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Electron Coupling of Nuclear Spins. VI. Relative Signs of

$J_{gem}^{HH}$ ,  $J_g^{HH}$  and  $J_t^{HH}$  in (2.2)Metacyclophane.

by

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ELECTRON COUPLING OF NUCLEAR SPINS. VI. RELATIVE SIGNS OF

$$J_{\text{gem}}^{\text{HH}}, J_{\text{g}}^{\text{HH}} \text{ and } J_{\text{t}}^{\text{HH}} \text{ in (2.2)Metacyclophane}^*$$

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The high resolution proton magnetic resonance spectrum of the methylene groups in (2.2)metacyclophane has been observed at 60 and 15 Mcs. In this compound, the C-CH<sub>2</sub>-CH<sub>2</sub>-C groups are fixed in position with the dihedral angle between alkyl C-C bonds slightly less than the symmetrical, staggered 60° and with little distortion from tetrahedral of the other bond angles in the group. Therefore, the HCCH coupling constants should be characteristic of ethanic trans and gauche orientations and the CH<sub>2</sub> should be comparable with the geminal coupling in methane.

A complete analysis of the A<sub>2</sub>X<sub>2</sub> and A<sub>2</sub>B<sub>2</sub> type spectra, in combination with previous, unambiguous experimental findings that  $|J_{\text{gem}}^{\text{HH}}| \cong |J_{\text{t}}^{\text{HH}}| > |J_{\text{g}}^{\text{HH}}|$ , leads to the following assignments in (2.2)metacyclophane:  $J_{\text{t}}^{\text{HH}} = +12.3$ ,  $J_{\text{g}}^{\text{HH}}$  (the coupling of the "central" pair of gauche protons) = +3.2,  $J_{\text{gem}}^{\text{HH}} = +12.0$ , and  $J_{\text{g}}^{\text{HH}} = +4.0$ , all ±0.1 cps. The magnitudes of these constants agree well with previous valence-bond calculations for CH<sub>4</sub> and the ethanic HCCH group. However, the opposite signs found for the large trans and geminal constants disagrees with the theoretical prediction that both are positive. The observed difference in sign can not be attributed to substituent effects, angular distortions, or to motional averaging. It is concluded that one of the two sets of calculations is in error; the implications of this result are discussed.

## 1. Introduction

This paper is concerned with the comparison between experiment and valence-bond calculations of the  $\sigma$ -electron contribution to the proton-proton coupling constants of  $\text{CH}_2$  and  $\text{HCCH}$  groups in high resolution nmr spectra.<sup>1</sup> Such calculations predicted the geminal coupling  $J_{\text{gem}}^{\text{HH}}$  to be +12.5 cps in methane,<sup>2</sup> and subsequent, more approximate, calculations<sup>3</sup> for the coupling of vicinal protons in the  $\text{HCCH}$  ethanic fragment with tetrahedral  $\text{HCC}$  bond angles gave the trans coupling  $J_{\text{t}}^{\text{HH}}$  to be about +9.2 cps and the gauche  $J_{\text{g}}^{\text{HH}}$ , +1.7 cps. The magnitudes of these values agree well with experiment except that the trans vicinal constants observed for ethanic groups<sup>4</sup> (and also both the cis and trans constants for ethylene<sup>3</sup>) are often about 50% larger than predicted.

In most cases, only the magnitudes of the coupling constants have been obtained from experiment; but increasing attention is being given to the importance of determining their relative signs. Several instances of substituted ethylenes have been reported<sup>5,6</sup> in which the sign of  $J_{\text{gem}}^{\text{HH}}$  (1 to 3 cps) is opposite to, and also the same as, that of  $J_{\text{cis}}^{\text{HH}}$  (5 to 11 cps) and  $J_{\text{trans}}^{\text{HH}}$  (12 to 18 cps). These results are compatible with the valence-bond calculations for the  $\text{CH}_2$  fragment,<sup>5</sup> which neglect substituent and  $\pi$ -electron effects, and which predict that  $J_{\text{gem}}^{\text{HH}}$  should become negative for  $\text{HCH}$  bond angles larger than about  $120^\circ$ .<sup>5,7</sup> In a similar vein, for the vicinal coupling, experiment has yielded instances of substituted ethanes in which the sign of  $J_{\text{g}}^{\text{HH}}$  (1 to 3 cps) is opposite to, and also the same as, that of  $J_{\text{t}}^{\text{HH}}$  (10 to 16.5 cps).<sup>4,6</sup> These results also are compatible with the predicted dependence of the coupling upon the dihedral angle  $\phi$ ,

$$J_{\text{vic}}^{\text{HH}} \cong 9\cos^2\phi - 0.3 \quad , \quad (1)$$

in view of the neglect in the valence-bond calculations<sup>3</sup> of substituent effects, and the assumption of tetrahedral  $\text{HCC}$  angles.

