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The Crystal Structures, Molecular Structures, and Absolute Configurations of the Hydrobromides of the Aporphine Alkaloids Leucoxine and Isoboldine*

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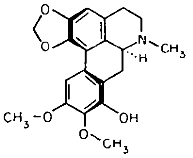
The X-ray crystal-structure analysis of leucoxine (I) hydrobromide ($C_{20}H_{21}O_5N.HBr$) completes the elucidation of the molecular structure of this alkaloid and establishes its absolute configuration as that of the *S* series of aporphines. The structure analysis of isoboldine (II) hydrobromide ($C_{19}H_{21}O_4N.HBr$) furnishes details of its molecular structure and confirms the absolute configuration (also *S* series) implied from the configurational assignment made previously for its isomer isoboldine from an optical rotatory dispersion study. The twist from coplanarity about the central bond of the biphenyl moiety is ~14° in (I).HBr and ~21° in (II).HBr (*cf.* ~30° in the *N*-methylbulbocapninium ion). The different twists result from the different substituents on the basic aporphine ring system. Both hydrobromides are orthorhombic ($P2_12_12_1$) with $Z = 4$. Cell parameters [$23 \pm 1{\cdot}5\,°C$, $\lambda(\mathrm{Cu}\,K\alpha_1) = 1{\cdot}54051$ Å] are: [(I).HBr] $a = 7{\cdot}1929\,(8)$, $b = 18{\cdot}3715\,(24)$, $c = 13{\cdot}8490\,(9)$ Å, $D_c = 1{\cdot}583$ g cm^{-3}; [(II).HBr] $a = 7{\cdot}543\,(1)$, $b = 21{\cdot}402\,(2)$, $c = 11{\cdot}503\,(1)$ Å, $D_c = 1{\cdot}486$ g cm^{-3}. $R(F)$ is 0·030 for (I).HBr and 0·056 for (II).HBr. E.s.d.'s of bond lengths not involving H atoms are 0·003 to 0·005 Å for (I).HBr and 0·005 to 0·011 Å for (II).HBr.

Introduction and structure analysis

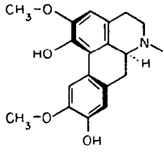
Leucoxine hydrobromide

Leucoxine ($C_{20}H_{21}O_5N$, formula I) is an alkaloid extracted from the leaves and stems of *Ocotea leucoxylon* (family Lauraceae). The preliminary characterization (Goodwin, Smith & Horning, 1960; Goodwin, 1965) by chemical, ultraviolet spectroscopic, and NMR methods indicated that it is a member of the aporphine series with a methylenedioxy group, two methoxyl groups, and a hydroxyl group. A structure such as (I) was postulated (Goodwin, 1965), but with ambiguity as to which of the three substituted positions on the lower benzenoid ring bears the hydroxyl group and without any conclusion as to absolute configuration.



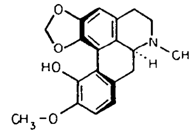
LEUCOXINE

(I)



ISOBOLDINE

(II)



BULBOCAPNINE

(III)

Two crystals, one about 0·2 × 0·1 × 0·1 mm and the other about 0·4 × 0·4 × 0·4 mm, were cut from prismatic specimens of leucoxine hydrobromide furnished by Dr S. Goodwin and used in the data collection with the Oak Ridge computer-controlled X-ray diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968). The larger crystal was used in the determination

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of the space group ($P2_12_12_1$) and cell dimensions (see *Abstract*). The only systematic absences were: $h00$ reflections with h odd, $0k0$ with k odd, and $00l$ with l odd. The cell parameters were refined by the method of least squares from the angle data ($2\theta,\chi,\varphi$) of six reflections in the 2θ range 125 to 134°.

Intensities of 2204 independent reflections were recorded (Cu $K\alpha$ radiation) by the θ–2θ step-scan method, with background counts at 2θ settings above and below each reflection peak. In an attempt to minimize extinction errors and at the same time maximize precision for the high-angle data, we used data from the smaller crystal for reflections with $2\theta < 85°$ and data from the larger crystal for the remaining reflections with $2\theta \leq 159{\cdot}5°$. The intensities from the two crystals were put on the same scale from the data of a few reflections recorded from both crystals. Absorption corrections calculated by the method of Busing & Levy (1957) were applied; the linear absorption coefficient was taken to be 36·9 cm^{-1}; the range of correction factors for the intensities was 1·46 to 1·54 for the smaller crystal and 2·27 to 3·07 for the larger.

