

Aug. 60

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Monthly  
Ecumenical  
Letters from  
Laboratories  
Of  
N - M - R  
No. 22

A monthly collection of informal private letters from laboratories of nmr.  
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PURDUE UNIVERSITY  
DEPARTMENT OF CHEMISTRY  
LAFAYETTE, INDIANA

June 23, 1960

Dr. B. L. Shapiro  
Mellon Institute  
4400 Fifth Avenue  
Pittsburgh, Pennsylvania

Dear Dr. Shapiro:

Perhaps some of the readers of MELLONMR may be interested in some additional values of  $C^{13}$ -H coupling constants which we may not have occasion to include in a formal publication for some time.

Several of the values in the table deserve special comment. The coupling in formyl fluoride, FCHO is the largest we have observed in any compound, and this seems to indicate that some other factor besides bond hybridization may influence the coupling constants. This molecule also has an astonishingly large H-F coupling constant. Perhaps both of these facts may be related to the possible existence of a low-lying electronic state, leading to an unusually low value of the quantity  $\Delta E$  which appears in the equations which result when perturbation theory is used to explain the spin coupling effect. It has been assumed that this average excitation energy varies little from molecule to molecule.

The  $C^{13}$ -H coupling observed in  $Al_2(CH_3)_6$  at room temperature represents an average for the terminal and the bridging methyl groups. At low temperatures where the two types of methyl proton yield distinct resonances, we could see  $C^{13}$  satellites only for the signal from the terminal methyl groups, but apparently the coupling constant is nearly the same for both types of bond.

With best regards,

Sincerely,

*Norbert Muller*

Norbert Muller  
Donald E. Fritchard

-2-

Observed Values of  $C^{13}$ -H Coupling Constants

| Compound   | $J_{C-H}$ (sec <sup>-1</sup> ) | Notes  |
|--|--------------------------------|--|
| $Al_2(CH_3)_6$   | 113                            | Room temp. Average of all proton positions                                       |
| $Al_2(CH_3)_6$   | 114                            | -60°. Terminal $CH_3$ groups   |
| Si $(CH_3)_4$  | 118                            |  |
| Ga $(CH_3)_3$  | 122                            |  |
| In $(CH_3)_3$  | 126                            |  |
| Paraldehyde  | { 127<br>159                   | Benzene Solution<br>$CH_3$ groups } $J_{H-H} = 5.2 \text{ sec}^{-1}$<br>Ring C-H |
| Hg $(CH_3)_2$  | 130                            | $J_{Hg-H} = 101.5 \text{ sec}^{-1}$  |
| CF <sub>3</sub> CH <sub>3</sub>  | 130                            | $J_{F-H} = 12.8 \text{ sec}^{-1}$  |
| H <sub>2</sub> C <sup>13</sup> (COOH) <sub>2</sub>                               | 132                            |  |
| C <sub>6</sub> H <sub>5</sub> N (CH <sub>3</sub> )C <sup>13</sup> H <sub>3</sub> | 135                            |  |
| (CH <sub>3</sub> ) <sub>2</sub> S  | 138                            | $J_{H-H} = 7.4 \text{ sec}^{-1}$   |
| CH <sub>3</sub> SH   | 138                            |  |
| (C <sup>13</sup> H <sub>3</sub> )(CH <sub>3</sub> )N CHO                         | 138                            |  |
| (CH <sub>3</sub> ) <sub>2</sub> SO <sub>2</sub>                                  | 140                            | Water solution   |
| Na B(OCH <sub>3</sub> ) <sub>4</sub>   | 142                            | Water solution   |
| 1,4-Dioxane  | 142                            |  |
| B(OCH <sub>3</sub> ) <sub>3</sub>  | 143                            |  |
| (CH <sub>3</sub> ) <sub>4</sub> NOH  | 144                            | Water solution   |
| H <sub>2</sub> C (CN) <sub>2</sub>   | 145                            |  |
| (CH <sub>3</sub> O) <sub>2</sub> CO  | 147                            |  |
| Ethylene Carbonate   | 157                            | $J_{H-H} = 7.9 \text{ sec}^{-1}$   |
| Trioxane   | 166                            | Benzene Solution   |
| p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> C <sup>13</sup> H <sub>3</sub>  | 173                            |  |
| C <sub>6</sub> H <sub>5</sub> C <sup>13</sup> H <sub>3</sub> O                   | 174                            |  |
| Ferrocene  | 175                            | CS <sub>2</sub> Solution   |
| CH <sub>2</sub> F <sub>2</sub>   | 185                            |  |
| Salicylaldehyde  | 194                            | Aldehyde C-H   |
| HCOOH  | 222                            |  |
| FCHO   | 267                            | $J_{H-F} = 181 \text{ sec}^{-1}$   |

(Contribution from Fairchild Camera and Instrument Corp.)

