

# The Relative Signs of the Nuclear Spin-coupling Constants in Tiglaldehyde as Determined by Selective Decoupling and Transitory Selective Irradiation (Nuclear Magnetic Double Resonance) Techniques

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By use of the selective decoupling technique it has been shown that the five-bond spin coupling in the fragment  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{CH}_3 \end{array}$  in tiglaldehyde (2-methyl-2-butenal) is of the same sign as the vicinal coupling in the fragment  $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$ . By means of a new technique employing transitory selective irradiation (TSI) the sign of the four-bond coupling in the fragment  $\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{CH}_3 \end{array}$  has been shown to be opposite to that of the five-bond coupling. The TSI method is based upon the fact that the application of a strong rf.-field can be used to produce a redistribution of the spin level populations in a nuclear spin system within a time that is short compared with the spin-lattice relaxation time  $T_1$ . These population changes will then cause intensity changes for those lines which have an energy level in common with the irradiated line(s) — and only for such lines — if the spectrum is recorded within a time that is short compared with  $T_1$ . The TSI method appears to be applicable in a variety of spin systems in which the spin-lattice relaxation times ( $T_1$ ) are long compared to the inverse of the apparent line-widths ( $T_2^*$ ).

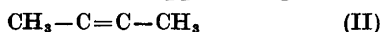
## I. INTRODUCTION

The theoretical estimates of nuclear spin coupling constants yield both the magnitudes and the signs of these parameters.<sup>1</sup> Since the predicted signs are more fundamental than the magnitudes, an experimental verification of the theoretical models should preferably involve sign determinations.

The long-range methyl group couplings in unsaturated compounds have been attributed to  $\pi$ -electron interactions.<sup>2-4</sup> On this model one would expect the long-range proton spin coupling in the allylic fragment



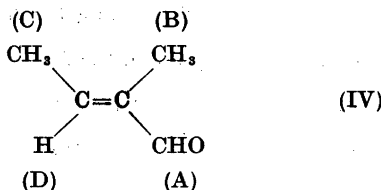
to be of about the same magnitude but of opposite sign to that in the fragment



The equality of the magnitudes has been experimentally verified in a number of cases (for references see Ref.<sup>3</sup>) and in several substituted propenes the long-range coupling in fragment I has been shown to be of opposite sign to the vicinal coupling in the fragment



by analysis of strongly coupled spectra (for a review see Ref.<sup>3</sup>) and by use of double irradiation techniques.<sup>5</sup> The long-range coupling in fragment II has been shown to be of the *same* sign as the vicinal coupling in fragment III by the analysis of the 40 Mc/s spectrum of tiglaldehyde (IV)



by use of second order perturbation theory.<sup>6</sup> The second order effects in the band from the hydrogens C are evident also in the 60 Mc/s spectrum (*cf.* Fig. 1).

Although long-range spin couplings both of the types occurring in fragment I and in fragment II are observed in this molecule, a direct comparison of their signs could not be obtained from the spectrum at 40 Mc/s.

However, by means of double irradiation techniques one may determine the relative signs of the three spin coupling constants observed in this molecule. The relative signs of  $J_{BC}$  and  $J_{CD}$ , previously known, may be obtained through the applications of the well known selective decoupling technique.<sup>5,7-13</sup> This method is not suitable for determining the sign of the third coupling  $J_{BD}$ , and therefore we have in the course of this work introduced a new technique for the determination of relative signs in multi-spin systems. In the following this latter technique will be called *transitory selective irradiation* (TSI).

## II. EXPERIMENTAL

The tiglaldehyde was a commercial product of highest quality (Eastman-Kodak) and used without further purification with a small amount of tetramethyl silane added. Only small amounts of impurities could be detected in the proton magnetic resonance spectrum. The chemical shifts and the spin coupling constants were measured on a Varian Associates model A-60 spectrometer operating at 60.007 Mc/s, calibrated with the common modulation side-band technique. Modulation side-bands were generated with a Hewlett-Packard function generator Model 202 A and the frequencies monitored with a Hewlett-Packard model 5512 A electronic counter.

The double resonance spectra were obtained using a Varian Associates model 4300 B (DP 60) spectrometer operating at a radiofrequency of 60.336 Mc/s. The nominal frequencies of the rf.-transmitters were checked with an electronic counter (Hewlett-Packard 524 D). The double resonance spectra were recorded using phase sensitive detection by operating the Varian V 3521 integrator in the lower sideband mode.<sup>14</sup> The irradiating rf.-field for the selective decoupling and TSI experiments was obtained through frequency modulation of the rf.-transmitter using a Hewlett-Packard 200 CD or 200 J Audio Oscillator. For further details of the experimental procedure see Ref.<sup>14</sup>

