

This chromatographic separation allowed the isolation of three main components. The major product⁷ was obtained as an amorphous powder in the initial fractions (benzene elution) whereas the remaining two alkaloids were isolated from the later fractions (benzene and benzene-ether elutions, respectively). The alkaloid isolated from the later benzene fractions was amorphous and showed an indole chromophore in the ultraviolet spectrum ($\lambda_{\text{max}}^{\text{MeOH}}$ 226, 285, and 293 m μ). The presence of an ester carbonyl infrared absorption ($\lambda_{\text{max}}^{\text{CCl}_4}$ 5.85 μ) and the stability of this ester group to acidic hydrolysis⁸ suggested that this alkaloid was probably a member of the Iboga series. Indeed, comparison (infrared and thin layer chromatography) of this amorphous alkaloid with an authentic sample of coronaridine (V)^{9,10} showed these to be identical. A further comparison (mixture melting point and infrared spectrum) of the crystalline hydrochlorides completely established the identity. The alkaloid isolated from the benzene-ether elution was crystalline, m.p. 143–145.5° (from petroleum ether, b.p. 60–80°), $[\alpha]^{25D} +49^\circ$ (CHCl₃), and its spectral properties (indole absorption in the ultraviolet and ester carbonyl absorption in the infrared) indicated another possible relative of the Iboga series, namely dihydrocatharanthine (VI). We prepared an authentic sample of dihydrocatharanthine by catalytic reduction of catharanthine^{1,11} and were able to confirm (mixture melting point, infrared spectrum, and thin layer chromatography) that the above mentioned product was indeed dihydrocatharanthine (VI).

The isolation of both coronaridine and dihydrocatharanthine from this transannular cyclization process indicates that isomerization at C-4 takes place during this reaction. This is not entirely unexpected since the iminium intermediate, assigned structure IV, could isomerize to an enamine bearing a double bond at the C-4–C-5 position. The mobility of the enamine-iminium system is well known.^{12,13}

We feel that the synthesis of these alkaloids provides an interesting synthetic approach to the Iboga alkaloids.

(8) This ester group was found to survive the acidic conditions normally used for the removal of the carbomethoxy group in vincadifformine.⁷

(9) M. Gorman, N. Neuss, N. J. Cone, and J. A. Deyrup, *J. Am. Chem. Soc.*, **82**, 1142 (1960).

(10) We are very grateful to Dr. M. Gorman for providing us with an authentic sample of coronaridine.

(11) The sample of catharanthine (as its hydrochloride) was kindly supplied by Dr. M. Gorman, Eli Lilly Laboratories. We cannot reconcile the difference in our melting point and rotation values with the reported¹ ones (m.p. 63–65°, $[\alpha]^{25D} +33^\circ$ (CHCl₃)) except to say that all our data are completely consistent with that expected for dihydrocatharanthine.

(12) N. J. Leonard, A. S. Hay, R. W. Fulmer, and V. W. Gash, *J. Am. Chem. Soc.*, **77**, 439 (1955).

(13) N. J. Leonard, W. J. Middleton, P. D. Thomas, and D. Choudhury, *J. Org. Chem.*, **21**, 344 (1956).

Since the decarboxylation of the C-18 carbomethoxy function is also well known,^{9,14} it is obvious that this sequence provides a synthesis of ibogamine¹⁵ and ep-ibogamine¹ as well.

Apart from its chemical interest, the above synthesis establishes the fact that the type of transannular cyclization reaction originally postulated in Wenkert's biosynthetic hypothesis³ can be realized in the laboratory. It will be of interest to determine whether nature follows this course as well.

Acknowledgment.—Financial aid from the National Cancer Institute of Canada and the National Research Council of Canada is gratefully acknowledged.

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(15) M. F. Bartlett, D. F. Dickel, and W. I. Taylor, *J. Am. Chem. Soc.*, **80**, 126 (1958).