However, while the present work was in progress a question less easy to dispose of was raised by reports<sup>8,9</sup> of relative sign determinations which conflict with the predictions<sup>2,3</sup> that large values of  $J_{gem}^{HH}$  and  $J_{vic}^{HH}$  should both be positive. In diethyl sulfite, the two protons in the  $CH_2$  groups are structurally non-equivalent because of the molecular asymmetry, so the spectrum is of the abc<sup>3</sup> type.<sup>1</sup> Because of this asymmetry,  $J_{gem}^{HH}$  could be determined in the  $CH_2$  group and its sign found with respect to  $J_{vic}^{HH}$  averaged over the  $CH_2$  group orientations.<sup>6</sup> The results are  $J_{gem}^{HH} = +10.45$  cps and  $J_{ac}^{HH} = J_{bc}^{HH} = +7.12$  cps. Similar results were found<sup>8</sup> for the  $-CH_2CHX-$  group of several 1,3-dioxo,5-X,cyclopentanes, in which the two slightly different vicinal constants are about 7 cps and opposite in sign to the 8 cps value for  $J_{gem}^{HH}$ . While these results indicate that something probably is intrinsically wrong with either the methane calculation<sup>2</sup> and/or that for the ethanic fragment,<sup>3</sup> the compounds studied are such that substituent effects, angular distortions and motional averaging are important, and their neglect in the theoretical treatment might be responsible for the apparent discrepancies in the relative signs.

A more convincing example is provided by the proton spectrum of the  $-CH_2CH_2-$  groups in (2.2)metacyclophane, the structure of which is sketched in Fig. 1. The spectrum of this compound was first reported by Wilson, Boekelheide, and Griffin,<sup>10</sup> in a study of chemical shifts produced by ring currents, and for which only a partial analysis was made. They gave the spatial relationships of the protons on the basis of an assumed model which led to the methylene groups being twisted about the  $CH_2-CH_2$  bond by about  $18^\circ$  from the symmetrically staggered conformation. However, an x-ray structural determination has been made for the solid compound,<sup>11</sup> and the C-C-C bond angles of the alkyl groups found to be  $109^\circ 49'$  and  $110^\circ 48'$ . Moreover, from the carbon positions given we have calculated the dihedral angle between the alkyl C-C-C bonds