Effect of Changes In Temperature On Field Trimmer

The magnet (which was insulated) was cycling with the room temperature. It appeared possible that the field trimmer was seeing a different  $\Delta t$  than the yoke and hence shifting the field. A five hundred watt hair dryer was used to blow warm air on the field trimmer plate when the pattern on the scope showed good resolution. As the plate warmed up, the ringing decreased and ultimately disappeared. The blower was then switched to cool and cool air blown on the field trimmer plate. As the plate cooled, ringing appeared and increased until we had a good pattern again. The change in resolution as the plate was warmed corresponded to the type of change that had been observed when the air conditioning failed. At least on my magnet, the field trimmer is one source of temperature instability. We now plan to insulate the field trimmer.

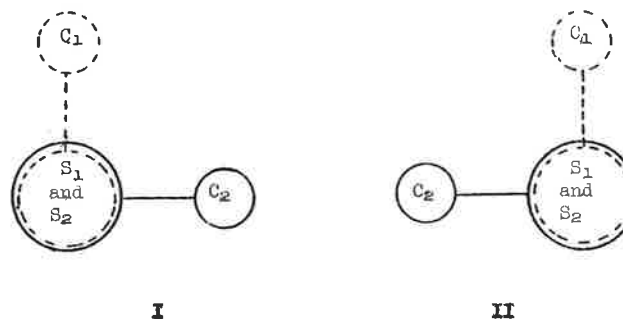
James E. LuValle  
Director of Basic Research

THE ENERGY BARRIER BETWEEN THE ENANTIOMERS OF 1,2-DITHIANE<sup>1</sup>

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

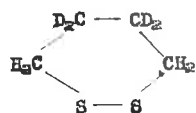
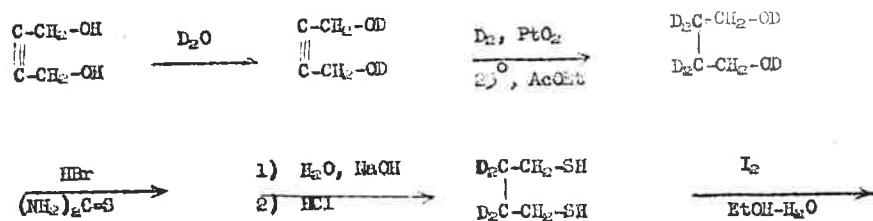
Sir:

The dihedral angle in an organic disulfide can produce two different molecular conformations, I and 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 NMR-spectrum, and therefore we prepared a deuterium-substituted derivative (III).



(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.<sup>2</sup>

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

At temperatures below  $-50^\circ$  the spectrum consists of a quartet of the AB type<sup>3</sup> (Fig. 1). The maximum separation of the two inner peaks is 10.4 c/sec,

- (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.

and the coupling constant is 13.0 c/sec. When the temperature is raised above  $-50^\circ$ , the peaks in the quartet start to converge, and at  $-45^\circ$  the spectrum consists of one single broad peak. As the temperature increases above  $-45^\circ$ , the peak sharpens and remains constant up to the highest temperature studied ( $150^\circ$ ).

From the low temperature pattern the chemical shift between the axial and equatorial hydrogens,  $\nu_a - \nu_e$ , was calculated as 18.5 c/sec. We

assumed that the following relation for the rate of interconversion<sup>4</sup> holds

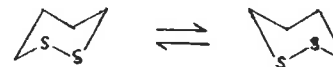
- (4) H. S. Gortowsky and C. H. Holm, J. Chem. Phys. 25, 1228 (1956).

approximately at  $-45^\circ$ , the temperature where the peaks coalesce:

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

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

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  $\Delta F^\ddagger = 11.6 \text{ kcal/mole}$ . Thus the molecular conformations have a very short lifetime. Even at  $-45^\circ$  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.<sup>5</sup>

- (5) C. Djerassi, 'Optical Rotatory Dispersion,' McGraw-Hill Book Company, New York, N.Y. (1954) p. 223.

The same measurements on cyclohexane<sup>6</sup> with similar assumptions give a value

- (6) F. R. Jensen, D. S. Koyce, C. H. Sederholm and A. J. Berlin, J. Am. Chem. Soc. 82, 1256 (1960).

4.

of 9.7 kcal/mole for  $\Delta F^\ddagger$ . 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  $\Delta F^\ddagger$  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  $60^\circ$ , the energy difference ( $\Delta F^\ddagger$ ) between  $0^\circ$  and  $90^\circ$  (assuming a cos dependence<sup>7</sup>) would be 12.5 kcal/mole.