The structure solution was found by the classic heavy-atom method. Eventually the H atoms were located and all 49 atoms in the asymmetric unit ($C_{20}H_{22}O_5NBr$) were included in full-matrix least-squares refinement. The sum minimized was $\Sigma\, w(|F_o|^2 - |F_c|^2)^2$, in which the weights w were set according to the equation $w(|F_o|^2) = 1/[\sigma_c^2(|F_o|^2) + (0{\cdot}03|F_o|^2)^2]$, where $\sigma^2(|F_o|^2)$ is the variance from counting statistics and the term $(0{\cdot}03|F_o|^2)^2$ is an empirical correction term (Peterson & Levy, 1957). In the final refinement cycles the following 333 parameters were optimized: one scale factor for each of the two crystal specimens; three coordinates for each of the 49 atoms; six anisotropic thermal parameters for each of the 27 non-H atoms; and a single isotropic thermal parameter for each of the 22 H atoms. The atomic scattering factors used were from *International Tables for X-ray Crystallography* (1962), except for H, for which the factors of Stewart, Davidson & Simpson (1965) were used. The dispersion corrections of Cromer & Liberman (1970) were used for Br^- ($\Delta f' = -0{\cdot}767$, $\Delta f'' = 1{\cdot}283$). The nine reflections with the highest intensity from the smaller crystal showed extinction effects and were given zero weights.

The final measures of goodness of fit for the correct absolute configuration are: $R(F) = 0{\cdot}030$; $R(F^2) = 0{\cdot}037$; $R_w(F^2) = 0{\cdot}060$; $\sigma_1 = 1{\cdot}300$ (standard deviation of an observation of unit weight). The corresponding measures obtained by refinement of the inverted structure are: $R(F) = 0{\cdot}042$; $R(F^2) = 0{\cdot}054$; $R_w(F^2) = 0{\cdot}089$; $\sigma_1 = 1{\cdot}927$. Applying the R-factor ratio test (Hamilton, 1965; *International Tables for X-ray Crystallography*, 1974), we find $\mathscr{R} = 1{\cdot}483$, much larger than the value $\mathscr{R}_{1,1862,0\cdot005} = 1{\cdot}002$ interpolated from Hamilton's tables for the 0·5% significant point of $\mathscr{R}$ for a hypothesis of one dimension and 1862 degrees of freedom. There is, therefore, a nearly zero probability for the hypothesis that the second, inverted configuration is correct. A final difference map for the correct configuration showed excursions of density from $-0{\cdot}33$ to $+0{\cdot}34$ e Å^{-3}. The coordinates for the non-H atoms are given in Table 1.[*]

Table 1. *Fractional coordinates* ($\times 10^5$) *for leucoxine hydrobromide*

	x	y	z
C(1)	54407 (49)	65158 (18)	23187 (19)
C(2)	55667 (44)	59560 (16)	16232 (19)
C(3)	55692 (61)	51723 (18)	19650 (22)
C(4)	62409 (52)	46457 (16)	12158 (21)
C(5)	58466 (38)	55315 (13)	−1219 (16)
C(6)	46727 (55)	56853 (15)	−10120 (20)
C(7)	50126 (45)	64426 (14)	−13774 (19)
C(8)	48201 (47)	65837 (15)	−23632 (19)
C(9)	50569 (47)	72822 (15)	−27298 (20)
C(10)	54404 (44)	78467 (15)	−20887 (20)
C(11)	56427 (43)	77143 (13)	−11117 (19)
C(12)	54126 (39)	70113 (14)	−7473 (18)
C(13)	55106 (41)	68461 (16)	2993 (20)
C(14)	54163 (36)	73776 (13)	10088 (17)
C(15)	53815 (45)	72073 (18)	19816 (21)
C(16)	56038 (38)	61155 (14)	6407 (17)
C(17)	50567 (55)	84078 (18)	18326 (23)
C(18)	58298 (59)	41866 (15)	−4333 (22)
C(19)	64965 (70)	74700 (22)	−42325 (26)
C(20)	56630 (64)	91177 (16)	−18302 (26)
N(21)	53314 (35)	47844 (13)	2637 (18)
O(22)	53157 (39)	81175 (12)	8877 (15)
O(23)	52685 (46)	78395 (14)	25185 (16)
O(24)	43697 (47)	60102 (11)	−29437 (14)
O(25)	48098 (40)	73879 (13)	−37062 (15)
O(26)	55754 (40)	85255 (11)	−24918 (15)
Br	9265 (5)	44903 (2)	−1562 (2)

