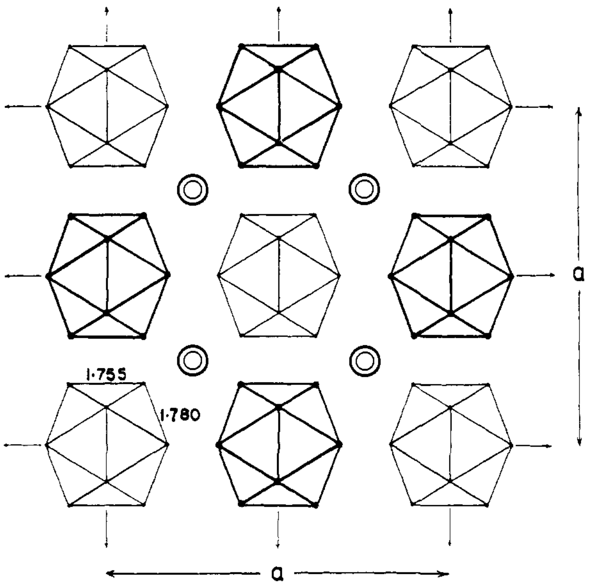

Fig. 1.—The unit cell of $K_2B_{12}H_{12}$, with the center of symmetry at the origin. The icosahedra have been drawn at two-thirds of their proper size in order to avoid overlap. Icosahedra at level zero are indicated by lighter lines, and those at level $^1/_2$ are indicated by heavier lines. Double circles indicate K^+ at levels $^1/_4$ and $^3/_4$.

by 24 H atoms at a distance of 2.29 Å. (σ = 0.06 Å.). The B–H bond length of 1.07 Å. (σ = 0.06 Å.) is short, but just within 3 standard deviations of the average B–H distance of 1.21 Å. found in boron hydrides and their derivatives.[6]

We wish to thank Dr. M. F. Hawthorne for supplying us with the sample, and the National Institutes of Health and the Air Force Office of Scientific Research for financial support.

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(6) W. N. Lipscomb, "Advances in Inorganic and Radiochemistry," Vol. I, Academic Press, New York, N. Y., p. 117.

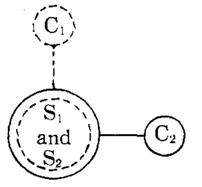
DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.
JEFFREY A. WUNDERLICH
WILLIAM N. LIPSCOMB

RECEIVED JULY 5, 1960

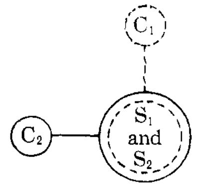
THE ENERGY BARRIER BETWEEN THE ENANTIOMERS OF 1,2-DITHIANE[1]

Sir:

The dihedral angle in an organic disulfide can produce two different molecular conformations, I and II.



I



II

These are optical antipodes, and their stability depends on the height of the rotational barrier hindering free rotation about the disulfide bond. We have studied the interconversion between the enantiomers of 1,2-dithiane by nuclear magnetic resonance. This molecule gives, however, a very complicated n.m.r. spectrum, and therefore we prepared a deuterium-substituted derivative (III).

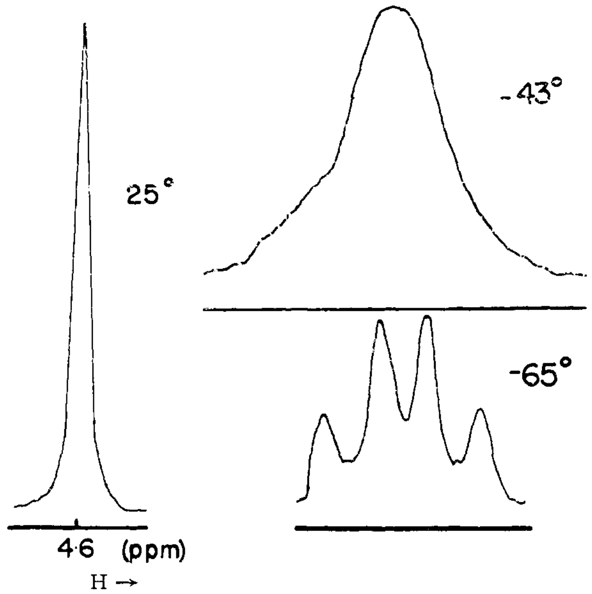
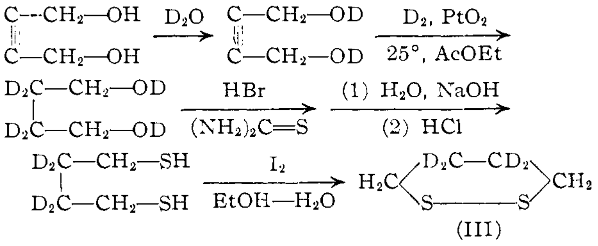


