

is in the *boat* conformation<sup>8</sup> and is slightly staggered to relieve the transannular strain due to the intraannular interactions of the hydrogen atoms on carbons 4, 5, 7 and 8. The interatomic distances and the relevant bond angles are summarized in Fig. 1.

The infrared spectra of the complexes were measured in potassium bromide. In all cases the absorption bands characteristic of the cyclooctadiene double bonds at 1660 cm.<sup>-1</sup> (C=C) and 710 cm.<sup>-1</sup> (=CH) were absent. New bands appearing at 1612 cm.<sup>-1</sup> and 746 cm.<sup>-1</sup> were assigned to the complexed olefin. The spectrum of Ia exhibited a pair of bands at 1230 cm.<sup>-1</sup> and 1192 cm.<sup>-1</sup> of equal intensity, complexes Ib and Ic exhibited a similar pair of bands at 1238 cm.<sup>-1</sup> and 1188 cm.<sup>-1</sup>, the intensity of the former being approximately twice that of the latter. A minor difference was also observed in a pair of bands that occurred at 971 cm.<sup>-1</sup> and 966 cm.<sup>-1</sup> in Ia and at 971 cm.<sup>-1</sup> and 957 cm.<sup>-1</sup> in Ib and Ic. X-Ray powder diffraction data also show that the structure of complex Ia is different from complexes Ib and Ic.

Hendra and Powell<sup>9</sup> have suggested that the cuprous chloride-COD-1,5-complex prepared from hydrochloric acid solution involves the *chair* conformer of the olefin rather than the *boat*. The infrared spectra of complexes Ia-c are virtually identical with that reported by these authors. Since the crystal structure determination of Ic has shown that the complexed olefin exists in the *boat* conformation, it would certainly appear that complexes Ia-c all involve the *boat* conformation of the olefin. If this were not the case, then the various complexes should exhibit major differences in the 1000-500 cm.<sup>-1</sup> region where most of the absorption bands are due to the skeletal vibrations of the eight-membered ring. We believe that the minor spectral differences observed between Ia and Ib and Ic may be attributed to two structurally different complexes. Complexes Ib and Ic possess the determined dimeric structure; complex Ia is polymeric and consists of COD molecules in the *boat* conformation joined by exocyclic cuprous chloride bridging. The spectral differences may then reside in the non-symmetrical nature of Ib and Ic as opposed to the more symmetrical structure of Ia.

A more complete structural analysis of this complex will be reported elsewhere.

(8) COD-1,5 has been found to exist in the *boat* configuration in its rhodium chloride complex; J. A. Ibers and R. G. Snyder, *Acta Cryst.*, **15**, 923 (1962).

(9) P. J. Hendra and D. B. Powell, *Spectrochim. Acta*, **17**, 913 (1961).

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## EVIDENCE FOR THE EXISTENCE OF AN ORGANODITIN DIHYDRIDE<sup>1</sup>

Sir:

We wish to record what we believe to be the first preparation of an organoditin dihydride, specifically, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.

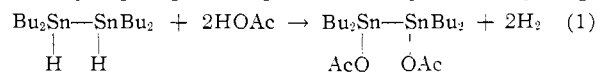
1,1,2,2-Tetra-*n*-butyl-1,2-dichloroditin,<sup>2</sup> prepared by treating 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin with hydrogen chloride in anhydrous ether, was reduced<sup>3</sup>

(1) We thank M and T Chemicals, Inc., for support of a portion of this work.

(2) A. J. Gibbons, A. K. Sawyer and A. Ross, *J. Org. Chem.*, **26**, 2304 (1961).

(3) This reduction was attempted by J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, Middlesex, England, 1958. It was later shown by the following workers that the compound which they believed to be 1,1,2,2-tetra-*n*-butyl-1,2-dichloroditin was in reality bis-(di-*n*-butylchlorotin) oxide: (a) ref. 2; (b) D. L. Alleston and A. G. Davis, *Chem. Ind.* (London), 949 (1961); (c) O. H. Johnson, *J. Org. Chem.*, **25**, 2292 (1960).

by lithium aluminum hydride in anhydrous ether to give the colorless liquid, 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin (76%) (found: Sn, 50.51; calcd. for C<sub>16</sub>H<sub>36</sub>Sn<sub>2</sub>H<sub>2</sub>: Sn, 50.75), *n*<sub>D</sub><sup>20</sup> 1.5205. A large Sn-H absorption band was found at 1795 cm.<sup>-1</sup> with a faint shoulder at 1835 cm.<sup>-1</sup>. The reaction of this hydride with a 100% excess of glacial acetic acid over that required by eq. 1 gave a quantitative yield of hydrogen



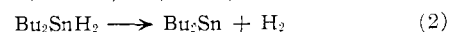
and 1,1,2,2-tetra-*n*-butyl-1,2-diacetoxyditin. That the product of this reaction is a ditin was shown by its quantitative reaction with bromine forming di-*n*-butylacetoxybromotin<sup>4</sup> isolated in 70% yield. In previous work it has been shown that di-*n*-butyltin dihydride reacts with two moles of acetic acid to produce di-*n*-butyltin diacetate.<sup>4</sup> It follows that di-*n*-butyltin dihydride is not present in appreciable amount in the reduction product, which, therefore, must be 1,1,2,2-tetra-*n*-butyl-1,2-dihydroditin.