Isoboldine hydrobromide

Isoboldine ($C_{19}H_{21}O_4N$, formula II) is an aporphine alkaloid of known chemical structure (for references see Shamma & Slusarchyk, 1964; and Shamma, 1967). The absolute configuration indicated in (II) is implied by the optical rotatory dispersion data (Craig & Roy, 1965) on boldine, which differs in structure from isoboldine only by the interchange of the OCH_3 and OH groups at the upper left of (II). Our sample of isoboldine was isolated by Professor R. Barnes[†] from the Brazilian plant *Croton celtidifolius* and was identified as isoboldine by mass spectroscopic analysis performed by Dr H. Fales[‡] (Barnes & Fales, 1966).

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[*] Lists of structure factors, H atom parameters, and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32384 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The crystal specimen of isoboldine hydrobromide used for precise determination of cell parameters (see *Abstract*) and for collection of intensity data measured about $0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}2$ mm. The space group was found to be $P2_12_12_1$, with $Z = 4$. The cell parameters in the *Abstract* were determined in the same way as those for leucoxine hydrobromide from the angle data of 12 reflections in the 2θ range 70 to 88°. Recording and processing of intensity data were as for leucoxine except that only one crystal specimen was used and absorption corrections were not made.*

Solution and refinement procedures were the same as those used for leucoxine hydrobromide, except that the H atoms could not be located. The 13 H atoms not on methyl or hydroxyl groups were included in the final least-squares calculations in fixed, calculated positions. They were given the anisotropic thermal parameters of the atoms bearing them, as determined at a near-final stage of the refinement. In the final refinement cycles the parameters adjusted were: a single scale factor on $|F_c|$ and three coordinates and six anisotropic thermal parameters for each of the 25 non-H atoms. The final measures of goodness of fit for the correct absolute configuration were: $R(F^2) = 0{\cdot}056$; $R(F^2) = 0{\cdot}095$; $R_w(F^2) = 0{\cdot}114$; $\sigma_1 = 2{\cdot}100$. For the alternative absolute configuration the corresponding measures were: $R(F) = 0{\cdot}064$; $R(F^2) = 0{\cdot}107$; $R_w(F^2) = 0{\cdot}1276$; $\sigma_1 =$

