tube) for 6 hr. The dehydrogenation product consisted, according to glpc assay, of two compounds in the ratio of 1:4.5 which could be separated by chromatography on alumina. The compound formed in minor amount (yield 9%), mp 27°, was identified as the 2,3-dihydro derivative of **2**, while the major product (46%) proved to be **2**.

4,9-Methano[11]annulenone (**2**), which was obtained as lemon yellow crystals of mp 74° (from cyclohexane), is a perfectly stable compound, remaining unchanged even after prolonged exposure to air. The ir spectrum of **2** (neat) displays one broad band in the 6–7-μ region, at 6.22 μ (1607 cm^{-1}), which apparently arises from coupled carbonyl and carbon double bond vibrations. The uv spectrum is found to be strongly solvent dependent: λ_{max} (cyclohexane) 227 (ϵ 15,000), 285 (38,000), 330 (4900, shoulder), and 392 mμ (1250, shoulder); λ_{max} (methanol) 226 (ϵ 15,700), 250 (10,300, shoulder), 292 (34,000), 335 (5300, shoulder), and 393 mμ (2600, shoulder). In the mass spectrum prominent peaks appear at *m/e* 170 (molecular ion), 142 (M − CO), and 141 (M − CO − H, base peak).

The nmr spectra of **2** in carbon tetrachloride and in acidic solvents confirm the proposed structure (Figure 1). The spectrum in carbon tetrachloride shows an AA′BB′ system at τ 2.79 and 3.1 (H_6, H_7 and H_5, H_8, respectively), an AB system at 2.82 and 3.98 with J = 12.2 Hz (H_3, H_{10} and H_2, H_{11}),[12] and another AB system at 8.32 and 9.96 with J = 11.4 Hz [*anti*-H_{12} (anti with respect to the cycloheptatriene system) and *syn*-H_{12}]. The assignments of both the olefinic protons H_5–H_8 and the bridge protons are based on the long-range couplings between H_5, H_8 and *anti*-H_{12} (J = 1.5 Hz). From a detailed analysis of the 100-MHz nmr spectrum[13] it appears that the ground state of the molecule is best represented by the polyenone structure **2**.[14] When the spectrum of **2** is recorded in deuteriotrifluoroacetic acid dramatic shifts are exhibited in accord with the expected formation of the aromatic 4-hydroxybicyclo[5.4.1]dodecapentaenylium ion (**10**). The most noticeable effect on the spectrum caused by the protonation of **2** is the large downfield shift of all the olefinic protons which now give rise to an AB system at τ 1.03 and 1.98 with J = 11.0 Hz (H_3, H_{10} and H_2, H_{11})[12] and to a singlet at 1.65 (H_5, H_6, H_7, H_8). The bridge protons on the other hand experience an upfield shift and give an AB system at τ 10.2 and 10.6 with J = 11.0 Hz. The opposite directions of shift for the protons in and above the plane of the peripheral 11-membered ring clearly indicate the presence of an induced diamagnetic ring current in the ion **10**. The aromatic stabilization of the ion **10** derives additional support from the finding that the pK_a of **10**, determined to be −0.6 ± 0.1,[15] compares well with that of protonated tropone (pK_a = −0.6 ± 0.3).[16]

4,9-Methano[11]annulenone (**2**) exhibits normal reactivity toward carbonyl reagents, *e.g.*, it forms an orange oxime (mp 197–198°) and a bright red phenylhydrazone (mp 178–179°).

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[12] This assignment is based on a comparison with the spectrum of 2,11-dideuterio-4,9-methano[11]annulenone.

[13] The analysis provides the following vicinal coupling constants for the olefinic protons H_5, H_6, H_7, and H_8 of **2**: $J_{5,6} = J_{7,8} = 6.74$ Hz and $J_{6,7} = 10.5$ Hz. These values are in close agreement with the corresponding constants of the parent hydrocarbon bicyclo[5.4.1]dodeca-2,5,7,9,11-pentaene[3] (6.02 and 10.58 Hz), but differ markedly from the nonalternating constants of the ion **1** (9.46 and 9.46 Hz) (these findings will be the subject of a separate forthcoming publication by K. Müllen, H. Günther, and E. Vogel).