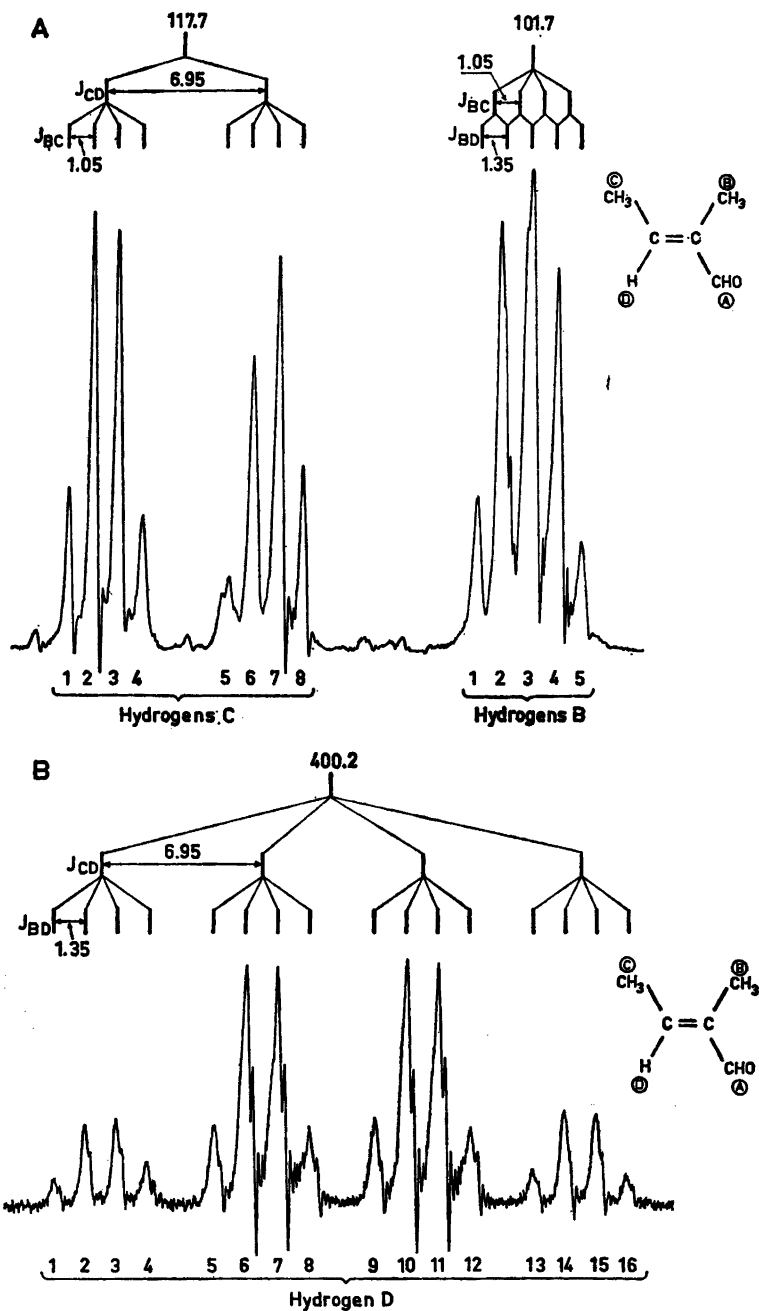
All the double irradiation experiments described in this work were carried out with field sweep methods, *i.e.* a fixed frequency difference was maintained between the strong and weak rf.-fields and the field sweep was used to scan the spectrum.

In order to check the reproducibility of the double irradiation spectra at least three recordings were obtained for each setting of the irradiating frequency. In all *ca.* six hundred spectra were obtained. In the course of the work a progressive deterioration in the performance of the recorder utilized was noted, manifested by a marked non-linearity of the recorder. Although this precluded a strictly quantitative verification of the predicted intensity changes in the TSI-experiments, the potentialities of this latter method could be verified in a semi-quantitative way and the results as to the signs of the spin coupling constants are unambiguous. In the selective decoupling and also in the TSI experiments the strengths of the rf.-fields  $H_1$  and  $H_2$  were maintained constant during the whole series of experiments and furthermore precautions were taken to maintain the sweep rate as constant as possible, in particular during the TSI experiments.

The relaxations times reported in section IV.2 below were measured by a study of the recovery of the signal after saturation.

## III. SELECTIVE DECOUPLING EXPERIMENTS

1. *The method.* The principles of the selective decoupling method for the determination of the relative signs of spin coupling constants in molecules containing three groups of mutually coupled nuclei has been described by Freeman and Whiffen<sup>5,8,9</sup> and by Manatt and Elleman.<sup>10,11</sup> From the papers cited above it is evident that, for a double resonance determination of the relative signs of the coupling constants  $J_{BC}$  and  $J_{CD}$  in IV, it is necessary to carry out double irradiation between the groups B and D. In order to avoid residual splittings,<sup>9,15</sup> such as occur in multispin groups ( $A_n$ ) it should (according to Ref.<sup>9</sup>) be advantageous to irradiate selected lines in the spectrum of the group B while observing the spectrum of the hydrogen D with a weak rf.-field. In the present case, however, the total width of the band assigned to hydrogen D is considerably larger than the band assigned to hydrogens B (*cf.* Fig. 1) and therefore in a field sweep experiment selective decoupling would only be detectable in a small part of the D-hydrogen spectrum. Furthermore, the near equality in magnitude of the coupling constants  $J_{BC}$  and  $J_{BD}$  causes accidental overlapping of pairs of lines in the band due to the B-hydrogens (*cf.* Fig. 1). We have therefore carried out



*Fig. 1.* The 60 Mc/s NMR spectrum of tiglaldehyde. The chemical shifts refer to the internal tetramethylsilane reference at 60.336 Mc/s (see text).

the reverse experiment and selectively decoupled each of the four subquartets in the D-hydrogen band while observing the changes in the spectrum of the hydrogens B. This does not cause any difficulties in the present case because of the relatively small value of the coupling  $J_{BD}$  compared to the magnitude of the coupling  $J_{CD}$ . This makes possible a selective decoupling experiment with rather strong irradiation fields ( $H_2$ ) such that  $\gamma H_2$  might be three to four times the magnitude of  $2\pi J_{BD}$ . For example if  $\gamma H_2/2\pi J_{BD} = 3$  a "collapsed" doublet in the spectrum of the hydrogens B will consist of a quintet with the approximate relative intensities 1:1:3:1:1 and the outer lines will be separated from the center line by less than  $0.25$  c/s ( $< 0.18 J_{DB}$ ) if the offset parameter  $^{15}(\Delta^1)$  equals zero, thus producing only a small broadening of the central line.

On the other hand, the sign of the spin coupling constant  $J_{BD}$  is not readily deduced from selective decoupling experiments. For example, in order to determine the sign of  $J_{BD}$  relative to  $J_{BC}$  one should perform double irradiation experiments between the groups D and C, which is not very favourable since  $J_{CD}$  is very much larger than both  $J_{BD}$  and  $J_{BC}$ . A second possibility might be to perform double irradiation experiments between the methyl groups B and C in order to determine the relative sign of  $J_{BD}$  relative to  $J_{CD}$ . This is, however