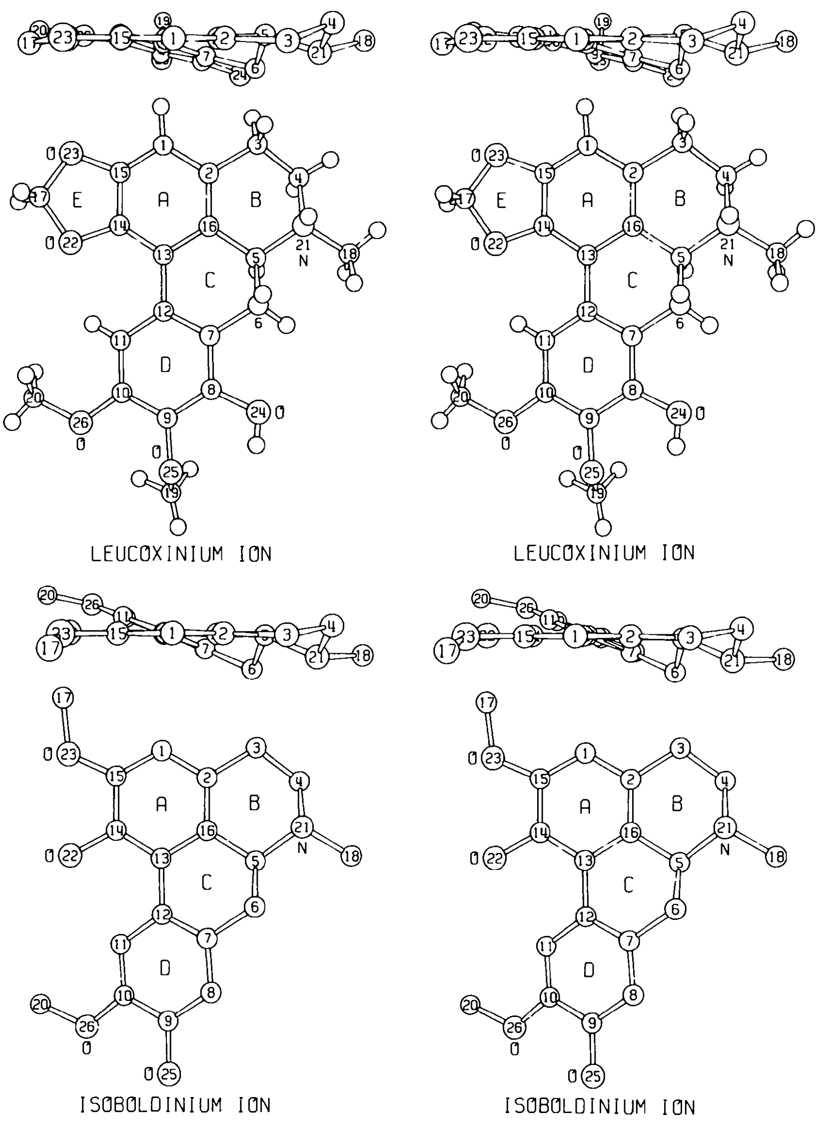

Fig. 1. Stereoscopic views of the alkaloid cations in leucoxine hydrobromide and isoboldine hydrobromide. Two views in directions at right angles to each other are shown for each cation. H atoms are included only in the lower view for the leucoxinium ion.

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* Absorption corrections were desirable ($\mu = 35{\cdot}3$ cm^{-1}), but it was not practical to make them because the crystal was inadvertently stuck on the side of a rather thick glass fiber. None of a half-dozen other crystals that were examined as possible replacements gave satisfactory diffraction patterns.

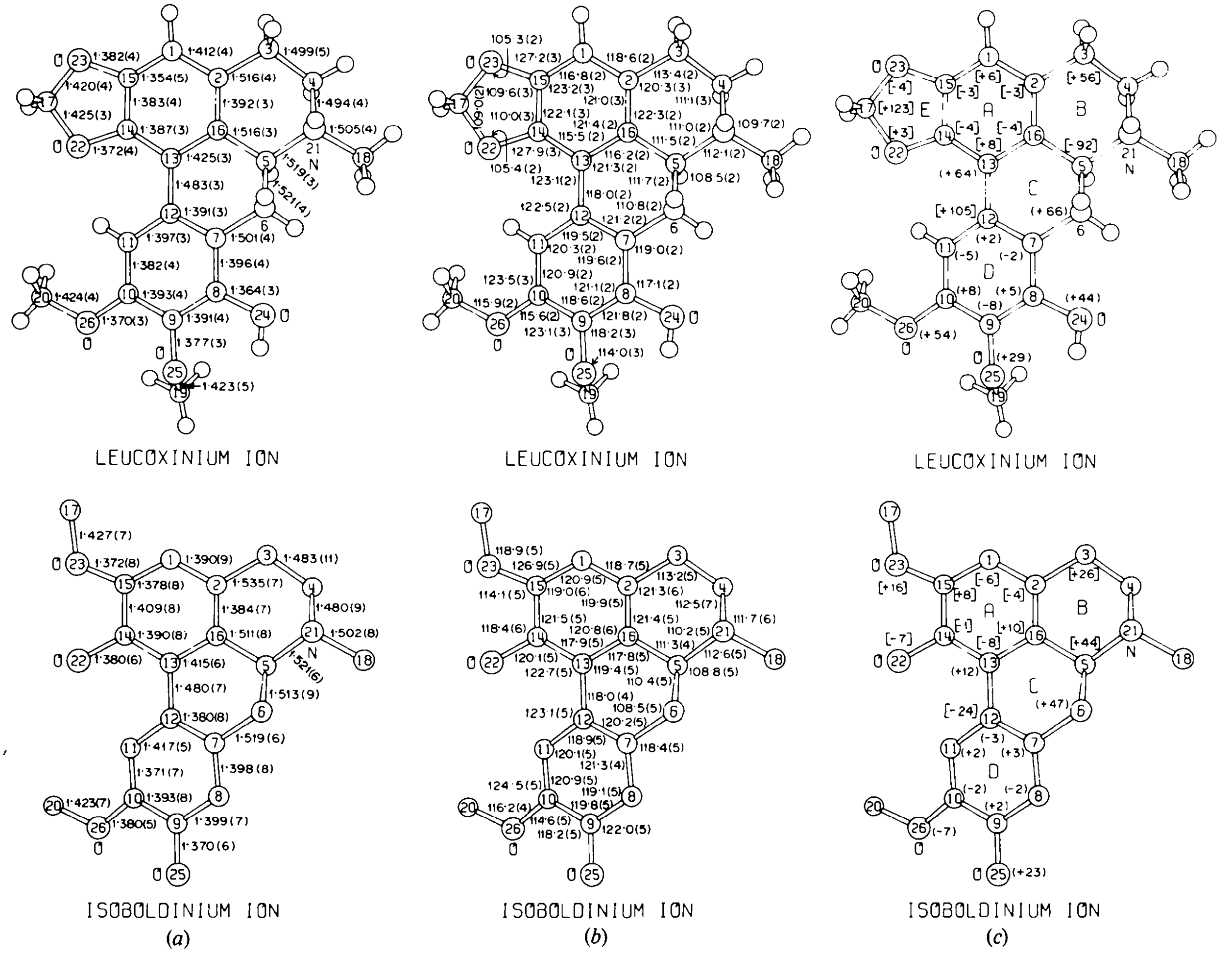
2·360. Comparison of the experimental R-factor ratio $\mathscr{R} = 1\cdot124$ with the significance point $\mathscr{R}_{1,1907,0\cdot005} = 1\cdot002$ shows that the probability of the alternative configuration is very much less than 0·005. The indication of absolute configuration is not so striking as in the case of leucoxine hydrobromide, presumably because of the perturbations of absorption and the omission of nine H atoms, but it is nevertheless satisfactory. A final difference map showed excursions of density from $-0\cdot58$ to $+0\cdot83$ e Å^{-3}. The coordinates are given in Table 2.*