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RECEIVED APRIL 2, 1964

The Geometry of Manganese Pentacarbonyl Hydride. An X-Ray Diffraction Study¹

Sir:

The geometry and the nature of the metal-hydrogen bond in the hydride complexes of the transition metals have been the subjects of intense study in recent years.² We report here the results of an X-ray diffraction study of the crystal structure of manganese pentacarbonyl hydride, Mn(CO)₅H, which was undertaken preparatory to a neutron diffraction study intended to determine a precise value for the Mn—H bond length. Inasmuch as this represents the first crystallographic study of a typical, simple, transition metal carbonyl hydride, and because the results will help to clarify or nullify a great deal of the speculation which has appeared in the literature regarding the geometry of these compounds, we feel that a communication at this time is warranted.

Manganese pentacarbonyl hydride³ is typical of a group of compounds ML_nH_x, where M is a transition metal, the ligand L is usually cyclopentadienyl, carbonyl, or cyano, and x is usually 1 or 2. The electron diffraction investigation⁴ of Fe(CO)₄H₂ and Co(CO)₄H, the classic compounds of this type, seemed to indicate that the carbonyls are disposed in a tetrahedral arrangement about the metal atom; the hydrogen atoms were not located, although Ewens and Lister assumed that the hydrogen atoms must be attached *via* C=O—H bonds. High resolution nuclear magnetic resonance studies of this group of compounds⁵ indicate that the hydrogen atom is always highly shielded and hence in a region of high electron density. It thus seems certain that a metal-hydrogen bond is involved, and some investigators⁶ have proposed an abnormally short length (1.2 Å. or less) for this bond. Lohr and Lipscomb⁵ have shown, however, that a simple molecular orbital description of the bond-

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. Chatt, *Proc. Chem. Soc.*, 318 (1962).

(3) W. Hieber and G. Wagner, *Z. Naturforsch.*, **13b**, 339 (1958).

(4) R. V. G. Ewens and M. W. Lister, *Trans. Faraday Soc.*, **35**, 681 (1939).

(5) L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, **3**, 22 (1964), and references quoted therein.

(6) F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 4425 (1958).

ing, with normal covalent bond lengths of about 1.5–1.6 Å., can lead to the observed high shielding.

$\text{Mn}(\text{CO})_5\text{H}$ crystallizes in the monoclinic space group $I2/a$ with cell constants $a = 12.18 \pm 0.02$, $b = 6.35 \pm 0.01$, $c = 19.20 \pm 0.03$ Å., and $\beta = 93.3 \pm 0.5^\circ$. There are eight molecules in the unit cell, and the calculated density is 1.75 g/cm³. Crystals were grown from the liquid phase by cooling in a stream of cold nitrogen gas, and the sample temperature was held constant at -75° during the X-ray photography. The intensities of 594 independent reflections were recorded photographically with a Buerger precession camera, using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å.). The intensities were visually estimated and reduced to structure amplitudes in the usual way. The Mn atom was located from the Patterson function, the carbon and oxygen atoms from an electron density map with the Mn atom subtracted, and the complete structure, including anisotropic temperature factors, but omitting the hydrogen atom, was refined by the least-squares method. The final value of the agreement factor $R = \sum ||F_{\text{obsd}}| - |F_{\text{calcd}}|| / \sum |F_{\text{obsd}}|$ is 0.045. The standard deviations in the final coordinates are about 0.0015 Å. for Mn and 0.007 Å. for the light atoms. A difference electron density synthesis calculated at this point exhibited a few peaks as high as 0.35 electron/Å.³, but there was no convincing indication of the hydrogen atom position.

The molecule has the geometry and dimensions indicated in Fig. 1. The proposed hydrogen position (for which there is no direct evidence) is also indicated. The molecular symmetry departs insignificantly from C_{4v} , and, if the hydrogen is in the suggested position, the coordination about the manganese atom is octahedral, as suggested by Lohr and Lipscomb for the $\text{CoH}(\text{CN})_5^{-3}$ ion. C_{4v} symmetry is not consistent with the interpretations offered by Wilson⁷ and by Cotton, Down, and Wilkinson⁸ for the gas-phase infrared spectrum of the compound. We consider it unlikely that the configuration in the gas phase is different from that in the solid, and suggest that a reinvestigation of the complex infrared spectra is in order.