Fig. 1.—Proton magnetic resonance spectra at 60 Mc./sec. of 1,2-dithiane-4,5-H^2_4 referred to benzene.



$$\begin{array}{l}C—CH_2—OH\\ \;\|\!|\\ C—CH_2—OH\end{array} \xrightarrow{D_2O} \begin{array}{l}C—CH_2—OD\\ \;\|\!|\\ C—CH_2—OD\end{array} \xrightarrow[25°,\ AcOEt]{D_2,\ PtO_2}$$

$$\begin{array}{l}D_2C—CH_2—OD\\ \;|\\ D_2C—CH_2—OD\end{array} \xrightarrow[(NH_2)_2C{=}S]{HBr} \xrightarrow[(2)\ HCl]{(1)\ H_2O,\ NaOH}$$

$$\begin{array}{l}D_2C—CH_2—SH\\ \;|\\ D_2C—CH_2—SH\end{array} \xrightarrow[EtOH—H_2O]{I_2} H_2C\begin{array}{c}D_2C—CD_2\\ S\text{———}S\end{array}CH_2$$

(III)

From low temperature studies of a 1 *M* solution in carbon disulfide we obtained data which provide an estimate of the rotational barrier for this molecule.[2]

At temperatures below −50° the spectrum consists of a quartet of the AB type[3] (Fig. 1). The maximum separation of the two inner peaks is 10.4 c./sec., and the coupling constant is 13.0 c./sec. When the temperature is raised above −50°, the peaks in the quartet start to converge, and at −43° the spectrum consists of one single broad peak. As the temperature increases above −43°, the peak sharpens and remains constant up to the highest temperature studied (150°).

From the low temperature pattern the chemical shift between the axial and equatorial hydrogens, γ_a–γ_e, was calculated as 18.5 c./sec. We assumed that the following relation for the rate of interconversion[4] holds approximately at −43°, the temperature where the peaks coalesce

$$k = \pi(\nu_a - \nu_e)/\sqrt{2}$$

From this we calculated the rate constant k = 41.1 sec.$^{-1}$.

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(1) The work described in this paper was supported in part by the U.S. Atomic Energy Commission.

(2) A Varian high-resolution n.m.r. spectrometer V-4311, operating at 60 Mc./sec. was used to obtain the spectra.

(3) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, New York, N.Y., 1959, p. 119.

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

If the interchange from one isomer to the other

is treated as a typical rate process, and the transmission coefficient is equal to unity, then Eyring's equation gives $\Delta F = 11.6$ kcal./mole. Thus the molecular conformations have a very short lifetime. Even at $-43°$ the half-life for the enantiomers is only 0.02 sec.

Rotatory dispersion in a disulfide absorption band indicating the asymmetry resulting from restricted rotation about the disulfide bond has indeed been observed in substances containing another asymmetric-inducing center.[5]

The same measurements on cyclohexane[6] with similar assumptions give a value of 9.7 kcal./mole for ΔF^*. If the six-membered rings are inverted by passing through intermediate boat forms, only one methylene opposition is involved in the transition through the maximum barrier in dithiane as compared to four in cyclohexane. Thus, one estimation of the ΔF^* for disulfide rotation alone (in the cyclic compound) might be about 9.2 kcal./mole. Since the maximum dihedral angle in the six ring is likely to be about 60°, the energy difference (ΔF^*) between 0° and 90° (assuming a cos dependence[7]) would be 12.3 kcal./mole. The entropy of activation (ΔS^*) for this reaction is, however, not known, and we must await a direct measurement of the temperature coefficient to evaluate the heat term.[8] Since the entire transition in the spectrum from a single line to a quadruplet occurs between -40 and $-50°$, precise temperature control and simpler spectra would be desirable. Experiments toward this end are in progress.

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(5) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Company, Inc., New York, N. Y., 1960, p. 223.

(6) F. R. Jensen, D. S. Noyce, C. H. Sederholm and A. J. Berlin, THIS JOURNAL, **82**, 1256 (1960).

(7) W. G. Dauben and K. S. Pitzer in "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 55.

