Fig. 1.—Cyclooctane at −135°: (1) C_8H_{16}; (2) $C_8D_{15}H$; (3) $C_8D_{15}H$, D decoupled.

of the massively deuterated[3] hydrocarbon. Hexa-deuterio-1,3-butadiene[4] was photodimerized in the presence of acetophenone[5] to give a 6:1 mixture of the *trans*- and *cis*-1,2-divinylcyclobutanes. The *cis* compound is readily converted to 1,5-cyclooctadiene.[5,6] The *trans* compound isomerized on heating overnight at 190° to give a mixture of 1,5-cyclooctadiene and 4-vinylcyclohexene.[7] The deuterated cyclooctadiene was chromatographically separated and reduced with deuterium gas in the presence of Adams' catalyst. Mass spectrographic analysis[8] on the resulting cyclooctane yielded the following: C_8D_{16}, 39.9%; C_8HD_{15}, 36.1%; $C_8H_2D_{14}$, 16.1%; $C_8H_3D_{13}$, 5.29%; $C_8H_4D_{12}$, 2.21%.

The n.m.r. spectra were taken in vinyl chloride solution on a Varian Model V-4302 60 Mc./sec. spectrometer equipped with a "deuterium decoupler."[9] The deuterated cyclooctane gave a broad line (8.56 τ) at −50°; this became quite sharp under double irradiation at the deuterium resonance frequency. As the temperature was lowered, the sharp line broadened and separated into two distinct lines, in the usual manner.[10] The coalescence temperature, T_c, was −111.5 ± 0.5° Below −135°, the chemical shift between the peaks remained constant at 18.8 ± 0.1 c.p.s. (Fig. 1).

From the changes in signal shape between −101° and −118°, the rates of ring inversion at various temperatures were calculated. The method of Gutowsky and Holm[11] was used below T_c; above T_c, an equation of line-broadening derived from eq. 10-29, ref. 10, was applied and corrected for the effects of the transverse relaxation time by a calculation based on eq. 10-23, ref. 10. From the Arrhenius plot of the results (Fig. 2), the activation energy for the ring inversion process was

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(4) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961); A. T. Morse and L. C. Leitch, *ibid.*, **23**, 990 (1958).

(5) G. S. Hammond, N. J. Turro and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(6) E. Vogel, *Ann.*, **615**, 1 (1958).

(7) The latter probably resulted from reversion to butadiene, followed by Diels-Alder dimerization.

(8) Kindly carried out by Dr. F. P. Lossing of the National Research Council of Canada.

(9) Manufactured by NMR Specialties.

(10) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N.Y., 1959, Chapter 10.

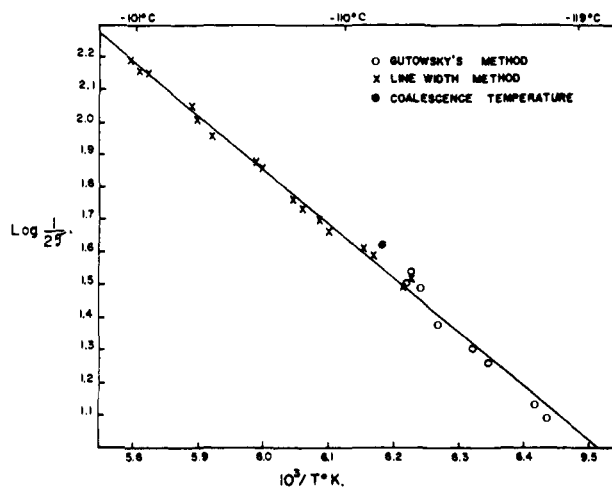(11) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

Fig. 2.—Temperature dependence of the inversion rate constant, $1/2\tau$; 2τ is the average lifetime in seconds of a proton on either site in the molecule.

calculated to be 7.7 ± 0.3 kcal./mole. Application of transition state theory showed that, at T_c, the free energy of activation was 8.1 kcal./mole and the entropy of activation was −4.4 e.u.