This hydride is more reactive toward acid than is di-*n*-butyltin dihydride, and, on exposure to air, rapidly forms a white solid whose tin analysis corresponds to that for di-*n*-butyltin oxide.

Formation of this ditin dihydride, or a polytin dihydride,<sup>5</sup> is indicated in other reactions of di-*n*-butyltin dihydride.

(a) Di-*n*-butyltin dihydride reacts with acetone to form isopropyl alcohol and di-*n*-butyltin.<sup>6</sup> Infrared spectra of the reaction product mixture taken at intervals showed not only the disappearance of Sn-H absorption of di-*n*-butyltin dihydride at 1835 cm.<sup>-1</sup> but also the simultaneous appearance of new Sn-H absorption at about 1785 cm.<sup>-1</sup>.

(b) Decomposition of di-*n*-butyltin dihydride at 100° constitutes a method for the preparation of di-*n*-butyltin. (Found: C, 41.34; H, 7.78; Sn, 51.10. Calcd.



for C<sub>8</sub>H<sub>18</sub>Sn: C, 41.45; H, 7.79; Sn, 50.96.) Infrared spectra of the reaction product mixture taken during the decomposition showed a decrease in the intensity of the Sn-H absorption at 1835 cm.<sup>-1</sup> accompanied by the appearance and increase in intensity of a Sn-H band at 1780 cm.<sup>-1</sup>; when the decomposition was somewhat more than 70% complete, only the latter band remained. Decrease in intensity of this band required prolonged heating.

(c) Treatment of di-*n*-butyltin with di-*n*-butyltin dihydride in a 1:1 molar ratio results in new Sn-H absorption at about 1780 cm.<sup>-1</sup>.

It has been reported by Neumann and König<sup>5</sup> that, in the case of diphenyltin dihydride, substitution of one hydride hydrogen by tin results in a lowering of the frequency of Sn-H absorption to about 1790 cm.<sup>-1</sup>.

(4) (a) A. K. Sawyer and H. G. Kuivila, *J. Am. Chem. Soc.*, **82**, 5958 (1960); (b) A. K. Sawyer and H. G. Kuivila, *J. Org. Chem.*, **27**, 610 (1962).

(5) W. P. Neumann and K. König, *Angew. Chem.*, **74**, 215 (1962).

(6) H. G. Kuivila and O. F. Beumel, *J. Am. Chem. Soc.*, **83**, 1246 (1961).

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## THE ASSIGNMENT OF N.M.R. SPECTRA USING THE NUCLEAR OVERHAUSER EFFECT

Sir:

In the analysis of nuclear magnetic double resonance (n.m.d.r.) experiments, three main effects must be considered: the perturbation of individual spin systems by the second r.f. field which gives rise to transitions



Fig. 1.—Frequency sweep n.m.r. spectra of *cis*-CHFCHF in  $\text{CCl}_3\text{F}$  at 60.0 Mc.: (A) single resonance spectrum, and double resonance spectra with strong irradiation at (B) line a, (C–D) line h and (E–F) line i.

not present in the single resonance spectrum; the effect of a strong r.f. field on the mean lifetime of states, or nuclear "stirring"; and changes in intensity in the presence of the second r.f. field due to deviations of steady-state populations from the Boltzmann distribution, or the Overhauser effect. In general, some combination of these effects will be observed.<sup>1,2</sup>

In the limit of short relaxation times the Overhauser effect is less important than the perturbation of individual spin systems. This case has been analyzed carefully for several types of spin systems.<sup>1,3–6</sup> If at least some of the relaxation times of a system are sufficiently long, it should be possible to observe an Overhauser effect in the presence of a second r.f. field of such low amplitude that the individual spin systems are not perturbed. Since transitions which have no energy levels in common may exhibit an Overhauser effect, energy level relationships which are not revealed

by perturbing individual spin systems<sup>7</sup> should be important in the limit of long relaxation times. The information that can be obtained from the nuclear Overhauser effect in *cis*-1,2-difluoroethylene is described in this note.