(8) D. W. Scott, H. L. Finke, M. E. Gross, G. R. Guthrie and H. M. Huffman, THIS JOURNAL, **72**, 2424 (1950); D. W. Scott, H. L. Finke, J. P. McCullough, M. E. Gross, R. E. Pennington and G. I. Waddington, *ibid.*, **74**, 2478 (1952); G. Bergson and L. Schotte, *Arkiv. Kemi*, **13**, 43 (1958).

(9) Postdoctoral Fellow 1959–1960. On leave of absence from the University of Uppsala, Uppsala, Sweden. Appointment supported by the International Cooperation Administration under the Visiting Research Scientists Program administered by the National Academy of Sciences of the United States of America.

DEPARTMENT OF CHEMISTRY AND LAWRENCE RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA
GÖRAN CLAESON[9]
GAYLORD M. ANDROES
MELVIN CALVIN

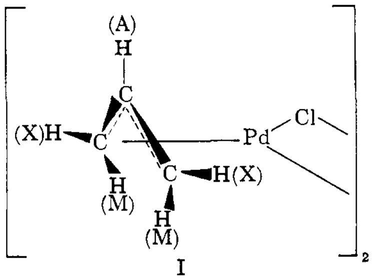
RECEIVED JUNE 23, 1960

STRUCTURES OF THE ALLYL AND CROTYL PALLADIUM CHLORIDE COMPLEXES

Sir:

The allylpalladium chloride (I) and crotylpalladium chloride (II) complexes[1] are unusually stable for organometallic halides. Our nuclear magnetic resonance (n.m.r.) results favor a non-classical structure for each compound.[2] Infrared spectra also support these assignments.

The 60-mc. spectrum shows that I has three types of protons in the ratio of 1:2:2. Several structures can be eliminated immediately. The structure with the allyl group σ-bonded to Pd should have four types of protons. The structure which has an additional π-Pd bond should have four or five different kinds of protons. Also excluded is the possibility of rapid allylic rearrangement observed[3] for allylmagnesium bromide which has only two types of protons. The structure consistent with the observed n.m.r. spectrum is the non-classical one shown where the dotted lines are electron deficient bonds.



I

In the calculation of the AM_2X_2 system, all off-diagonal matrix elements between Ψ_m and Ψ_n were neglected when they differed in any of the total spin components $F_z(A)$, $F_z(M)$ or $F_z(X)$ because the chemical shifts between protons were many times greater than the coupling constants. At 60 mc. the spectra parameters in c.p.s. are

$$\delta_A = 52.5,\ \delta_M = 135.2,\ \delta_X = 197.4$$

$$|J_{AM}| = 6.4,\ |J_{AX}| = 12.8 \text{ and } |J_{MX}| \approx 0$$

The corresponding values obtained at 15.1 mc. are

$$\delta_A = 13.0,\ \delta_M = 33.8\ \delta_X = 51.0$$

$$|J_{AM}| = 6.5,\ |J_{AX}| = 12.9 \text{ and } |J_{MX}| \approx 0$$

From the 60-mc. spectrum of II it is clear that one of the X-protons has been replaced by the methyl group. In place of the 135.2–c.p.s. doublet in I, resulting from the two equivalent M-protons, is now a group of peaks centered at 146 c.p.s. produced by protons M and M′. (The M′ proton and the methyl group are bonded to the same carbon atom.) The total area is still equivalent to two protons. The nuclear system excluding the methyl group is considered to be AMM′X. The spectra parameters in c.p.s. are

$$\delta_A = 57.9,\ \delta_{M'} = 146.1,\ \delta_M = 143.1,\ \delta_X = 209.7$$

$$\delta_{CH_3} = 299,\ |J_{AM}| = 6.3,\ |J_{AM'}| = 12.0$$

$$|J_{AX}| = 11.5,\ |J_{M'CH_3}| = 6.0, \text{ and } |J_{MX}| \approx 0$$

The protons M and X bonded to the same carbon atom in I differ by 62.2 c.p.s. in their chemical shift values. A similar large difference of 40.2 c.p.s. between the α- and the β-protons in the C_5H_6 ring was observed in $(\pi\text{-}C_5H_5)(C_5H_6)Co$.[4] H$\alpha$, which has a higher chemical shift value than Hβ, is on the

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(1) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959).

(2) A Varian Associates 60-mc. and 15.1-mc. high resolution n.m.r. spectrometer and a Beckmann IR-7 spectrometer were used in this work. All solutions were 10% in $CDCl_3$. The n.m.r. peaks were referred to an external benzene standard. The complexes I and II were prepared as described previously[1] and gave correct analyses.

(3) J. E. Norlander and J. D. Roberts, THIS JOURNAL, **81**, 1769 (1969).

(4) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).