Discussion

The molecular geometry for each of the alkaloid cations is shown in correct absolute configuration in the stereoscopic drawing of Fig. 1. Bond lengths and angles and deviations from the best least-squares planes through the benzenoid rings are shown in Fig. 2 for the C, N and O atoms. No data relating to the H atoms are included in Fig. 2, since in the case of isoboldine hydrobromide no H parameters were refined and most of the H atoms were omitted, and in the case of leucoxine hydrobromide the H parameters were not determined very accurately. However, for leucoxine hydrobromide the H atoms are shown in Figs. 1 and 2. The apparent C–H bond lengths for this compound range from 0·86 to 1·12 Å (average 0·99 Å); the apparent N–H and O–H lengths are 0·98 and 0·84 Å.

The agreement between corresponding bond lengths and valence angles in the two alkaloid cations is reasonably good in relation to the standard errors, and all bond lengths and valence angles are close to the expected values.

According to the system for specification of molecular chirality developed by Cahn, Ingold & Prelog (1966), the absolute configuration for each of the two cations is specified as 5S, meaning that in each



(a) (b) (c)

Fig. 2. (a) Bond lengths in Å, with standard errors. (b) Angles in degrees, with standard errors. (c) Deviations from least-squares best planes through the aromatic rings, in units of 10^{-3} Å. Deviations from rings A are enclosed in square brackets, and those from ring D are enclosed in parentheses. H atom positions are shown for the leucoxinium ion.

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* See first footnote on p. 2052.

Table 2. *Fractional coordinates* (×10⁴) *for isoboldine hydrobromide*

Atom numbers correspond to those for leucoxine hydrobromide, and there are no atoms 19 and 24.