[14] For a similar evaluation of the electronic structure of tropone see: D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969), and D. J. Bertelli, T. G. Andrews, Jr., and P. O. Crews, *ibid.*, **91**, 5286 (1969).

[15] Determined spectrophotometrically in aqueous sulfuric acid solution using Hammett's H_0 acidity values.

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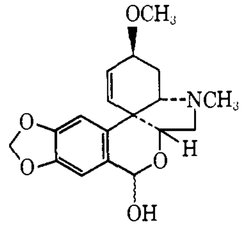
Molecular Structure and Absolute Configuration of Alkaloids Related to 5,10-Ethanophenanthridine[1]

Sir:

Previous chemical transformations have interrelated the alkaloids pretazettine (**1**), haemanthamine (**2a**), and montanine (**3**) as well as the artifact, tazettine (**4**).[2] Absolute configurations for these alkaloids and **4** were originally assigned by empirical arguments based on Mill's rule.[3] Extension of these observations in ORD and CD spectra[4,5] of the compounds led to ambiguous results. The elegant and detailed chemical degradations of dihydrotazettine[6] indicate that the assignments of absolute configurations shown for **1**–**4** were indeed correct. Because of biosynthetic interest in several laboratories concerning the mechanism of *in vivo* benzylic oxidation, and for better correlations of ORD and CD data with the absolute configuration and physiolog-



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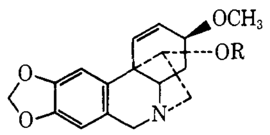
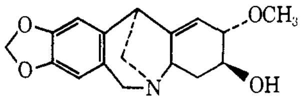


2a, R = H
b, R = COC_6H_4Br (para)



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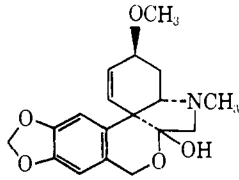

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 2796. Additional support was derived from a grant from the National Institutes of Health (HE-07503).

[2] W. C. Wildman and D. T. Bailey, *J. Amer. Chem. Soc.*, **91**, 150 (1969). For a summary of these alkaloid interconversions see: W. C. Wildman, *Alkaloids*, **6**, 343 (1960).

[3] J. A. Mills, *J. Chem. Soc.*, 4976 (1952).

[4] G. G. DeAngelis and W. C. Wildman, *Tetrahedron*, **25**, 5099 (1969).

[5] K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hameda, R. Mitsui, and K. Takeda, *J. Chem. Soc. B*, **46** (1967).

[6] R. J. Highet and P. F. Highet, *Tetrahedron Lett.*, 4099 (1966).

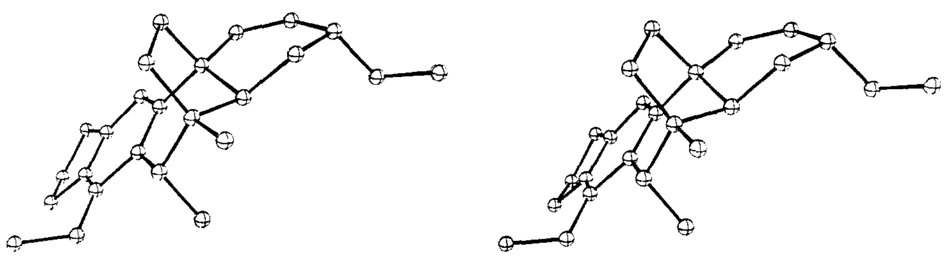


Figure 1. Stereoscopic plot of 6-hydroxybuphanidrine (**5**) methiodide.

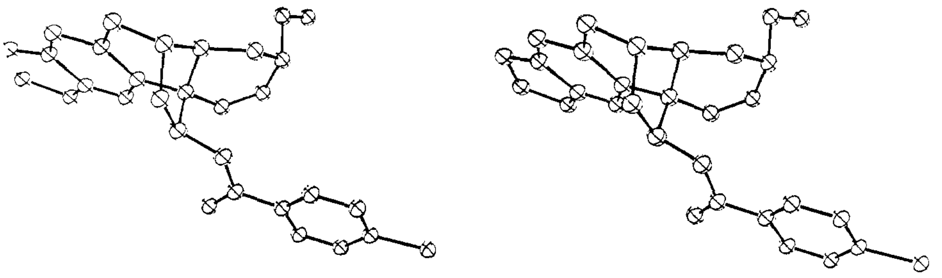
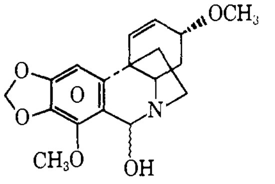


Figure 2. Stereoscopic plot of haemanthamine *p*-bromobenzoate (**2b**).

ical activity of these and related compounds, independent proof of absolute configuration by X-ray crystallographic methods was most desirable.

