in the near infrared corresponding to the $b_2 \rightarrow b_1$ (σ^*) "d–d" transition. Such a band is observed at 10,250 cm.$^{-1}$ (ϵ = 8.3 in acetone), in excellent quantitative agreement with theory. All other "d–d" bands are expected to be hidden under the intense charge transfer spectrum.

An acetone solution of $Fe(NO)[S_2CN(CH_3)_2]_2$ shows a sharp e.s.r. spectrum consisting of three bands spaced by 12.5 gauss with $\langle g \rangle = 2.04$. The $\langle g \rangle$ factor is expected for the $^2B_1$ ground state; the hyperfine splitting is due to the nitrogen of the NO group. The calculated one electron m.o. energies may be used, along with an estimate of 50 cm.$^{-1}$ for the spin–orbit coupling constant for Fe^+ in $Fe(NO)^{2+}$ to predict the anisotropy of the $\langle g \rangle$ value[8]; this gives $g_{\parallel} = 2.04$, $g_{\perp} = 2.03$. By analyzing the e.s.r. spectrum of $Fe(NO)[S_2CN(CH_3)_2]_2$ in Styrofoam,[9] the experimental values $g_{\parallel} = 2.04$, $g_{\perp} = 2.02$ were obtained, in close agreement with theory.

For the $Mn(CO)_5X$ series, radiocarbon monoxide exchange experiments indicate that the axial CO is bound much more strongly than the other four CO groups,[10] and thus these compounds fit the description of the model. There are six electrons from Mn to place in the m.o.'s, giving a $^1A_1\{[e(\pi^b)]^4[b_2]^2\}$ ground state. The first charge transfer band for solutions of these compounds in chloroform is observed[11] at 26,670 cm.$^{-1}$ (ϵ = 1200, $X^- = NO_3^-$), 26,520 cm.$^{-1}$ (ϵ = 620, $X^- = Cl^-$), 25,870 cm.$^{-1}$ (ϵ = 420, $X^- = Br^-$) and 24,750 cm.$^{-1}$ (ϵ = 390, $X^- = I^-$). These bands are assigned to the $b_2 \rightarrow e(\pi^*)$ transition. The $n \rightarrow \pi^*$ assignment also is supported by the fact that the maximum of the band for $Mn(CO)_5Br$ is shifted to higher energies on increasing the polarity of the solvent employed (350 cm.$^{-1}$ shift from benzene to ethanol).

The m.o. energy level scheme also has been used successfully to account for the spectral and magnetic properties of $M(H_2O)_5NO^{n+}$ [12] and $M(CN)_5NO^{n-}$ [12,13] type complexes.

---

[8] A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc.* (*London*), **A205**, 135 (1951).

[9] I. Bernal and H. B. Gray, to be published.

[10] A. Wojcicki and F. Basolo, *J. Am. Chem. Soc.*, **83**, 525 (1961).

[11] C. C. Addison, M. Kilner and A. Wojcicki, *J. Chem. Soc.*, 4839 (1961).

[12] H. B. Gray and P. T. Manoharan, unpublished results.

[13] H. B. Gray and C. J. Ballhausen, *J. Chem. Phys.*, **36**, 1151 (1962).

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK 27, NEW YORK

HARRY B. GRAY
IVAN BERNAL
ERNST BILLIG

RECEIVED APRIL 16, 1962

ON THE SIGNS OF CH AND HH COUPLING CONSTANTS

Sir:

Although theoretical calculations have indicated that both geminal and vicinal HH coupling constants should be positive in sign,[1] it has been found recently that their signs are opposite in several typical molecules.[1] In order to determine which of the two theoretical calculations leads to the correct result, one must know the absolute signs of the HH coupling constants. Karplus[1] has suggested that these signs may be obtained by comparisons with directly-bonded CH coupling constants, whose signs are almost certainly positive. We have determined the relative signs of directly-bonded CH and vicinal HH coupling constants in several molecules by double resonance experiments similar to those proposed by Karplus,[1] with the results outlined below.

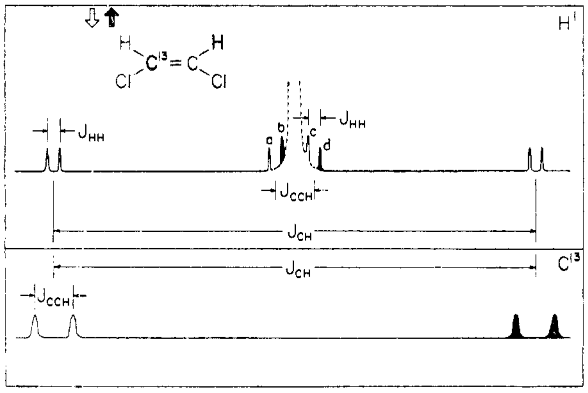
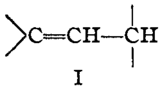


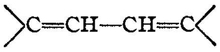
Fig. 1.—Diagrammatic spectra.