	x	*y*	*z*
C(1)	9321 (9)	58185 (25)	24172 (61)
C(2)	9263 (8)	59545 (23)	12360 (57)
C(3)	9013 (12)	66363 (25)	8566 (66)
C(4)	8706 (12)	67061 (24)	−4100 (77)
C(5)	9463 (9)	56138 (22)	−8617 (56)
C(6)	10817 (9)	52108 (21)	−14788 (49)
C(7)	10424 (9)	45306 (21)	−12034 (53)
C(8)	10638 (10)	40875 (23)	−20855 (55)
C(9)	10338 (10)	34566 (24)	−18347 (50)
C(10)	9818 (10)	32807 (21)	−7202 (53)
C(11)	9608 (8)	37174 (21)	1407 (53)
C(12)	9906 (8)	43582 (19)	−984 (49)
C(13)	9720 (8)	48546 (21)	7890 (49)
C(14)	9784 (9)	47340 (24)	19752 (56)
C(15)	9595 (9)	52158 (25)	27999 (58)
C(16)	9478 (8)	54812 (22)	4286 (54)
C(17)	9894 (12)	54716 (35)	48313 (72)
C(18)	9773 (13)	64512 (23)	−23818 (56)
C(20)	9314 (15)	24371 (26)	5862 (66)
N(21)	9872 (7)	62969 (18)	−11101 (47)
O(22)	10031 (8)	41314 (17)	23710 (36)
O(23)	9693 (7)	50177 (19)	39327 (38)
O(25)	10558 (9)	29979 (17)	−26524 (39)
O(26)	9549 (8)	26477 (16)	−5768 (40)
Br	13841 (1)	65573 (4)	−2573 (7)

cation the configuration of the single asymmetric C atom, C(5), is *S*. The chirality of the twisted biphenyl system (rings *A* and *D*) embedded in each cation is stereospecifically linked with the chirality of the asymmetric C; that is, the former is uniquely determined by the latter (Goodwin, 1958; Shamma, 1960, 1962; Djerassi, Mislow & Shamma, 1962), and no diastereoisomerism is possible in the aporphine series. Even so, since the twisted biphenyl system is a structural feature of great interest in the aporphine alkaloids, it may be useful to specify explicitly that the axial chirality in the Cahn, Ingold & Prelog (1966) notation is 12,13-*aR* for the leucoxinium and isoboldinium cations and that the complete specification of configuration is 12,13-*aR*,5*S*.

The absolute configurations of the two alkaloid cations may also be specified as '*S* series', in a less specific use of the Cahn–Ingold–Prelog notation common in aporphine chemistry (see, for example, Vernengo, 1961; Craig & Roy, 1965). In this kind of notation, *S* series or *R* series specifies directly the axial chirality of the basic aporphine nucleus only (substituent groups on the nucleus considered replaced by H atoms), but in view of the stereospecific linking the chirality at C(5) is also specified (*S* series implies 5*S*, *etc.*). There is no conflict with our more specific notation.

The configurational assignments made in this work apply also to the free alkaloids leucoxine and isoboldine. The information is new for leucoxine. For isoboldine the assignment confirms by an independent, absolute method the assignment implied from that made for its isomer boldine from relative configurational studies with the method of optical rotatory dispersion (Craig & Roy, 1965). The only other X-ray crystallographic determination of absolute configuration in the aporphine series known to us is that of bulbocapnine (III), determined as the methiodide by Ashida, Pepinsky & Okaya (1963). The assignments made by Craig & Roy are based in part on the known absolute configuration of bulbocapnine.

In neither of the two alkaloid hydrobromides are the atoms C(1), C(13), C(12) and C(9) collinear, as they are in an isolated molecule of biphenyl. The departures from collinearity are easily discernible in Fig. 1 and are reflected in some of the deviations from coplanarity given in Fig. 2. The angle between vectors C(13) → C(1) and C(12) → C(9) is 176·2 (2)° in isoboldine.HBr and 173·7 (1)° for leucoxine.HBr. The angles C(1)···C(13)–C(12) and C(9)···C(12)–C(13) are 178·2 (4) and 177·5 (4)° in isoboldine.HBr and 174·4 (1) and 177·1 (2)° in leucoxine.HBr.