Two alkaloid derivatives (**2b** and the methiodide of **5**) were selected for study. Chronologically, **2b** was examined first, but preliminary crystallographic data suggested inconclusive results might be obtained concerning the absolute configuration of the molecule. With the recent isolation of **5** and its chemical structure known with certainty from degradative studies,[7] the absolute configuration of a suitable derivative of **5** was undertaken as well.



5

The methiodide of 6-hydroxybuphanidrine (**5**) belongs to the orthorhombic system with $a = 20.02 \pm 0.01$, $b = 13.62 \pm 0.01$, and $c = 7.24 \pm 0.01$ Å. Density measurements indicated four molecules per unit cell and the systematic extinctions $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), and $00l$ ($l = 2n + 1$) uniquely determine the space group as $P2_12_12_1$ ($D_2{}^4$). The unique reflections ($2\theta \leq 110°$) were collected on an automated Hilger–Watts diffractometer using filtered Cu (1.5418 Å) radiation. Of the 1229 reflections measured, 1178 were judged observed after background and LP corrections. During data collection a right-handed coordinate system was used. The iodine position was determined from a three-dimensional Patterson synthesis, and the remaining 24 nonhydrogen atoms were located in subsequent electron-density syntheses. Full-matrix least-squares refinements in which all atomic positions and anisotropic temperature factors were successively varied (255 parameters) and in which the iodine scattering factor was corrected for an anomalous contribution[8] were performed for the structure and its enantiomer. The final unweighted R factors were 0.083 and 0.052 for the 1178 observed data. A list of reflections with significant differences between Friedel pairs was made, and these reflections and their Friedel pairs were remeasured on the diffractometer. The observed differences in the Friedel pairs indicated that the structure with the lowest R factor was correct.[9] A computer-generated stereoscopic drawing[10] of the correct absolute configuration (less the iodine atom) is given in Figure 1. The only detail, other than the absolute configuration of this alkaloid, which was in doubt was the configuration of the 6-hydroxyl group. This hydroxyl group is quasi-axially oriented and the O–O distance to the *O*-methyl is 3.04 Å, which is too long for a strong hydrogen bond[11] to the neighboring aromatic methoxyl group. This observation is consistent with the infrared spectrum.

The second alkaloid examined was haemanthamine *p*-bromobenzoate (**2b**). Preliminary photographs indicated that the crystal system was monoclinic with $a = 9.11 \pm 0.01$, $b = 13.13 \pm 0.01$, $c = 8.91 \pm 0.01$ Å, and $\beta = 85.57 \pm 0.04°$. Systematic extinctions ($0k0$ for k odd) and density measurements indicated space group $P2_1$ ($C_2{}^2$) and one molecule per asymmetric unit. Data collection was performed as described above; of the 1626 measured data, 1350 were retained after background and LP corrections. The position of the bromine was determined from the three-dimensional Patterson synthesis. Despite the pseudomirror plane, 30 nonhydrogen atoms were located in subsequent normal and difference electron-density syntheses. Both the structure and its mirror image were fully refined by full-matrix least squares to unweighted R factors of 0.058

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[7] M. Slabaugh, unpublished Ph.D. Thesis, Iowa State University, Ames, Iowa, 1970.

[8] K. Lonsdale, Ed., "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

[9] W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

[10] C. K. Johnson, Oak Ridge National Laboratory, Oak Ridge, Tenn., Report No. ORNL-3794, 1965.

[11] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 87.

and 0.059, respectively, for the observed data. Friedel pairs were checked and results indicated that the structure with the smaller R possessed the correction absolute configuration.[9] A computer-generated drawing[10] of this configuation of haemanthamine p-bromobenzoate is given in Figure 2.