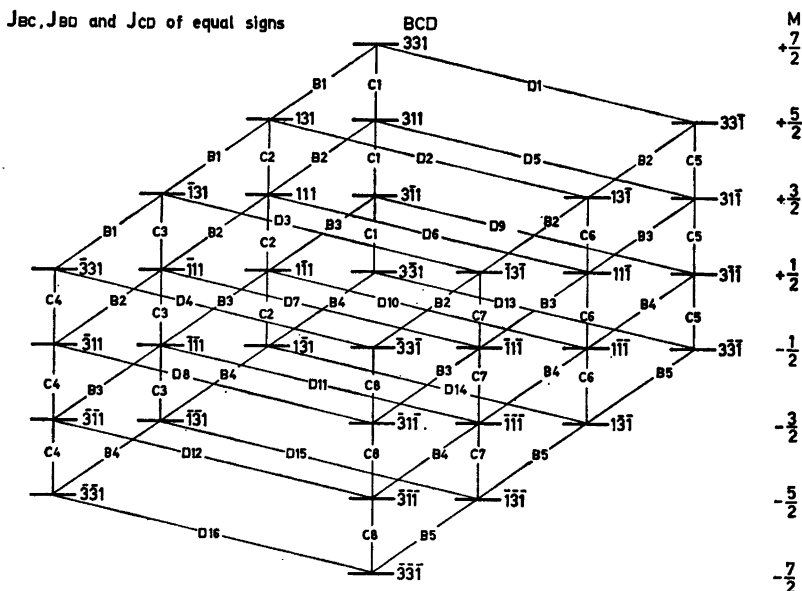


Fig. 2. The schematic energy level diagram (neglecting second order effects) of the ethylenic (D) and methyl group (B and C) proton spins of tiglaldehyde for the hypothetical case when  $J_{BC}$ ,  $J_{BD}$  and  $J_{CD}$  carry the same sign. The labelling of the energy states has been abbreviated.

Thus, for example,  $\bar{3}\bar{3}1$  represents the state in which  $M_Z(B) = +\frac{3}{2}$ ,  $M_Z(C) = -\frac{3}{2}$  and  $M_Z(D) = +\frac{1}{2}$  etc. B-transitions are represented by diagonal lines with a positive slope ( $\nearrow$ ), C-transitions are represented by vertical lines and D-transitions by diagonal lines with a negative slope ( $\searrow$ ).

The total magnetic quantum number (M) of the levels are given in the right hand part of the figure.

an even more unfavourable experiment since this corresponds to a spin decoupling experiment in an  $A_3X_3$  system with a rather small  $A-X$  shift, and in addition selective decoupling irradiation in the C-hydrogen band is hampered by the large value of  $J_{CD}$  compared to  $J_{BC}$ , while selective decoupling of  $J_{BC}$  in the B-hydrogen band is impeded by the accidental overlap of pairs of lines.

In an attempt to overcome these difficulties we decided to undertake a double irradiation experiment using a weak rf.-field.<sup>16</sup> In order to overcome the complications arising from accidental overlap of line-pairs we decided to perform this experiment between the groups C and D. This approach has the additional advantage that it permits a *direct* comparison in a single experiment of the signs of the two long-range couplings in the fragments I and II in one and the same molecule.

Irradiation of one single line in the D-hydrogen band would affect only one of the four energy levels involved in any of the triply degenerate transitions of the C-methyl group (*cf.* Figs. 2–5). For example, irradiation of the line D 1

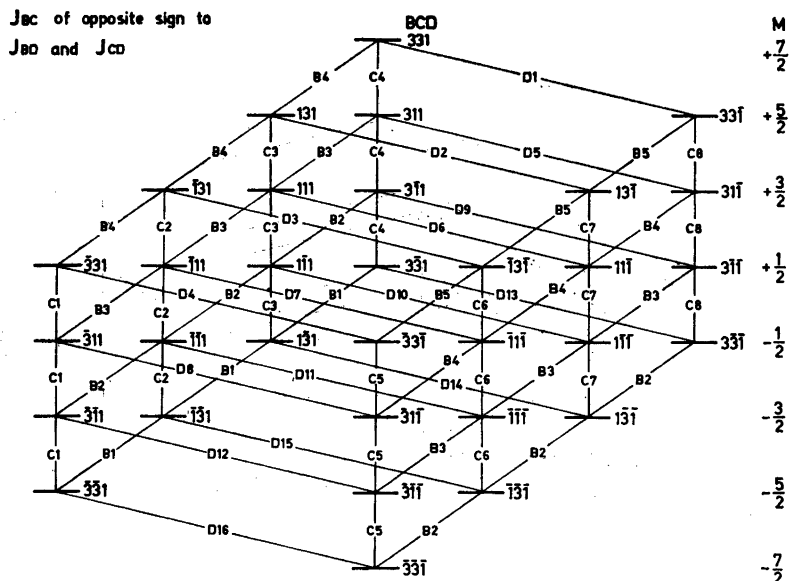


Fig. 3. The schematic energy level diagram (neglecting second order effects) of the ethylenic (D) and methyl group (B and C) proton spins of tiglaldehyde for the hypothetical case when  $J_{BC}$  is of opposite sign to  $J_{CD}$  and  $J_{BD}$ . The same symbols as in Fig. 2 have been used.

would, according to Fig. 4, affect only the highest level involved in the transitions C 4 and C 8. It was thought that these effects would be more difficult to detect than would be the effects of the reverse experiment in which a single line in the C-methyl spectrum is irradiated while observing the effects in the D-hydrogen band. A detailed theoretical analysis of this experiment would

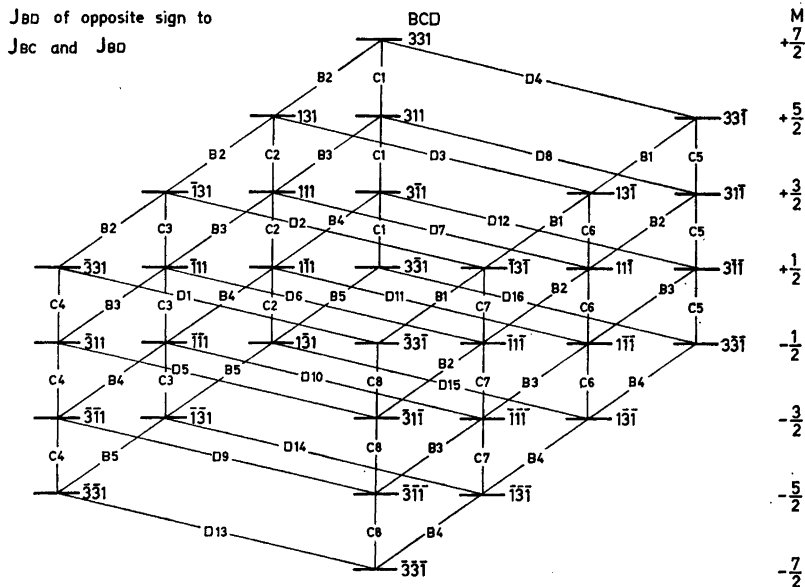


Fig. 4. The schematic energy level diagram (neglecting second order effects) of the ethylenic (D) and methyl group (B and C) proton spins of tiglaldehyde molecule in which  $J_{BD}$  is of opposite sign to  $J_{BC}$  and  $J_{CD}$ . The same symbols as in Fig. 2 have been used.