The single resonance frequency sweep spectrum<sup>4,7</sup> for *cis*-1,2-difluoroethylene in  $\text{CCl}_3\text{F}$  solution is shown in Fig. 1, A.<sup>8</sup> The assignment of this AA'XX' system has been described previously.<sup>9,10</sup> The double resonance spectrum obtained by irradiation of line a is shown in Fig. 1, B. Lines c, d, g, h and j decrease in intensity while the remaining lines are essentially unchanged. The double resonance spectra obtained by irradiation of line h for two different values of the amplitude of

(7) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

(8) These traces are recorded by sweeping the audio frequency which modulates the magnetic field and observing the first sideband. Since the modulation index is proportional to the inverse of the modulating frequency, the amplitude and phase of the sideband change as the frequency is swept. This effect can be distinguished from the Overhauser effect by comparing changes in relative intensity with respect to the single resonance spectrum. The spurious features appearing between peaks c and d and near peak i in all the spectra occur at modulating frequencies of precisely 600.0 and 666.7 c.p.s. for any sample.

(9) G. W. Flynn, M. Matsushima, J. D. Baldeschwieler and N. C. Craig, *J. Chem. Phys.*, in press.

(10) G. W. Flynn and J. D. Baldeschwieler, *ibid.*, **38**, 226 (1963).

(1) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, **37**, 85 (1962).

(2) B. D. Nageswara Rao and J. D. Baldeschwieler, unpublished work.

(3) J. D. Baldeschwieler, *J. Chem. Phys.*, **36**, 152 (1962).

(4) R. Freeman and D. H. Whiffen, *Proc. Phys. Soc. (London)*, **79**, 794 (1962).

(5) B. D. Nageswara Rao and J. D. Baldeschwieler, *J. Chem. Phys.*, **37**, 2473 (1962).

(6) A. L. Bloom and J. N. Shoolery, *Phys. Rev.*, **97**, 1261 (1955).

the second r.f. field,  $H_2$ , are shown in Fig. 1, C and D. In Fig. 1, C, line d decreases in intensity while the remaining lines are essentially unchanged. When  $H_2$  is increased, line d almost disappears while line c splits into a broad doublet. The double resonance spectra obtained by irradiation of line i are shown in Fig. 1, E and F. The behavior of these spectra is complementary to those for irradiation of line h.

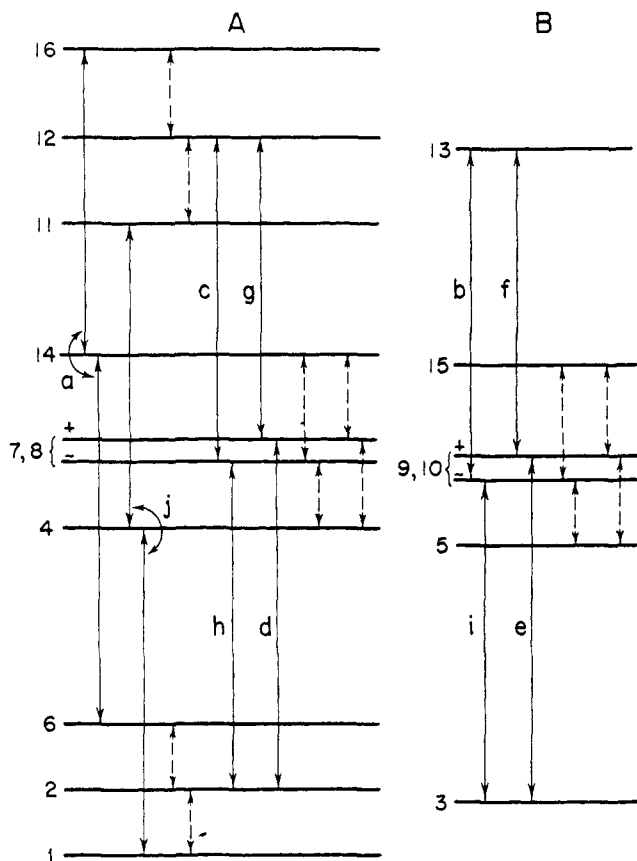


Fig. 2.—Schematic energy level diagram for an AA'XX' system of spins  $1/2$ .