These results show that the correct absolute configuration of the crinine-, tazettine-, and montanine-type Amaryllidaceae alkaloids are in complete agreement with the degradation studies performed by Highet and Highet.[6]

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Preparation of Some Ditertiary Phosphine and Arsine Derivatives of Dicobalt Octacarbonyl. The Structure of $(CH_3)_2As\overline{C{=}CAs(CH_3)_2CF_2C}F_2Co_2(CO)_6$

Sir:

Many examples of tertiary phosphine and arsine derivatives of dicobalt octacarbonyl are now known. Some of these contain bridging carbonyl groups,[1,2] some do not,[3] and others are thought to exist in solution as an equilibrium mixture containing both carbonyl-bridged and nonbridged species.[4] This behavior is similar to that of the parent cobalt carbonyl which has been shown to exist in solution as a mixture of bridged and nonbridged species.[5]

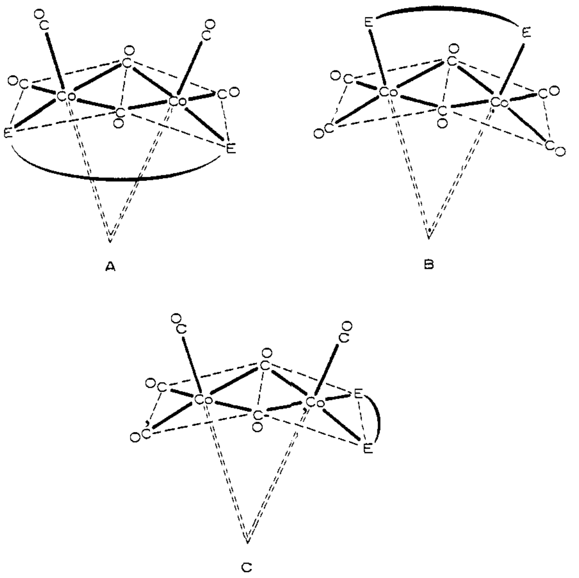


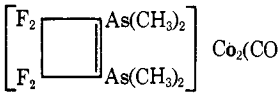
Figure 1. Possible structures for (ligand)$Co_2(CO)_6$. The ligand is represented by EE.

Table I. C–O Stretching Frequencies of (Ligand)$Co_2(CO)_6$[a]

Compd	Terminal CO				Bridging CO	
I	2052 (6)	2020 (8)	1996 (10)		1842 (3)	1786 (3)
II	2066 (1)	2052 (5)	2022 (8)	1998 (10)	1842 (2)	1798 (2)
III	2068 (5)	2006 (6)	1996 (10)		1812 (1)	1800 (3)
IV	2072 (6)	2007 (8)	2000 (10)		1816 (2)	1802 (4)

[a] Spectra were run on a Perkin-Elmer Model 457 spectrometer in C_6H_{12} solution. Values are listed in cm^{-1} and relative intensities are given in parentheses.

We have prepared a series of disubstituted ditertiary phosphine and arsine cobalt carbonyl derivatives which exist in solution exclusively as the carbonyl-bridged form; furthermore we have evidence to show that these compounds have a structure where the bifunctional ligand as well as the two carbonyl groups bridge the cobalt atoms. The fluorocarbon-bridged ligands used in this investigation reacted with dicobalt octacarbonyl in hexane at room temperature, to give, after purification, the following reddish crystalline solids. Purification was effected by chromatography on Fluorisil followed by crystallization from hexane. All compounds decomposed on heating to about 100°. Analyses for the species prepared are as follows: calcd for I: C, 27.1; H, 1.9; F, 12.3; found: C, 27.3; H, 2.0; F, 12.0; calcd for II: C, 52.3; H, 2.6; F, 9.7; found: C, 52.0; H, 2.5; F, 9.8; calcd for III: C, 25.6; H, 1.8; F, 17.3; found: C, 25.7; H, 1.9; F, 17.0; calcd for IV: C, 24.2; H, 1.9; F, 17.7; found:



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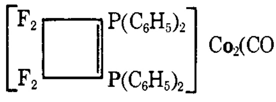

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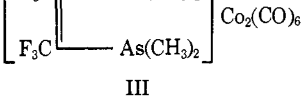

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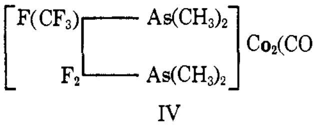

IV

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