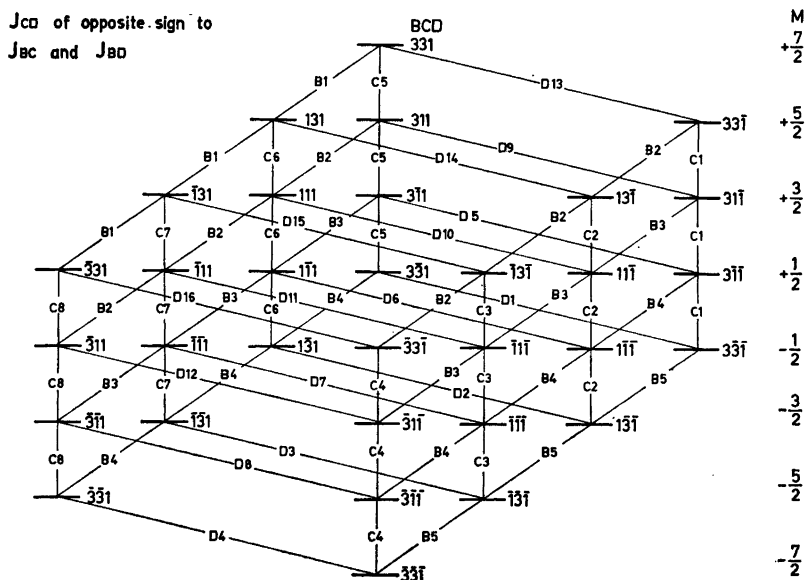


Fig. 5. The schematic energy level diagram (neglecting second order effects) of the ethylenic (D) and methyl group (B and C) proton spins of tiglaldehyde for the hypothetical case when  $J_{CD}$  is of opposite sign to  $J_{BC}$  and  $J_{BD}$ . The same symbols as in Fig. 2 have been used.

involve the solution of a fourth order secular equation. However, one may expect that the application of a sufficiently weak irradiation field should cause a *broadening* of lines having an energy level in common with the irradiated lines. This latter statement follows from the general principle that only lines having an energy level in common with the irradiated line will be affected by the irradiation.<sup>16</sup>

2. *Results.* The effect of the selective decoupling irradiation in the D-hydrogen band as observed in the band of the B-methyl group is displayed in Fig. 6, in which the predicted multiplet patterns are indicated schematically above each of the observed double resonance bands. In these schematic spectra we have neglected all residual splittings and indicated only the complete coalescence of "collapsed" line pairs. The numerical results are summarized in Table 1. Owing to the fact that a rather strong irradiating field ( $H_2$ ) was used ( $\gamma H_2 > 6 \pi J_{BD}$ ) the observed patterns resembled the theoretically predicted ones over a region  $\pm 1$  c/s from the optimum value.

As is evident from Table 1 the selective irradiation experiments unequivocally confirm the earlier reports<sup>6</sup> that  $J_{BC}$  and  $J_{CD}$  carry the same sign.

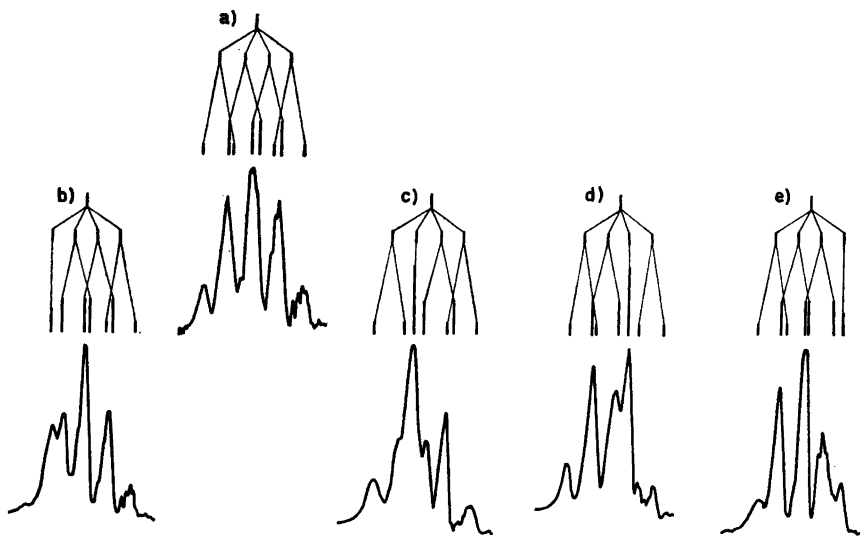


Fig. 6. Results of the selective decoupling experiments. 6a shows the appearance of the unperturbed B-methyl group quintet. In 6b the frequency difference  $\nu_1 - \nu_2$  was adjusted so as to center the decoupling rf.-field between the lines D2 and D3 while observing the B-methyl group. In 6c the irradiating field is centered between the lines D6 and D7 when the methyl group is observed with a weak rf.-field. In d the irradiating field is centered between the lines D10 and D11 and in e between the lines D14 and D15 (see text and Table 1).



*Table 1.* The results of the spin decoupling experiments when the four D-hydrogen quartets are successively decoupled and the effects of the B-methyl group quintet are observed.

Collapse of line as indicated in Figs. 6b–6e.	Predicted frequencies in c/s		Observed frequencies in c/s
	like signs of $J_{BC}$ and $J_{CD}$	unlike signs of $J_{BC}$ and $J_{CD}$	
6 b	307.3	286.5	307.1
6 c	301.5	294.5	301.4
6 d	295.5	302.5	295.4
6 e	289.7	310.5	289.6

#### IV. TRANSITORY SELECTIVE IRRADIATION EXPERIMENTS

1. *Method.* As indicated in section III:1 one should expect that irradiation of a single line in the C-hydrogen band would cause broadening of those lines in the D-hydrogen band which have an energy level in common with the irradiated line. In our initial studies of this type of experiment, the frequency difference between the observing and irradiating fields was adjusted so as to irradiate one of the lines C1–C4 while observing the lines D5–D8. Because of the occurrence of repeated spacings it follows that the same frequency setting allows irradiation of one of the lines C5–C8 while the lines D9–D12 are observed (*cf.* Fig. 1). Then, for certain frequency settings a reduction was observed in the peak heights of the lines that would be affected according to the level assignments in Fig. 3 or Fig. 4. It was observed, however, that this effect was dependent on whether the spectrum was recorded with a field-sweep from low to high fields or *vice versa* — a phenomenon that is not in accordance with the predictions of the model outlined in section III:1. Furthermore, for other combinations of the irradiating and observing frequencies, some lines would *increase* in heights and other lines would display *negative* intensities. It thus became evident that a new phenomenon was involved.

