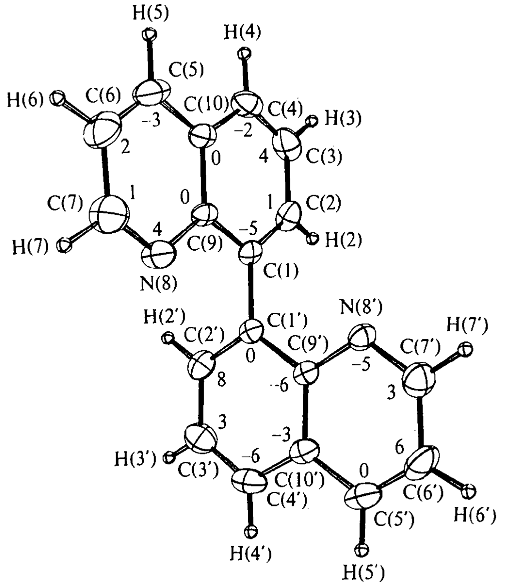

Fig. 1. The molecular structure of 8,8′-biquinolyl with the deviations in Å (× 10^3) from the least-squares planes noted.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31704 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.