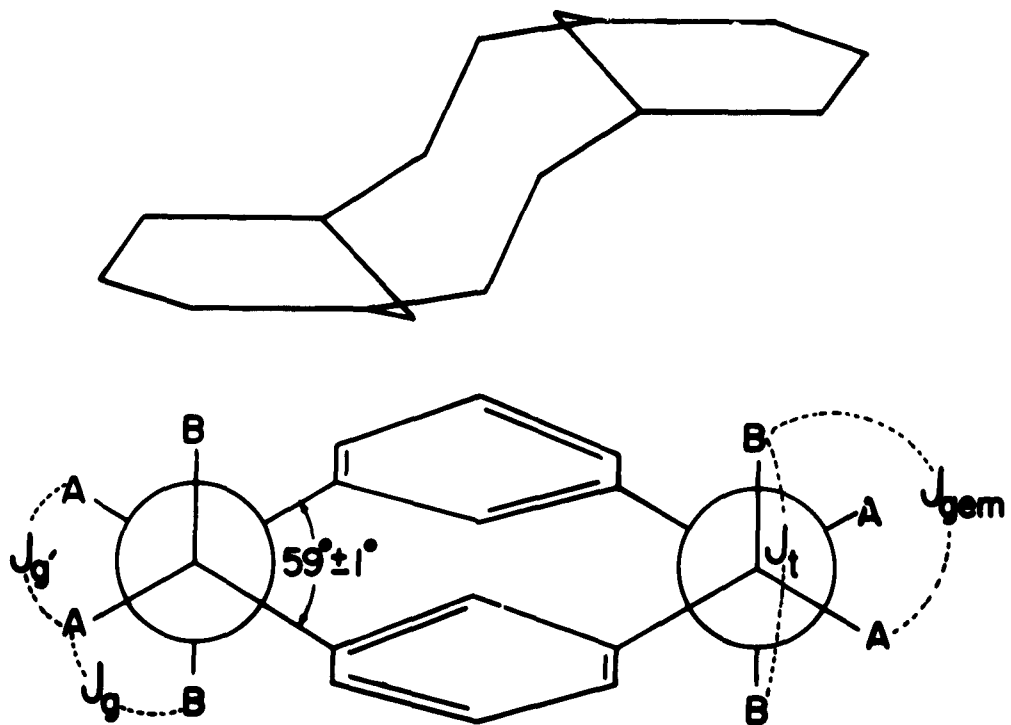


Fig. 1. The molecular geometry of (2.2)metacyclophane. The bottom part of the figure is a projection in the plane perpendicular to the C-C bond of the  $-\text{CH}_2\text{CH}_2-$  groups; it includes definitions of the symbols used for the coupling constants.

and found it to be  $59 \pm 1^\circ$ , which means that the methylene protons are in virtually a symmetrical staggered conformation. Therefore, this compound has the advantage that angular distortion effects should be minimal for the  $-\text{CH}_2\text{CH}_2-$  groups. Moreover, the latter are locked into position so that individual values can be obtained for  $J_t^{\text{HH}}$  and  $J_g^{\text{HH}}$  instead of some uncertain kind of average; and, finally, only carbon and hydrogen atoms are bonded to the methylene groups, so substituent effects should be small. For these reasons, a complete analysis of the  $-\text{CH}_2\text{CH}_2-$  spectrum was undertaken.

## II. Experimental Results

The sample of (2.2)metacyclophane used in these experiments was very kindly provided by Wilson, Boekelheide, and Griffin.<sup>10</sup> The high resolution proton spectra were observed at room temperature using 10% solutions in  $\text{CCl}_4$ . The spectra at 60 Mcs were run locally on Varian Associates HR-60 and A-60 spectrometers. The 15.083 Mcs spectrum was obtained through the courtesy of Dr. J. N. Shoolery at Varian Associates, where it was run on a V-4300 spectrometer system with a 12" magnet. The spectra were calibrated by the usual audiofrequency sideband method.<sup>1</sup>

The over-all procedure used to determine the magnitudes and relative signs of the coupling constants in the  $-\text{CH}_2\text{CH}_2-$  group is the following. At a resonance frequency of 60 Mcs, the chemical shift  $\nu_0\delta$  between the  $A_2$  and  $B_2$  sets of protons, defined in Fig. 1, is sufficiently large that the quite simple observed spectrum is a good approximation to the  $A_2X_2$  type.<sup>1</sup> From it, the magnitudes of  $\nu_0\delta$  and of the four coupling constants are determined readily, as well as the relative signs for each of two pairs of coupling constants. In part, the 60 Mcs spectrum is easy to analyze because it is insensitive to one of the relative signs. However, the latter becomes important at lower resonance frequencies, where the spectrum is of the  $A_2B_2$  type.<sup>1</sup> Therefore, the magnitudes

and signs obtained from the 60 Mcs spectrum were used to calculate 15.083 Mcs spectra for the remaining relative sign permutations, and comparison of these with the observed spectrum completes the analysis.

We will not repeat here the theoretical expressions for the transition energies and intensities of  $A_2X_2$  and  $A_2B_2$  spectra, which are available in several publications<sup>1</sup> along with some methods for analyzing the spectra. However, determining the relative signs and magnitudes of all four coupling constants in such a 4-spin system is sufficiently complex that it seems desirable to outline all of the steps followed in the present case.<sup>12</sup>

It is convenient to use parameters in the analysis which are the sum and difference of pairs of the coupling constants.<sup>1</sup> For our case, these parameters are

$$\begin{aligned} K &= \pm |J_t + J_{g'}| & N &= |J_g + J_{gem}| \\ M &= |J_t - J_{g'}| & L &= |J_g - J_{gem}| \end{aligned} \quad (2)$$

where the coupling constants are defined in Fig. 1. In principle, each of the constants, and also the chemical shift, has both magnitude and sign. However, the spectrum is independent of the sign of the chemical shift and insensitive to inverting the signs of all coupling constants. This leaves the appearance of the spectrum governed by the magnitudes of the five quantities and by the three relative signs of the four coupling constants.