An aspect of structure of considerable interest in the aporphine alkaloid series is the degree of twist about the chiral axis C(12)–C(13). It may eventually be possible to correlate twist angles with the optical rotatory dispersion properties. The angle between the normals to the best least-squares planes through rings *A* and *D* is an approximate measure of the twist. This angle is 15·5° for leucoxine.HBr and 21·1° for isoboldine.HBr. A better measure, less subject to perturbation because of the non-collinearity of C(1), C(13), C(12) and C(9) discussed above, is the average of the two torsion or conformation angles C(16)–C(13)–C(12)–C(7) and C(14)–C(13)–C(12)–C(11) (Klyne & Prelog, 1960). These angles are 13·6 (4) and 15·0 (5)° for leucoxine.HBr (average 14·3°); and 21·2 (8) and 20·5 (1·0)° for isoboldine.HBr (average 20·9°). These twist angles are to be compared with an angle of 29·9° reported by Shamma & Slusarchyk (1964) from Ashida, Pepinsky & Okaya's (1963) determination of the structure of bulbocapnine methiodide. The three different angles (14·3, 20·9 and 29·9°) can be rationalized on the basis of the differences in the substituents on the aporphine nucleus in the three cases. There is relatively little interference in leucoxine.HBr between O(22) and the H atom on C(11); the twist is determined by the attachment of the rings *B* and *C* to the biphenyl nucleus, possibly with a slight effect from packing in the crystal. In isoboldine.HBr, however, atom O(22) is closer to the H on C(11), not being pulled away from it by ring closure with C(17); the angle C(13)–C(14)–O(22) is 120·1 (5)° in isoboldine.HBr and 127·9 (3)° in leucoxine.HBr. As a result, there is significantly more twist in the former. The C(11)···O(22) distance is 2·733 (7) in isoboldine.HBr and 2·876 (3) Å in leucoxine.HBr, indicating more in-

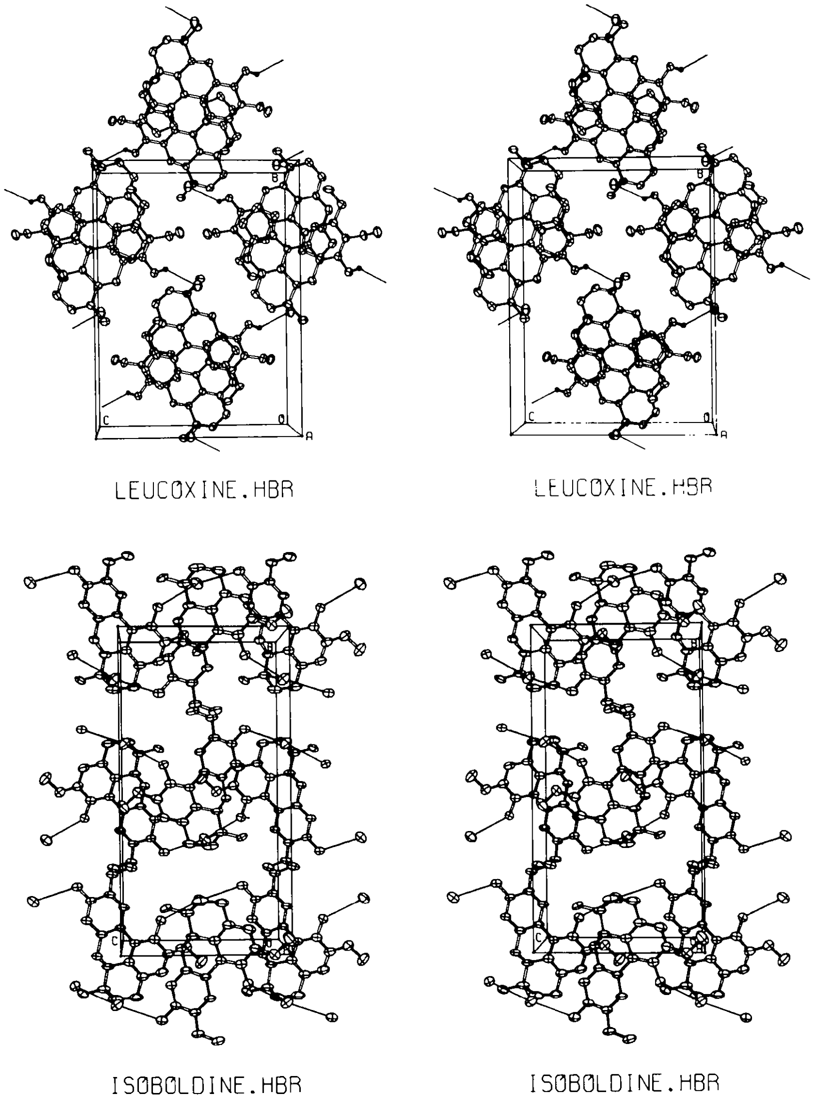

Fig. 3. Stereoscopic views showing the packing and hydrogen bonding in leucoxine hydrobromide and isoboldine hydrobromide.