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

The entropy of activation ( $\Delta S^\ddagger$ ) for this reaction is, however, not known, and we must await a direct measurement of the temperature coefficient to evaluate the heat term.<sup>8</sup> Since the entire transition in the spectrum from a single line

- (8) D. W. Scott, H. L. Finkle, M. E. Gross, G. R. Guthrie and H. M. Huffman, J. Am. Chem. Soc. 72, 2424 (1950). D. W. Scott, H. L. Finkle, J. P. McCullough, M. E. Gross, R. E. Pennington and G. I. Waddington, J. Am. Chem. Soc. 74, 2478 (1952). G. Bergson and L. Schotte, Arkiv. Kemi, 13, 43 (1958).

to a quadruplet occurs between  $-40^\circ$  and  $-50^\circ$ , precise temperature control and simpler spectra would be desirable. Experiments toward this end are in progress.

Department of Chemistry and  
Lawrence Radiation Laboratory,  
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Berkeley 4, California

Göran Claesson<sup>9</sup>  
Waylord M. Andrees  
Melvin Calvin

- (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.

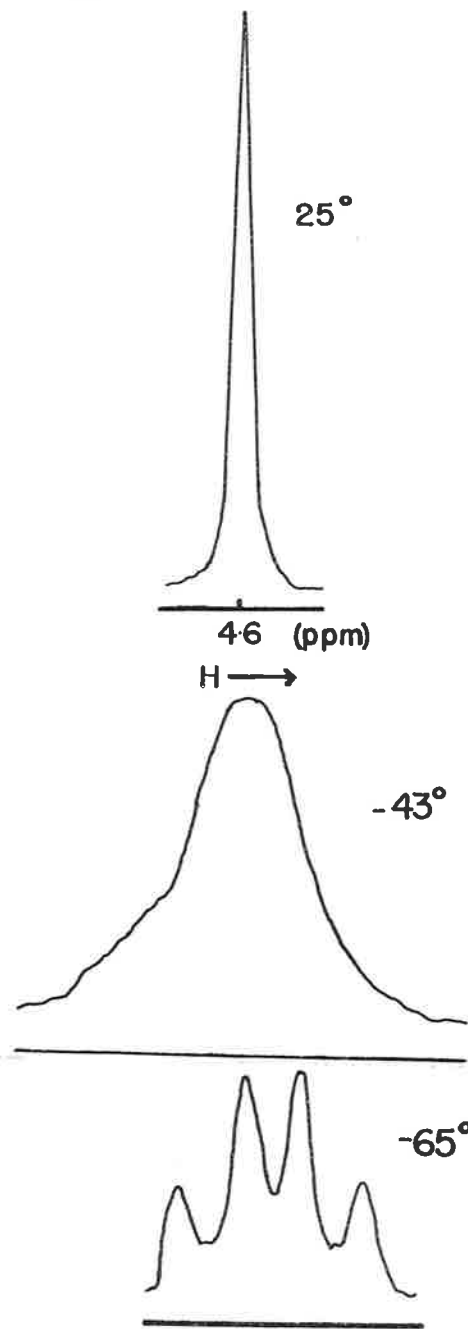


Fig. 1. Proton magnetic resonance spectra at 60 Mc/sec of 1,2-dithiane-4,5-d<sub>2</sub> referred to benzene.

HARVARD UNIVERSITY

DEPARTMENT OF PHYSICS

LYMAN LABORATORY OF PHYSICS  
CAMBRIDGE 38, MASSACHUSETTS

25 July 1960

Dr. A.A. Bothner-By  
Mellon Institute  
Pittsburgh, Pa.

Dear Dr. Bothner-By,

I thought you might like to include in MELLONMR the following coupling constants calculated from the enclosed spectrum of 1,1,4,4-tetramethylcyclohexyl-cis-2,6-diacetate. The peak positions are indicated in c/s at 60Mc/s from internal hexamethyldisiloxane and the figures in parentheses indicate the standard deviation of the experimental values.

$$J_{AB} = J(\phi_{H-C-H} = 109^\circ 28') = 12.36 \pm 0.2 \text{ c/s}$$

$$J_{AX} = J_{aa} = J(\phi_{H-C-H} = 180^\circ) = 12.35 \pm 0.1 \text{ c/s}$$

$$J_{BX} = J_{ea} = J(\phi_{H-C-H} = 60^\circ) = 4.25 \pm 0.1 \text{ c/s}$$

The difference in chemical shift between axial and equatorial protons is 0.131 ppm with the axial proton lying to higher field.