It appears that the observations hitherto made can be rationalized in terms of a very simple model: The intensity of an absorption line is directly proportional to the difference in population between the two levels involved in the transition. A strong transient irradiation of a single line in the NMR spectrum will perturb the populations of the irradiated levels while the non-irradiated levels retain their populations unchanged, provided the irradiation lasts for a time which is short compared to the relaxation times. Then, if a second line having an energy level in common with the transiently irradiated line is observed with a weak rf-field shortly after the irradiation, intensity changes which can be estimated from the population changes will occur.

It should be pointed out here that the transitory selective irradiation experiments work well only if the inverse of the apparent linewidth ( $T_2^*$ ) is small compared to the spin lattice relaxation time ( $T_1$ ). The reasons for this

will become obvious in the following. Under experimental conditions normally encountered this last mentioned condition is usually fulfilled.

We may consider two extreme situations both of which may be approximately realized in practice. In the first case (case I) the signal to be irradiated remains unperturbed until the time  $t = 0$  when a strong irradiating field ( $H_2$ ) is applied at exact resonance and remains on for a time of the order of  $T_2^*$ . This type of experiment is most easily performed with a frequency sweep spectrometer. In the second case (case II) the line to be irradiated is traversed by the strong irradiating field so as to fulfil the conditions of adiabatic fast passage.<sup>17-19</sup> This latter type of experiment may be performed on both frequency sweep and field sweep spectrometers. To get a simple picture of the processes involved in the first case we may consider these processes phenomenologically in a frame of reference rotating with the angular frequency,  $\omega_2$ , of the irradiating rf-field  $H_2$ . In this frame the net magnetization,  $M$ , resulting from the difference in populations of the irradiated levels will precess around the direction of  $H_2$  (see Fig. 7) with the angular frequency  $\gamma H_2 T_2^*$ . When  $\gamma H_2 T_2^*$  is not large compared to unity the line broadening will produce a spread in the precession frequencies in the order of  $1/T_2^*$  and thus the net magnet-

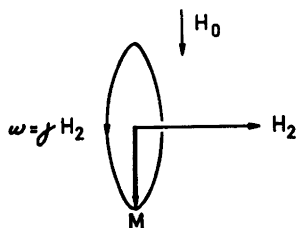


Fig. 7. A schematic diagram illustrating the motion of the net magnetization  $M$  as viewed in a coordinate system rotating with the angular frequency  $\omega_2$  of the irradiating field  $H_2$ .

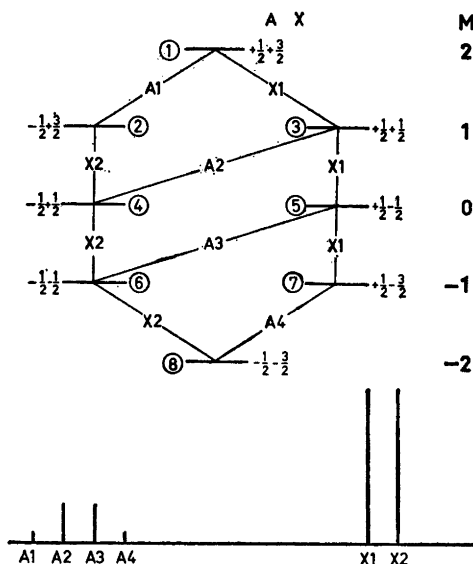


Fig. 8. Energy level diagram and schematic spectrum of an  $AX_3$  spin system.

ization — *i.e.* the population differences — will be extinguished within a time of the order of  $T_2^*$ . Thus the effect of the irradiation is an equilibration of the populations in the energy levels involved; *i.e.*, transitory selective saturation has been accomplished.

In the second case the result of the adiabatic fast passage is an inversion of the effective magnetic field in the rotating frame. The population changes may be calculated simply by exchanging the magnetic quantum numbers ( $m_i$ ) of the irradiated group ( $i$ ) for  $-m_i$  in the Boltzman factors governing the populations for the levels involved.

As an example we may consider the case of an  $AX_3$  system, the level scheme of which is indicated in Fig. 8. The population  $N_p$  in the energy level  $p$  is proportional to a degeneracy parameter  $\eta$  and a Boltzmann factor

$$N_p = C \cdot \eta \exp \left( - \frac{\mu H_0}{kT} \times \frac{M}{I} \right) \quad (1)$$

where  $C$  is a constant of proportionality common to all states,  $\mu$  is the magnetic moment,  $H$  the applied magnetic field,  $k$  the Boltzmann constant,  $T$  the absolute temperature, and  $I$  the spin quantum number. For brevity the exponent will in the following be designated by  $-\kappa M$ . Since  $\kappa$  is very small compared to unity under normal experimental conditions, the deviation of the population ( $N_p$ ) for any one level ( $p$ ) from the average ( $N_0$ ) will be proportional to  $-M$ .

$$N_p - N_0 = -C \cdot \eta \cdot M \cdot \kappa \quad (2)$$

Selective irradiation of the line X1 will cause a redistribution of the population in the levels 1, 3, 5, and 7 such that

in case I	in case II
$N_1 - N_0 = -0.5 C\kappa$	$N_1 - N_0 = + C\kappa$
$N_3 - N_0 = -1.5 C\kappa$	$N_3 - N_0 = 0$
$N_5 - N_0 = -1.5 C\kappa$	$N_5 - N_0 = -3 C\kappa$
$N_7 - N_0 = -0.5 C\kappa$	$N_7 - N_0 = -2 C\kappa$

immediately after the irradiation \* as compared to the original populations

$$\begin{aligned} N_1 - N_0 &= -2 C\kappa \\ N_3 - N_0 &= -3 C\kappa \\ N_5 - N_0 &= 0 \\ N_7 - N_0 &= + C\kappa \end{aligned}$$

The relative intensities for the lines A1–A4 will then be

in case I	in case II
for A1 -0.5	for A1 -2.0
for A2 + 1.5	for A2 0
for A3 + 4.5	for A3 + 6.0
for A4 + 2.5	for A4 + 4.0

\* Note that the levels 3, 4, 5, and 6 are triply degenerate.

instead of the 1:3:3:1 intensity pattern in the unperturbed case. It may be noted that for a discussion of the relative intensity *change* in any one line the degeneracy in the levels may be neglected.