The first experiment, carried out on *cis*-1,2-dichloroethylene, containing C^{13} in natural abundance, will be described in some detail to illustrate the techniques and principles involved. Diagrammatic spectra are shown in Fig. 1. The black peaks in the H^1 and C^{13} spectra correspond to the "up" orientation of the proton directly bonded to C^{13}. Irradiation of the high field (low frequency) doublet in the C^{13} spectrum at a frequency of about 15.085 Mcps. and an rf. field of about 10 to 20 milligauss while observing the inner C^{13} satellites in the H^1 spectrum at 60 Mcps. caused peaks b and d to move inward. Irradiation of the low-field C^{13} doublet, at a frequency about 200 cps. (J_{CH}) higher, caused peaks a and c to draw together. It follows that the sign of the HH coupling constant is the same as that of the one-bond CH coupling constant. *trans* HH couplings in substituted ethylenes have been found to be of the same sign as *cis* couplings,[2] as have couplings between protons in the relationships I[3] and II.[4]



$$>C{=}CH{-}\overset{|}{\underset{|}{C}}H$$

I



II

All, therefore, probably are positive.

To determine the signs of vicinal couplings in saturated compounds, a double resonance experiment similar to that described above was performed on 1,2-dichloroethane. The sum of the vicinal HH couplings was found to have the same sign as the CH coupling. Since large geminal couplings

---

[1] See M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962), for a review and references.

[2] S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958); C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960); E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); S. Castellano and C. Caporiccio, *J. Chem. Phys.*, **36**, 566 (1962).

[3] F. S. Mortimer, *J. Mol. Spectroscopy*, **3**, 335 (1959); A. D. Cohen and N. Sheppard, *Proc. Roy. Soc.*, **A252**, 488 (1959); B. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **30**, 944 (1959); A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); R. Freeman, *Mol. Phys.*, **4**, 385 (1961).

[4] J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959).

in several representative saturated compounds have been found to be of sign opposite to the large vicinal couplings,[5] it seems very likely that the former are negative and the latter positive, as Karplus suggested.[1]

An apparent exception to these generalizations is found in the spectra of substituted ethylene oxides, in which the geminal and both vicinal coupling constants have been reported to be of the same sign.[6] Furthermore, an analysis of the spectrum of epichlorohydrin appears to show that the coupling constants among the ring protons are of the same sign as the large geminal coupling constant in the chloromethyl group,[7] although the vicinal couplings to that group are of opposite sign. If the spectral analyses were correct and the geminal coupling constant in the chloromethyl group is normal, both the geminal and the vicinal coupling constants in the epoxide ring would be negative. This apparent anomaly was investigated by a double resonance experiment on ethylene oxide, in which the vicinal coupling constants[8] are about the same as in epichlorohydrin.[7] We found that the CH coupling constant and the sum of the vicinal HH coupling constants are of the same sign, presumably positive. It seems likely, therefore, that the analysis of the epichlorohydrin spectrum was in error.[9]

The authors wish to thank Nuclear Magnetic Resonance Specialties for making double resonance equipment available for this work, Mrs. Jane Ratka for some of the samples, and Mr. Charles B. Krabek for measurements on some of the spectra.

---

(5) R. R. Fraser, R. U. Lemieux and J. D. Stevens, *J. Am. Chem. Soc.*, **83**, 3901 (1961); F. Kaplan and J. D. Roberts, *ibid.*, **83**, 4666 (1961); K. A. McLauchlan, J. I. Musher, K. G. R. Pachler and R. Freeman, *Mol. Phys.*, in press.

(6) H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959); C. A. Reilly and J. D. Swalen, *ibid.*, **32**, 1378 (1960); **34**, 980 (1961).

(7) C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, **35**, 1522 (1961).

(8) N. Sheppard and J. J. Turner, *Proc. Royal Soc.*, **A252**, 506 (1959).

(9) It has been found recently that a calculation assuming opposite signs for the $-CH_2Cl$ and ring geminal coupling constants gives a better fit to the observed spectrum: C. A. Reilly and J. D. Swalen, private communication.

(10) Multiple Fellowship on Silicones sustained by the Dow Corning Corporation and Corning Glass Works.

(11) This work was supported in part by a grant from the National Science Foundation.

MELLON INSTITUTE
DEPARTMENT OF CHEMISTRY
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURGH 13, PA.