In terms of the parameters K, L, M and N, which we treat as positive quantities except for K in the one circumstance noted below, the relative signs of each pair of coupling constants in Eq. (2) is determined by the relative values of the corresponding two parameters. Thus, if  $J_g$  and  $J_{gem}$  have the same sign,  $N > L$ ; and if opposite,  $N < L$ . Identical relations involving K and M hold for  $J_t$  and  $J_{g'}$ . In addition, the spectrum is sensitive to the actual relative signs of  $K = (J_t + J_{g'})$  and  $N = (J_g + J_{gem})$ . Whether the observed spectrum is fitted by

K positive or negative, while treating N as positive, determines the third relative sign. If K negative applies, then the constant of largest magnitude in K is of opposite sign to the constant of largest magnitude in N, while they are of the same sign for a positive K. Finally, the magnitudes of the coupling constants are obtained by means of Eq. (2) from the numerical (positive) values for K, L, M, and N; however, the spectrum alone does not tell which constant is which within each pair and supplemental information about the relative magnitudes of the constants is required to complete the assignment.

#### A. 60 Mcs Spectrum

The proton spectrum observed at 60 Mcs is shown in Fig. 2. To a first approximation it is of the  $A_2X_2$  type,<sup>13</sup> consisting of "mirror image"  $A_2$  and  $X_2$  multiplets whose centers are separated by  $[(\nu_{0\delta})^2 + N^2]^{1/2}$ . In general, each of these two multiplets has ten lines, two quartets and a doublet with a common center. The splitting of the outer pairs of lines in one quartet is K, and of the other, M; while the splitting of the inner pair is  $(K^2+L^2)^{1/2}-K$  and  $(M^2+L^2)^{1/2}-M$  respectively, for the two quartets. The lines of the doublet are the strongest transitions; their splitting is  $N$ .<sup>1,12</sup>

In the observed spectrum, the  $A_2$  and  $X_2$  multiplets have two rather broad, very strong lines at the center, with two weaker lines at each side. Obviously, the inner lines of the two quartets fall on top of or very close to the strong N-doublet, and only the outer lines of the quartets are resolved. Therefore, the  $\sim 8$  cps splitting of the strong center pair of lines undoubtedly is N. Also, the outer splittings of the two quartets are  $\sim 9$  and  $\sim 15$  cps but at this point it is uncertain which is K and which is M. These values, in combination with the expressions for the central splitting of the two quartets and their observed values of  $\sim 8$  cps, give an unambiguous value for L of  $15 \pm 2$  cps. Also, the separation between the centers of the two multiplets is approximately the chemical shift, which gives  $\nu_{0\delta} \approx 60.3$  cps.