The crystal structure is markedly similar to that of $\text{Mn}_2(\text{CO})_{10}$.⁹ If one breaks the Mn—Mn bond in the latter compound and moves the $\text{Mn}(\text{CO})_5$ fragments apart by about 3 Å., one obtains very nearly the structure found here. Two $\text{Mn}(\text{CO})_5\text{H}$ molecules are related by a twofold axis, much as the two halves of the $\text{Mn}_2(\text{CO})_{10}$ molecule are related, so that the fourfold axes of the molecules are directed toward the crystallographic twofold axis. This implies that the molecules pack so that the hydrogen atoms of the two molecules are probably in contact.

If we assume that the H atoms lie along the $\text{O}_1\text{—C}_1\text{—Mn}$ line and further assume that, as seems reasonable, the hydrogen atoms are in van der Waals contact at a distance between 2.2 and 2.6 Å., we can calculate that the Mn—H bond length lies between 1.6 and 1.4 Å. We feel that the value of 1.6 is an upper limit, but we can be considerably less certain about the lower value.

The short intermolecular $\text{H} \cdots \text{H}$ distance is perhaps

(7) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958).

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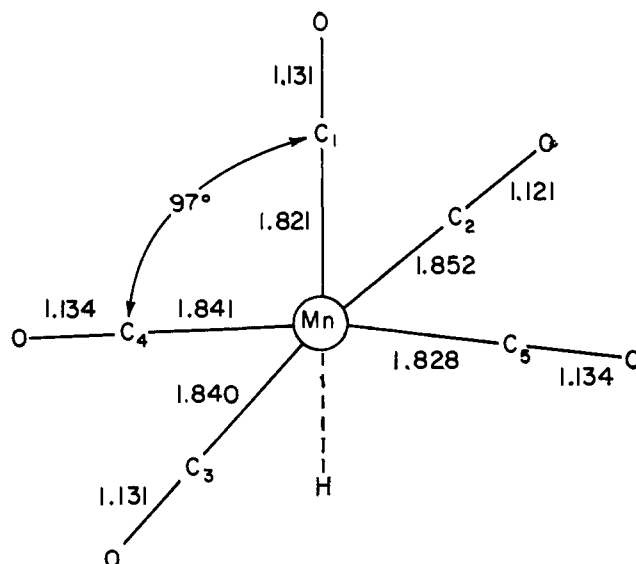


Fig. 1.—Geometry of the $\text{Mn}(\text{CO})_5\text{H}$ molecule. The position of the hydrogen atom is assumed. The molecule has approximate C_{4v} symmetry. The estimated standard deviations of the bond lengths are about 0.01 Å. The 97° angle indicated for the angle $\text{C}_1\text{—Mn—C}_4$ is an average of the four values actually found for $\text{C}_1\text{—Mn—C}_{\text{base}}$: $97.4, 96.9, 95.9,$ and 96.7° , each with an estimated standard deviation of 0.4° .

pertinent with regard to the conclusions drawn from the broad line n.m.r. spectrum of $\text{Fe}(\text{CO})_4\text{H}_2$,¹⁰ where the assumption that the observed second moment was due only to an intramolecular $\text{H} \cdots \text{H}$ distance forced the authors to derive a low value (1.88 Å.) for this distance and hence a bond length in the neighborhood of 1.1 Å. for the geometries assumed. In view of the result here, we consider it a strong possibility that the observed line width of the n.m.r. spectrum in $\text{Fe}(\text{CO})_4\text{H}_2$ is due to a sum of contributions from an intramolecular interaction at a distance corresponding to a more reasonable bond length^{11,12} and an intermolecular contact of the magnitude inferred here.

In conclusion, we feel that the results of this investigation should encourage further investigations of these compounds by structural chemical techniques. In addition to a neutron diffraction investigation, we are contemplating a broad-line n.m.r. study, which together with an assumption of C_{4v} symmetry will allow a determination of the Mn—H bond length.

Acknowledgment.—We wish to thank Professor W. N. Lipscomb for providing us with a sample of $\text{Mn}(\text{CO})_5\text{H}$ and to Dr. Kohji Shimaoka for the design of the low temperature apparatus.

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RECEIVED MARCH 31, 1964

The Molecular Structure of the Methyl Ester of *o*-Nitrobenzenesulfenic Acid¹

Sir:

There have been no reports of definitive molecular structures for sulfenic acids or their esters. We

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.