The presence of only two lines in the low temperature spectrum indicates that only one conformation, or one group of easily interconverted conformations, exists. This is in accord with fairly well established evidence of a skewed crown conformation in cyclooctane and its derivatives.[12] A further investigation supplied additional evidence for the crown model. Deuterated 1,5-cyclooctadiene was reduced with non-deuterated diimide.[13] This reduction has been shown[14] to give exclusively *cis* addition of hydrogen. The cyclooctane product must therefore contain two groups of *cis* vicinal protons at the 1,2 and 5,6 positions. The dihedral angle between *cis* protons in the crown conformation is expected to be close to 90°; hence, according to the Karplus relationship,[15] the vicinal coupling should be small. At −135°, the low field peak showed splitting of 2.85 ± 0.4 c.p.s.; this was obscured in the high field peak. This small splitting may be due to coupling of *cis* vicinal protons. It could also be due to the presence of two distinct species in which the two pairs of *cis* vicinal protons are *cis* or *trans* to each other. In either case, the absence of large *cis* vicinal coupling supports a crown or skewed crown conformation.

(12) N. L. Allinger, S. P. Jindal and M. A. DaRooge, *J. Org. Chem.*, **27**, 4290 (1962), and papers cited therein.

(13) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

(14) E. J. Corey, D. J. Pasto and W. L. Mock, *ibid.*, **83**, 2957 (1961); S. Hünig, H.-R. Müller and W. Thier, *Tetrahedron Letters*, **11**, 353 (1961).

(15) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

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STEREOCHEMISTRY OF THE MANGANESE(II)-PYRIDOXYLIDENEVALINE CHELATE[1]

Sir:

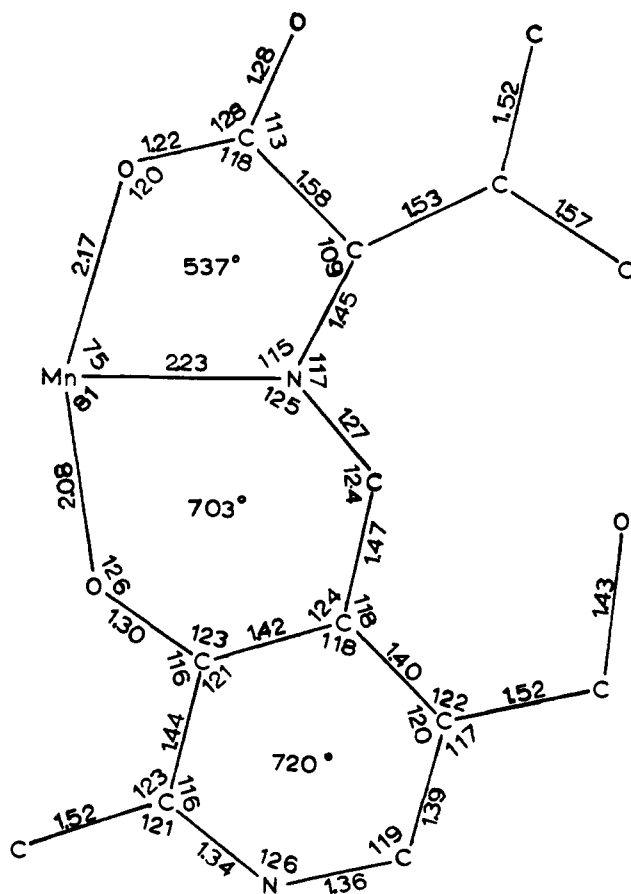Chelation of the Schiff bases derived from pyridoxal and amino acids to transition-period cations gives rise to

Fig. 1.—The *quasi*-planar ring skeleton of one PyrVal⁻ chelated to Mn⁺⁺. Bond lengths and angles are as shown; the sum of the interior angles in each ring appears at the ring center. The pyridine ring, including all directly attached atoms, is essentially flat; the other rings, which include Mn(II), are necessarily somewhat folded and twisted (see text). Bond lengths (with standard deviations mostly >0.015 Å.) are generally compatible with the model postulated by earlier workers.

complexes which have received attention as model substances for the transaminase enzyme systems.[2-5] Christensen's appraisal[4] of the stereochemical possibilities open to these complexes poses several rather fundamental questions which we have undertaken to answer through X-ray analysis of crystalline structure. Preliminary results are reported herein for the manganese(II) chelate of pyridoxylidenevaline, Mn(Pyr-Val)₂, prepared following Christensen[4] except for the use of D,L-valine instead of L-valine as a starting material[6]; the special virtue of this preparation was to furnish crystals usable for structure determination.