In practice it will be difficult to attain these predicted intensity changes due to several causes. Thus it is always necessary to maintain a finite time difference between the application of the irradiating and observing rf.-fields to allow for the time required to accomplish the population redistributions and also in order to avoid line-broadenings or line-splittings<sup>16</sup> due to "tickling"\*. During the time interval between the irradiation and the detection, the spin level populations will tend to revert to their equilibrium values through spin-lattice relaxation. It should be noted that during the relaxation process not only the originally irradiated levels will change their populations but also the originally unperturbed levels will be affected. For example, in the case just considered the levels 2, 4, 6, and 8 will have their populations changed if the spin-lattice relaxation time  $T_{1A}$  of the A-nucleus is not very long compared to the corresponding time  $T_{1X}$  for the X-nuclei.

In the present study the emphasis has been on the determination of the relative signs of the spin coupling constants and on the qualitative aspects of the transitory selective irradiation (TSI) method. Most of the experimental results were obtained at a time when we had no detailed comprehension of the phenomena involved. Therefore we have not optimized the experimental conditions and it seems probable that considerably larger intensity changes than those observed in the present study could be obtained with this molecule.

2. *Results.* In order to determine the relative signs of the two long range spin couplings  $J_{BC}$  and  $J_{BD}$  we perform a TSI in the C hydrogen band and observe the changes in the D-hydrogen band. We may then consider the NMR spectrum of the C and D hydrogens as that of four superimposed  $AX_3$ -systems, one for each of the four different spin orientations of the B-hydrogens. The gross structure of the bands due to the hydrogens C and D is that of an  $AX_3$ -system and the small splittings caused by the long-range couplings produce a quadruplication of the  $AX_3$  case. The results of the TSI experiments are conveniently discussed with reference to the energy level diagrams in Figs. 2–5. The diagrams in Figs. 2 and 5 correspond to equal signs of the two long-range couplings compared, and the diagrams of Figs. 3 and 4 correspond to opposite signs of these two couplings. Since we have already shown in section III:2 that  $J_{CD}$  and  $J_{BC}$  are of the same sign we need actually only consider the diagrams in Figs. 2 and 4.

The results of the TSI experiments are summarized in Table 2 and some representative spectra are shown in Figs. 9–16. These spectra were all obtained using a sweep from low to high field and a sweep speed of 0.30–0.36 c/s.<sup>2</sup> The variations in the sweep speed was caused by the random drift of the magnetic field. However, these variations are small enough not to cause

\* In our experiments the possible occurrence of tickling also imposes a restriction of the amplitude of the irradiation field  $H_2$ . A compromise has to be reached between this restriction and the requirement<sup>17–19</sup> of adiabaticity:

$$\frac{dH_0}{dt} \ll \gamma H_2^2$$

Table 2. The results of the transitory selective irradiation experiments. The frequency differences  $\nu_1 - \nu_2$  given are those which give the smallest offset required to produce a definite intensity change. The entries printed in italics refer to experiments in which the sweep goes from high to low field.

In the second column the following abbreviations have been used, "red" for an intensity reduction, "enh" for an intensity enhancement and "neg" for a negative intensity. The lines affected are listed immediately after these symbols.

$\nu_1 - \nu_2$ in c/s	Observed effects in the D-hydrogen bond	Peak irradiated in the C-hydrogen bond	$\nu_{Cl} - \nu_{D1}$ in c/s	Offset in c/s	Offset in sec.	Fig.
300.20	enh D1	C8	300.00	0.20	0.6	
297.8	enh D2	C7	297.60	0.20	0.6	
295.4	enh D3	C6	295.20	0.30	0.9	
293.5	enh D5	C8	293.05	0.45	1.4	
293.5	neg D1	C4	293.05	0.45	1.4	
290.85	neg D2	C3	290.65	0.20	0.6	
288.45	enh D7	C6	288.25	0.20	0.6	16
288.45	neg D3	C2	288.25	0.20	0.6	16
286.35	red D5	C4	286.10	0.25	0.8	12
286.35	red D9	C8	286.10	0.25	0.8	12
283.9	red D6	C3	283.70	0.20	0.6	11
283.9	red D10	C7	283.70	0.20	0.6	11
283.4	red D6	C3	283.70	0.30	0.9	
283.4	red D10	C7	283.70	0.30	0.9	
281.35	red D7	C2	281.30	0.05	0.2	10
281.35	red D11	C6	281.30	0.05	0.2	10
280.85	red D7	C2	281.30	0.45	1.4	
280.85	red D11	C6	281.30	0.45	1.4	
279.45	enh D9	C4	279.15	0.30	0.9	15
279.45	neg D13	C8	279.15	0.30	0.9	15
279.0	red D8	C1	278.90	0.10	0.3	13
279.0	red D12	C5	278.90	0.10	0.3	13
278.45	enh D9	C4	279.15	0.70	2.1	
278.45	neg D13	C8	279.15	0.70	2.1	
277.0	neg D14	C7	276.75	0.25	0.8	
276.1	neg D14	C7	276.75	0.65	2.0	
274.6	neg D15	C6	274.35	0.25	0.8	14
274.05	neg D15	C6	274.35	0.30	0.9	
272.4	enh D13	C4	272.20	0.20	0.6	
272.05	neg D16	C5	271.95	0.10	0.3	
271.8	neg D16	C5	271.95	0.15	0.4	
271.8	enh D13	C4	272.20	0.40	1.2	
269.8	enh D14	C3	269.80	0	0	
267.55	enh D15	C2	267.40	0.15	0.4	

any difficulties in the interpretation of the spectra. Fig. 9 displays the spectrum of the D-hydrogen band as obtained under the same conditions as Figs. 10–16, except for the absence of the perturbing rf.-field at the C-hydrogen band.