A schematic energy level diagram for an AA'XX' system, assuming K, L, M and N positive, is shown in Fig. 2. The diagram is separated into states belonging to the  $A_1$  and  $B_1$  representations of the symmetry group  $C_{2v}$ . The transitions indicated by solid lines represent proton single resonance transitions and are labeled a through j in correspondence with Fig. 1, A. Fluorine single resonance transitions are indicated by dashed lines. Since transitions a and j have no energy levels in common with proton transitions of different frequencies, an Overhauser effect on the remaining proton lines when line a or j is irradiated can occur only if the fluorine relaxation times are much shorter than the proton relaxation times. If line a is irradiated, the population of level 6 will be decreased and that of level 16 will be increased. Fluorine relaxations can restore the Boltzmann distribution among levels 1, 2 and 6, and independently among levels 11, 12 and 16. Thus the populations of levels 1, 2 and 6 will be decreased, while the populations of levels 11, 12 and 16 are increased and transitions c, g, h, d and j will all be decreased in intensity as in Fig. 1, B. Since transition a belongs to the  $A_1$  symmetry representation, this result unambiguously identifies the other transitions belonging to the  $A_1$  representation. The assignment of the lines to symmetry representations enables the parameters K and M to be distinguished, and shows that  $J_{HH}$  and  $J_{FF}$  are opposite in sign.<sup>9</sup>

Spectra C–F of Fig. 1 are consistent with the above assignment. For these experiments some of the pertinent transitions have energy levels in common. Thus, in the estimation of intensities from peak heights, perturbations of individual spin systems must be considered.<sup>7</sup> For instance, when line h is irradiated, the intensity of line c should increase, but for sufficiently large  $H_2$  it splits into a broad doublet. Thus, while the intensity may be increased by the Overhauser effect, the relation of peak height to intensity is obscured by the change in line shape. On the other hand, line d should decrease in intensity when line h is irradiated, and for larger  $H_2$ , line d should be split into a sharp doublet. In this case the Overhauser effect is clear. The interpretation of spectra E and F of Fig. 1 is entirely complementary to that of spectra C and D.

From the qualitative interpretation of these experiments it is possible to obtain the relative sign of two coupling constants and information on the relative fluorine and proton relaxation times. It is apparent from these spectra that even in the liquid phase there is no important relaxation mechanism connecting states belonging to different symmetry representations.<sup>11</sup>

The sample of *cis*-1,2-difluoroethylene was kindly supplied by Professor Norman C. Craig of Oberlin College. The financial support of the National Science Foundation and an Alfred P. Sloan Grant to J. D. B. are gratefully acknowledged.

(11) G. W. Flynn and J. D. Baldeschwieler, *J. Chem. Phys.*, **37**, 2907 (1962).

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IDENTITY OF SYNTHETIC N<sup>6</sup>-β-GLYCERYLLYSINE AND THE C<sup>14</sup>-LABELED AMINO ACID OBTAINED ON SODIUM BOROHYDRIDE REDUCTION AND HYDROLYSIS OF A COMPLEX FROM C<sup>14</sup>-FRUCTOSE 6-PHOSPHATE-TRANSALDOLASE INTERACTION<sup>1</sup>

Sir:

The results of recent investigations of the interaction of rabbit skeletal muscle aldolase and yeast (*Candida utilis*) transaldolase with dihydroxyacetone phosphate and fructose 6-phosphate, respectively, have indicated that certain intermediates in these reactions are Schiff bases—formed in each instance by reaction of an ε-amino group of a lysine residue of the enzyme and the carbonyl function of the substrate.<sup>2–4</sup> Thus, for example, sodium borohydride reduction of a protein complex from the reaction of C<sup>14</sup>-fructose 6-phosphate with the yeast transaldolase, followed by complete acid hydrolysis of the resulting modified protein, gave a radioactive amino acid which was identical in two-dimensional chromatography with the labeled amino acid obtained by the same treatment of a C<sup>14</sup>-dihydroxyacetone phosphate aldolase complex.<sup>2,3</sup> Periodate oxidation of this C<sup>14</sup>-amino acid gave C<sup>14</sup>-formaldehyde and a non-radioactive amino acid which was indistinguishable from lysine on chromatography, electrophoresis, or bioassay with a lysineless mutant of *Escherichia coli*.<sup>4</sup> The behavior of the radioactive amino acid toward periodate was that expected of N<sup>6</sup>-β-glyceryllysine (I) (N<sup>2</sup>-β-glyceryllysine was ruled out as a possibility because neither the transaldolase nor the aldolase appears to have an N-terminal lysine residue), and the reactions indicated in the following scheme were suggested for the formation of this substance.

(1) Supported by grants-in-aid from the National Institutes of Health.

(2) B. L. Horecker, S. Pontremoli, C. Ricci and T. Cheng, *Proc. Natl. Acad. Sci. U. S. A.*, **47**, 1942 (1961).

(3) E. Grazi, T. Cheng and B. L. Horecker, *Biochim. Biophys. Res. Commun.*, **7**, 250 (1962).

(4) E. Grazi, P. T. Rowley, R. Cheng, O. Tchola and B. L. Horecker, *ibid.*, **9**, 38 (1962).