The Mn(II) chelate crystallizes in the space group *Pcan* with $a = 9.15 \pm 0.02$, $b = 16.84 \pm 0.01$, $c = 19.765 \pm 0.01$ Å. The unit cell contains 4Mn(Pyr-Val)₂ and, in principle, 16H₂O (one set of eight fold positions is incompletely filled). Three-dimensional

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(3) J. B. Longenecker and E. E. Snell, *ibid.*, **79**, 142 (1957).

(4) H. N. Christensen, *ibid.*, **79**, 4073 (1957).

(5) E. E. Snell and W. T. Jenkins, *J. Cellular Comp. Physiol.*, **54**, Supplement. 161 (1959).

(6) The use of L-valine gave crystals of the Mn(II), Cu(II), and Fe(III) chelates agreeing closely with Christensen's description of his products, of which none was usable for structure determination; the Fe(III) chelate, for example, displayed an astonishing internal disorder. The use of D,L-valine gave crystals of the Mn(II) and Cu(II) chelates which, at least superficially, were very different from those obtained with L-valine. These unanticipated observations suggest incomplete racemization of the amino acid prior to crystallization of the chelate, and are to receive further study.

intensity data from a crystal plate having about one-tenth of the optimum volume wanted with MoKα radiation in the technique described earlier[7] were counter-recorded for the range, $(\sin\theta)/\lambda < 0.65$. Some 1100 independent {*hkl*}, about 40% of normal expectancy, were measurable above background; the use of an alternative radiation was impracticable for various reasons. The intensity data sufficed, nonetheless, for structure determination by Patterson and Fourier methods to give results which are qualitatively certain and quantitatively illuminating. At a late stage of refinement, with use of anisotropic thermal parameters for individual atoms, the conventional R is 0.10 for the 1100 observable {*hkl*} amplitudes. The more pertinent bond parameters of the molecule are shown on Fig. 1.

Octahedral coördination for manganese is achieved with the one pattern (apart from its enantiomorph) which can allow essential planarity of the fused ring systems; a twofold axis bisecting opposite pairs of octahedral edges renders the two PyrVal⁻ of a molecule structurally equivalent. The distortion from planarity in the ring skeleton of a PyrVal⁻ chelated to the excessively large Mn⁺⁺ is bound to be significant, with the detailed pattern determined in part by packing relations in the crystal. A bowing of the fused ring system along its principal axis and a rather more important twisting about this axis combine to give a dihedral angle of roughly 150° between the mean planes of the pyridine and valinate rings. Of interest in this connection is the following intermolecular hydrogen bonding: carboxylate oxygen to pyridine nitrogen at 2.68 Å., the second carboxylate oxygen to a water molecule at 2.69 Å., and this same water molecule to methanolic oxygens of two complexes at 2.65 and 2.74 Å. It is readily calculable that the use of cations small enough to give complexing bonds averaging <2.0 Å. would go far toward minimizing ring strain in a chelated Pyr-Val⁻.

Christensen's studies[4] led him to postulate especially weak complexing of phenolic oxygen to M(II) ions (excepting Cu(II) in the 1:1 chelate), but our data (Fig. 1) lead to precisely the opposite conclusion. Although detailed correlations with bonding theory must await a full report, our stereochemical data seem generally to qualify the chelate type of Fig. 1 for the postulated role of catalytic intermediate in the reactions of interest.[2,3,5] We hope to learn more about the disconcerting behavior of these systems during crystallization,[6] and to obtain internally well ordered crystals suitable for the authoritative evaluation of bond parameters.

(7) J. V. Silverton and J. L. Hoard, *Inorg. Chem.*, **2**, 243 (1963).

(8) Author to whom correspondence should be addressed.

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BON-BON, A NOVEL 6-MEMBERED HETEROCYCLE CONTAINING BORON, OXYGEN AND NITROGEN

Sir:

In a study of the reaction between nitric oxide and tri-*n*-butyl-borane which will be described elsewhere, we have obtained some new boron compounds which, upon hydrolysis, yield di-*n*-butylborinic acid and N-*n*-butyl-hydroxylamines. It is the purpose of this communication to describe the synthesis and characterization of these compounds.

The addition of an alcoholic solution of hydroxylamine to di-*n*-butylborinic acid results in the immediate