Table 3. *Lengths of hydrogen bonds in leucoxine*.HBr *and isoboldine*.HBr

Leucoxine.HBr		Isoboldine.HBr	
N(21)···Br⁻	3·267 (3) Å	N(21)···Br⁻	3·199 (5) Å
O(24)···Br⁻	3·206 (2)	O(22)···Br⁻	3·215 (4)
		O(25)···Br⁻	3·177 (5)

terference in the former between O(22) and the H on C(11). The twist is greatest in bulbocapnine methiodide because of the replacement of the H on C(11) by the larger OH group, even though the five-membered ring is present in this compound, as in leucoxine. In bulbocapnine methiodide, O(22) is 0·17 Å above the plane of ring *A* and the O atom on C(11) is 0·20 Å below the plane of ring *D*. Consistent with the smaller twist angles and lesser strain in leucoxine.HBr and isoboldine.HBr, the deviation of atom O(22) from the plane of ring *A* is small in each case (see Fig. 2).

In each of the two compounds studied there appear to be weak hydrogen bonds involving N—H and OH groups as donors and bromide ions as acceptors (see Table 3). The packing and the hydrogen bonding are shown stereoscopically in Fig. 3, which shows the thermal ellipsoids of 50% probability (Johnson, 1976). The fact that for isoboldine hydrobromide the ellipsoids appear generally to be elongated in the *x* direction probably results because absorption corrections were not applied in this case. The rather thick glass fiber mentioned in a footnote above was stuck on a side of the crystal prism approximately parallel to **b**, the prism axis.

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The Crystal and Molecular Structure of Dicarbonylbis(η-cyclopentadienyl)-μ-(2,3-η-1,1,1,4,4,4-hexafluoro-2-butenyl)-dirhodium

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The structure of (η-C_5H_5)$_2$$Rh_2(CO)_2(CF_3C_2CF_3)$ has been determined from 3893 diffractometer data and refined by least squares to $R = 0{\cdot}075$. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 9{\cdot}322$ (5), $b = 12{\cdot}139$ (6), $c = 8{\cdot}671$ (5) Å, $\alpha = 103{\cdot}60$ (5), $\beta = 68{\cdot}98$ (5), $\gamma = 109{\cdot}87$ (5)°, $Z = 2$. The two Rh atoms are essentially coplanar with the four C atoms of the $CF_3C_2CF_3$ ligand; the Rh–C distances are 2·031 (10) and 2·054 (10) Å. This geometry is consistent with attachment of the ligand to the Rh atoms by two σ bonds. The ligand is *cis* bent, and the distance between the ethenyl C atoms is 1·269 (14) Å. The distance of 2·682 (1) Å between the two Rh atoms is consistent with a Rh–Rh bonding interaction. One CO group is attached to each Rh and the Rh–C–O bonds are approximately normal to the Rh_2C_4 plane. Within each molecule, the two CO groups, and consequently the two (η-C_5H_5) groups, assume a *trans* arrangement.

Introduction

Alkyne–transition-metal complexes are important intermediates in synthesis. Complexes in which the alkyne adopts a μ-bridging position between two metal atoms are of particular interest. The structures of several of these complexes have been determined by X-ray diffraction, and a representation of the main structural features is shown in Fig. 1(*a*). The alkyne is positioned normal to and above the metal–metal bond axis. The C–C distance is longer in the coordinated alkyne than in the free alkyne, and the substituents assume a *cis* bent geometry. The Co complexes $Co_2(CO)_6(RC_2R)$ (Dickson & Fraser, 1974, Table VI) and the Ni complexes (η-C_5H_5)$_2$$Ni_2(RC_2R)$ (Mills & Shaw, 1968) are typical of this class of compound.

Studies of the structures of several hexafluorobut-2-yne–dimetal complexes have revealed a different bonding mode. $(Ph_3P)_2Au_2(CF_3C_2CF_3)$ (Gilmore & Woodward, 1971), $Fe_2(CO)_6(SCF_3)_2(CF_3C_2CF_3)$ (Davidson, Harrison, Sharp & Sim, 1972) and $(Ph_3P)_2Ir_2(NO)_2(CF_3C_2CF_3)$ (Clemens, Green, Kuo,