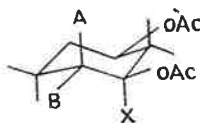
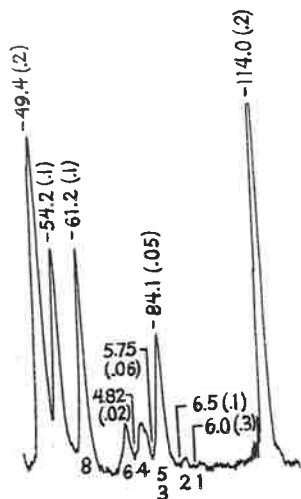
Based on the trans-isomer and two approximations which are probably quite valid, I get a  $J_{ee} = 2.8$  c/s and another  $J_{ea} = 3.8$  c/s. In this isomer the equatorial proton is most probably greater shielded than the axial proton contrary to most expectations.

I should appreciate a copy of the issue sent out in the end of June if there are any left.

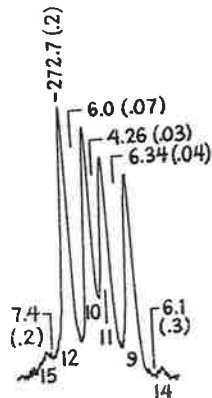
With best regards,

Yours sincerely,

*Jeremy*  
J. I. Musher



(b)



The Coupling of Proton Spins by  
pi-electron Interactions

Martin Karplus<sup>†</sup>

Noyes Chemical Laboratory  
University of Illinois, Urbana, Illinois

A theoretical formulation is developed for the pi-electron contribution,  $A_{HH}(\tau)$ , to the spin-coupling between pairs of protons in hydrocarbon molecules. By means of the correspondence between the  $\sigma$ - $\pi$  interaction in unsaturated molecules and related free radicals, the proton spin-coupling is expressed in terms of hyperfine constants and triplet state energies. With known values for these quantities,  $A_{HH}(\tau)$  is found to be in agreement with experimental measurements available for molecules in which the pi electrons are expected to dominate the coupling. Of particular interest are the large couplings (1.3 - 8 cps) calculated for certain systems with protons separated by three or four carbon atoms. Also absolute signs are predicted by the theory, with  $A_{HH}(\tau)$  equal to -6.7 cps for allene and +7.8 cps for butatriene.

Table 1. Hyperfine Constants

| Radical Fragment    | $a_H$ (cps)                          |
|---------------------|--------------------------------------|
| $H-\dot{C}(sp^2)^a$ | $-65 \times 10^6^b$                  |
| $H-\dot{C}(sp)^a$   | $-95 \times 10^6^c$                  |
| $H-C-\dot{C}$       | $+150 \cos^2 \phi \times 10^6^{d,e}$ |

<sup>a</sup>The symbol (sp<sup>2</sup>) and (sp) indicates the hybridization of the carbon C-H bond orbital.

<sup>b</sup>See References 13-16 in text.

<sup>c</sup>M. Karplus, unpublished calculations.

<sup>d</sup>The angle  $\phi$  is the angle between the H-C-C plane and the C  $\pi$ -orbital axis.

<sup>e</sup>See References 17-19 in text.

Table 2. Proton Spin-Coupling Constants

-23-

| Separation of Protons        | $A_{HH^1}(\tau)$ (cps)<br>(theor.) | $A_{HH^1}$ (cps)<br>(exp.)             |
|------------------------------|------------------------------------|--|
| <b>1. Two carbons</b>        |                                    |  |
| (a) H-C-C-H                  | +1.5                               | 5-11 (cis), 10-18 (trans) <sup>a</sup> |
| (b) H-C=C-H                  | +4.6                               | 9.1 <sup>b</sup>                       |
| <b>2. Three carbons</b>      |                                    |  |
| (a) H-C-C-C-H                | -1.7                               | -1.4 to -1.8 <sup>c</sup>              |
| (b) H-C=C-C-H                | -3.7                               | -2.1 to -2.9 <sup>d</sup>              |
| (c) H-C=C-C-H                | -6.7                               | 6.1 to 7.0 <sup>e</sup> (unknown sign) |
| <b>3. Four carbons</b>       |                                    |  |
| (a) H-C-C-C-C-H <sup>f</sup> | +2.0                               | 1.2 to 1.5 <sup>g</sup> (unknown sign) |
| (b) H-C-C=C-C-H <sup>f</sup> | +2.9                               | 2.9 <sup>h</sup> (unknown sign)        |
| (c) HC=C=C-C-H               | +7.8                               | - -                                    |

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DEADLINE!!

For issue No. 23 is Thursday,  
August 25.

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