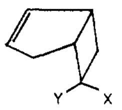
PAUL C. LAUTERBUR[10]
ROBERT J. KURLAND[11]

RECEIVED JULY 6, 1962

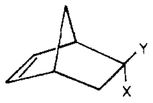
THE INTRAMOLECULAR THERMAL REARRANGEMENT OF THE BICYCLO[3.2.0]-HEPTENYL TO THE BICYCLO[2.2.1]HEPTENYL SYSTEM

Sir:

We wish to report the stereospecific thermal isomerization of *syn-cis*-bicyclo[3.2.0]hept-2-enyl-6-acetate (I) to *exo*-5-norbornenyl-2-acetate (III), an example of a new type of intramolecular rearrangement.[1,2]



I, X = H; Y = OAc
II, X = OAc; Y = H



III, X = H; Y = OAc
IV, X = OAc; Y = H

V

Reduction of the ketene–cyclopentadiene adduct[3–6] V with sodium borohydride[7] gives a mixture of alcohols I (Y = OH) (75%) and II (X = OH) (25%), whereas sodium–ethanol reduction of V gives 30% I (Y = OH) and 70% II (X = OH). Stereochemical equilibration[8] (fluorenone, aluminum *t*-butoxide–benzene) of the mixture of alcohols from the hydride reduction gives a I (Y = OH):II (X = OH) ratio of 45:55. Hydrogenation[9] of either the 75:25 or 30:70 mixture above and then stereochemical equilibration gives a dihydro-I (Y = OH):dihydro-II (X = OH) ratio of 48:52. The stereochemical assignments are based on the assumptions that hydride reduction occurs from the less hindered side[10] and that sodium reduction produces the more stable epimer.

Acetylation of the 75:25 mixture above and then preparative vapor chromatographic separation (3.7 m. × 2.2 cm. tri-β-cyanoethoxypropane (TCEP)-on-firebrick column at 120° and 1100 ml./min. helium flow) gives pure I,[9] $n^{20}\text{D}$ 1.4697, and pure II,[9] $n^{20}\text{D}$ 1.4652.

Heating a 0.6 *M* solution of I in decalin at 300° causes conversion to II, III, IV, vinyl acetate, and cyclopentadiene. Identification of the products is achieved by analytical vapor chromatography (46-m. capillary column at 120°, with TCEP as the stationary phase) of the reaction mixtures as such as well as after lithium aluminum hydride reduction to a mixture containing the four unsaturated alcohols (I–IV, OAc = OH) and subsequent hydrogenation to a mixture containing the four saturated alcohols (dihydro I–IV, OAc = OH). Under the same conditions of pyrolysis, II gives qualitatively the same mixture of products, but the reaction is slower and the proportions of products are different from those obtained from I.

Although cyclopentadiene and vinyl acetate do combine to give III and IV under these conditions, the major if not the entire path for the I→III conversion in the early stages of the reaction does not involve fragmentation to and Diels-Alder recombination of these addends: The III:IV (*exo:endo*) ratio from I is 9.4 after 60 minutes of pyroly-

---

(1) For a previous attempt to observe a reaction of this type, see C. A. Stewart, Jr., *J. Am. Chem. Soc.*, **84**, 117 (1962).

(2) For formal analogs, which however have not been shown to be intramolecular, see (a) J. J. Drysdale, U.S. Patent 2,861,095; C.A., **53**, 9102 (1959); (b) J. J. Drysdale, U.S. Patent 2,813,320; C.A. **54**, 11118 (1960).

(3) B. T. Brooks and G. Wilbert, *J. Am. Chem. Soc.*, **63**, 870 (1941).

(4) A. T. Blomquist and J. Kwiatek, *ibid.*, **73**, 2098 (1951).

(5) For further discussion of the structure of V, see J. D. Roberts and W. F. Gorham, *ibid.*, **74**, 2278 (1952).

(6) In a modification of the reported[3,4] conditions, we have prepared V by keeping a mixture of the reactants at room temperature rather than at 100°. The reaction seems to be exothermic, and in one run carried out *without solvent*, a serious explosion occurred.

(7) For a report of this reduction using lithium aluminum hydride, see H. L. Dryden and B. E. Burgert, *J. Am. Chem. Soc.*, **77**, 5633 (1955).

(8) W. von E. Doering and T. Aschner, *ibid.*, **71**, 838 (1949).

(9) The material obtained had the correct elementary analysis.

(10) For a reasonably close analogy, see O. L. Chapman, D. J. Pasto, G. W. Borden and A. A. Griswold, *J. Am. Chem. Soc.*, **84**, 1220 (1962).