Fig. 10 displays the effects of the TSI experiments when the frequency difference  $\nu_1 - \nu_2$  equals 281.35 c/s. It is seen that the intensities of the lines D7 and D11 are strongly reduced and that the intensities of the other lines in the spectrum are nearly unaffected. This fact alone shows that  $J_{BC}$  and  $J_{BD}$

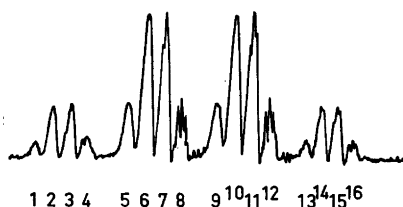


Fig. 9. The appearance of the 60.336 Mc/s NMR spectrum of the D-hydrogen band obtained using the Sanborn recorder. This spectrum was recorded under the same conditions as those used in obtaining the spectra shown in Figs. 10–16 except for the absence of any strong perturbing fields.

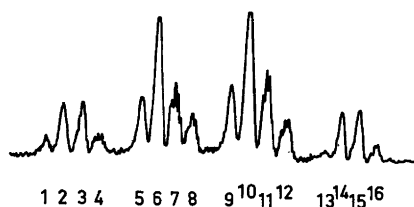


Fig. 10. The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2$  between the weak and the strong rf.-fields equals 281.35 c/s. The intensities of lines D7 and D11 are reduced due to the population changes caused by the preceding irradiation of lines C2 and C6, respectively.

have opposite signs, for had these coupling constants been of equal sign the near equality of the splittings ( $J_{BD} = 1.35$  c/s,  $J_{BC} = 1.05$  c/s) would have produced a spectrum in which all the lines D5–D12 would have had their intensities perturbed in a similar manner. The frequency difference  $\nu_1 - \nu_2 = 281.35$  c/s differs by 0.05 c/s from the measured line separations D7 to C2 or D11 to C6. A certain frequency difference is necessary to allow for the time needed to accomplish the population redistribution before the intensity change is studied. The result that a TSI at C2 reduces the intensity of line D7 is only consistent with a level scheme corresponding to  $J_{BC}$  and  $J_{BD}$  carrying opposite signs (Figs. 4). For example the level scheme displayed in Fig. 2 can be ruled out since according to this scheme a reduction of the inten-

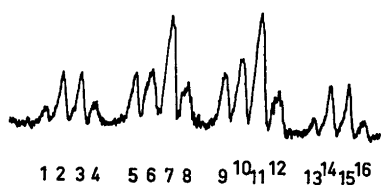


Fig. 11. The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2$  equals 283.9 c/s. The intensities of lines D6 and D10 are reduced due to the population changes caused by the preceding irradiation of lines C3 and C7 respectively.

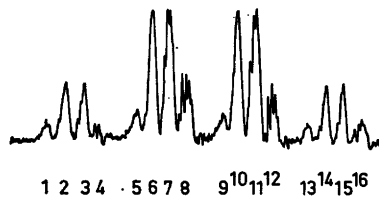


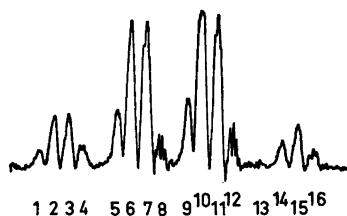
Fig. 12. The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2$  equals 286.35 c/s. The intensities of lines D4, D5 and D9 are reduced due to the population changes caused by the preceding irradiation of lines C1, C4 and C8 respectively (see text).

sity of line D7 would have required a previous irradiation of the line C3. However, line C3 is not irradiated until *ca.* 3 sec after the recording of line D7.

Fig. 11 shows the intensity changes of lines D6 and D10 which follow upon the TSI at C3 and C7 respectively.

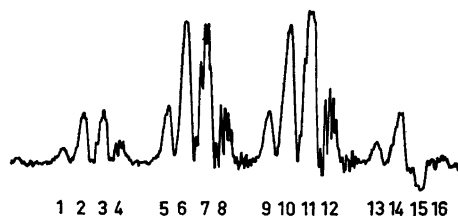
In the spectrum displayed in Fig. 12 lines C4 and C8 were irradiated shortly before recording lines D5 and D9. Owing to the near equality of the line separa-

tions C1—C4 and D4—D5 the irradiation field in this experiment will reach line C1 at about the time when D4 is recorded and therefore the intensity of line D4 is perturbed as well.



*Fig. 13.* The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2$  equals 279.0 c/s. The intensities of lines D8 and D12 are reduced due to the population change caused by the preceding irradiation of lines C1 and C5, respectively. A slight enhancement of the intensity of line D9 and intensity reductions of lines D13 and D14 caused by irradiations of lines C4 and C8 respectively, may be noted.

These latter lines are also irradiated with the above frequency setting, however, the frequency difference was not optimized for these lines. The last mentioned effects are better illustrated in Fig. 16.

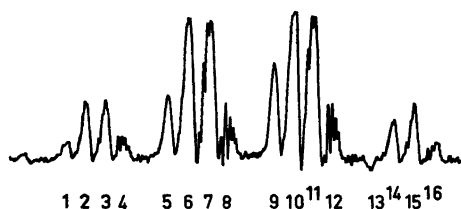


*Fig. 14.* The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2 = 274.6$  c/s. A negative intensity is observed for line D15 due to the previous irradiation of line C6. The intensity enhancement of line D11 is quenched due to the cut-off characteristics of the recorder amplifier (see section II).

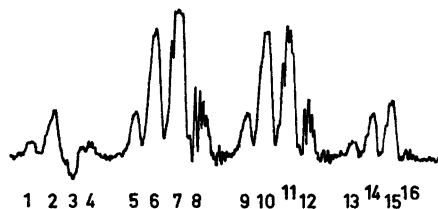
In the spectrum displayed in Fig. 13 the frequency difference  $\nu_1 - \nu_2$  was set so as to reduce the intensity of lines D8 and D12; however, for the same reasons that line D4 was reduced in Fig. 12, the intensity of line D13 is reduced in the present case and line D9 is *enhanced*. This is as one would expect from the level arrangement depicted in Fig. 4.

A *negative* intensity is obtained for line D15 when line C6 has been irradiated shortly before. This is shown in Fig. 14. The same frequency setting allows the irradiation of line C2 just before line D11 is recorded, and this would, according to Fig. 4, lead to an enhancement of line D11. This is not so convincingly shown in Fig. 14 because of the cut-off characteristics of the recorder used. However, in Fig. 15 the enhancement of the intensity of line D9 is evident as is the negative intensity of line D13. The corresponding C-lines irradiated in this latter case were C4 and C8 respectively.

In the spectrum displayed in Fig. 16 the frequency difference  $\nu_1 - \nu_2$  was set at 288.45 c/s. This differs by 0.20 c/s from the frequency difference D3—C2 or D7—C6, respectively, and therefore the line D3 has a negative intensity while the intensity of line D7 is enhanced. The intensity of line D16 is also strongly reduced owing to the fact that line B5 is irradiated just before the recording of line D16 (offset 0.15 c/s corresponding to  $\sim 0.5$  sec delay) and line D15 is somewhat enhanced owing to the previous irradiation of line B4 (offset 0.10 c/s). The intensity changes of lines D15 and D16 give further evidence for the



*Fig. 15.* The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2 = 279.45$  c/s. The intensity of line D9 is enhanced and line D13 displays a negative intensity due to the population changes caused by the preceding irradiations of lines C4 and C8, respectively.



*Fig. 16.* The appearance of the D-hydrogen band when the frequency difference  $\nu_1 - \nu_2 = 288.45$  c/s. A negative intensity is observed for line D3 due to the preceding irradiation of line C2. The intensity enhancement of line D7 is quenched due to the cut-off characteristics of the recorder amplifier (see section II). The intensity of line D15 is slightly enhanced and line D16 is extinguished because of irradiation of lines B4 and B5, respectively (see text).

equality of the signs of  $J_{BC}$  and  $J_{CD}$  since these latter changes can only be understood in terms of the level arrangements in Fig. 2 and Fig. 4.

A number of spectra were recorded with a sweep from high to low fields the amplitudes of the rf.-fields and the sweep rates in this series were the same as in the foregoing experiments. The results of the reverse-sweep experiments are also listed in Table 2, where they are printed in italics. It should be noted that the sense of the frequency offset here is the opposite of that in the forward-sweep experiments. In both series the offset parameter is of the order of 0.30 c/s with a maximum value of 0.70 c/s and a minimum value of 0 c/s. An offset parameter of this magnitude is what one would expect since the sweep rate in these experiments is 0.30–0.36 c/s,<sup>2</sup> the inverse linewidths about 1.3 sec and the spin-lattice relaxation times of the various groups:  $T_{1A} = 8.1$  sec,  $T_{1B} = 6.6$  sec,  $T_{1C} = 5.9$  sec and  $T_{1D} = 8.7$  sec.

## V. DISCUSSION

In this section we will consider two different aspects of the present work (1:o) the methods for determining the relative signs of spin coupling constants in multispin systems and (2:o) the implications of the fact that the five bond coupling,  $J_{BC}$ , carries the same sign as the vicinal coupling,  $J_{CD}$ , but is of opposite sign to the four bond coupling,  $J_{BD}$ .

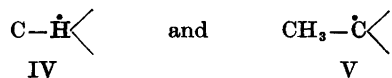
In section III we have shown that the selective decoupling<sup>5,8-11</sup> technique may successfully be applied to a seven spin system and that the residual splittings in  $A_n$ -groups reported by Anderson and Freeman<sup>15</sup> do not present any serious difficulties if the coupling constants of the irradiated group are sufficiently different in magnitude. In section IV we have developed a new application of irradiation with a weak rf.-field for the assignment of the level arrangements in nuclear spin systems. This method employs a transitory



selective irradiation to produce a redistribution of the energy level populations in a nuclear spin system and is applicable to systems in which the spin-lattice relaxation time  $T_1$  is long compared with the inverse of the apparent linewidths  $T_2^*$ . This latter requirement follows from the fact that a time of the order of  $T_2^*$  is needed to accomplish the redistribution of the spin populations and that these new populations are dissipated within a time of the order of  $T_1$  (hence the phrasing "transitory selective irradiation" for this technique). This condition should be distinguished from that required for the application of the nuclear Overhauser effect in spectral assignments.<sup>20</sup> The nuclear Overhauser effect provides unambiguous assignments in systems where at least some non-equivalent nuclei have widely different spin-lattice relaxation times. This is a more serious restriction than the condition  $T_1 \gg T_2^*$  since with present day techniques, field inhomogeneity broadening produces inverse linewidths which are smaller than the spin-lattice relaxation times in most organic liquids. Furthermore, the spin-lattice relaxation times can often be increased by carefully degassing the samples and by diluting the samples in suitable non-viscous aprotic solvents such as  $\text{CS}_2$ . For the analysis of certain NMR spectra with closely spaced lines it may be unfavourable to aim for too long relaxation times since this would complicate the interpretation of the results due to intricate after effects.

It appears that this new method may be applied to a variety of spectral assignment problems. A favourable feature of the TSI-technique is that only easily available commercial accessories are required.

The present study confirms the earlier reported assignments on the relative signs of the long-range coupling constants in the fragments I and II. Theoretical estimates of these coupling constants by Karplus<sup>4</sup> assign an absolute positive sign to the long-range coupling in fragment II and a negative to the long-range coupling in fragment I. Karplus' calculations involve only  $\pi$ -electron interactions and estimations of the hyperfine constants for the fragments



Karplus used experimental results derived from ESR and NMR data to estimate the signs and magnitudes of these constants, so it may be said that Karplus' results on  $\pi$ -electron couplings are among the most reliable of all calculations of indirect nuclear spin couplings made so far. Then the results of the present investigation may be taken together with Karplus' calculations to show that the vicinal coupling in fragment III is positive in sign, and the signs of other nuclear spin coupling constants may then be related to the sign of this spin coupling constant. This offers an alternative route to that of Lauterbur and Kurland<sup>21</sup> for the determination of the absolute signs of spin coupling constants.

*Note added in manuscript.* Recently a determination of the absolute sign of the *ortho*-coupling in substituted benzenes has been carried out by McLauchlan and Buckingham (private communication). We may therefore reverse the above argument so as to consider the present results as an additional experimental verification of the Karplus' theory for nuclear spin coupling by  $\pi$ -electron interactions.

*Acknowledgements.* Thanks are due to Dr. E. Forslind and to Professors O. Lamm and K. Siegbahn for their interest in this work and for providing excellent working facilities. We are indebted to Drs. I. Lindgren and T. Vänngård for valuable discussions.

Grants in aid of this work were provided by the *Knut and Alice Wallenberg Foundation*, *The Swedish Technical Research Council* and *The Swedish Natural Science Research Council*.

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Received September 24, 1963.