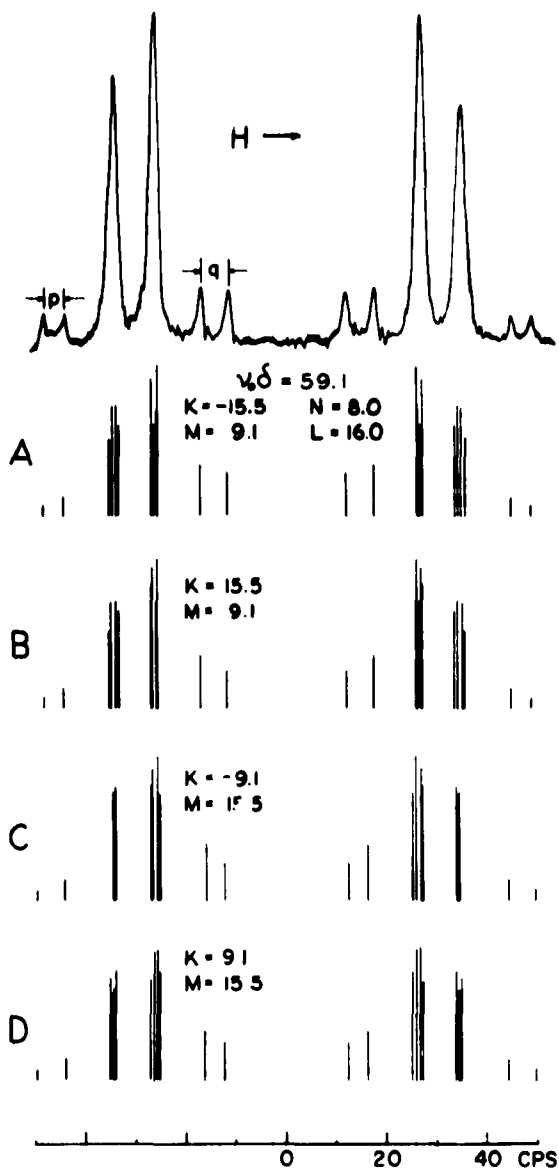


Fig. 2. At the top is the spectrum observed at 60 Mcs for the  $-\text{CH}_2\text{CH}_2-$  group protons in (2.2)metacyclophane. The line spectra shown below were calculated for the known values of N and L, 8.0 and 16.0 cps, and the four possible sign permutations,  $K = +15.5$ ,  $M = 9.1$  and  $K = +9.1$ ,  $M = 15.5$  cps. Only the first two, A and B, fit the splittings p and q.

Except for refinement of these numerical values, no further information could be obtained from the 60 Mcs spectrum if it were truly of the  $A_2X_2$  type.<sup>1,12</sup> However, second order effects are visible in the intensities of the  $A_2$  and  $X_2$  multiplets, which are peaked slightly towards one another. Also, the multiplets are asymmetric in that the separation between the outer lines from each quartet is less for the pairs of lines at the two ends of the spectrum than for the two pairs nearest the center, e.g.  $p < q$  as in Fig. 2. Because of these deviations, efforts were made not only to refine the numerical values of the parameters but also to extend the analysis.

Two major aspects of the spectrum remain to be determined. First, which of the  $\sim 9$  and  $\sim 15$  cps values is  $K$  and which is  $M$ ? Secondly, does the observed spectrum correspond to  $K$  positive or negative? Therefore, spectra were calculated, and compared with experiment, for all four remaining possible relative sign permutations,  $K \approx +9$ ,  $M \approx 15$ ; and  $K \approx +15$ ,  $M \approx 9$ . These calculations were made with the University of Illinois electronic digital computer, Illiac,<sup>14</sup> using a program written for the general 6-spin system.<sup>15</sup> More refined parameters were obtained by varying them systematically, comparing the resulting calculated spectra with experiment, and then interpolating. In this manner, the following best-fit, numerical values were obtained:  $\nu_{08} = 59.1$ ,  $N = 8.0$ ,  $L = 16.0$ , and  $K$  or  $M = 9.1$  or  $15.5$ , all in cps. More important, the calculated spectra given in Fig. 2 for the four possible sign permutations show that although the spectrum observed at 60 Mcs is too insensitive to the sign of  $K$  for its determination, the asymmetry in the splittings  $p$  and  $q$  in Fig. 2 is governed by the relative magnitudes of  $K$  and  $M$ . In order to have  $p < q$  as observed, it is necessary to have  $K > M$ ,<sup>16</sup> which requires that  $K$  be  $15.5$  and  $M$ ,  $9.1$  cps. Of the four calculated spectra in Fig. 2, A and B, with  $K = +15.5$  and  $M = 9.1$  cps, agree with experiment, while C and D, with  $K = +9.1$  and  $M = 15.5$  cps do not.

B. 15.083 Mcs Spectrum

In order to determine the relative sign of K, the spectrum was observed at 15.083 Mcs, where the chemical shift is small enough (14.7 cps) that the spectrum is definitely  $A_2B_2$ . The results are shown in Fig. 3. A complete analysis might very well have been obtained from a single,  $A_2B_2$  type spectrum at say 30 Mcs or even 40 Mcs.<sup>12</sup> However, the analysis of a spectrum run at a high, as well as a low frequency minimizes the possibility of error. Figure 3 includes the observed spectrum and also spectra calculated for the two remaining sign permutations,  $K = +15.5$  cps. It is seen that there is excellent agreement between experiment and the spectrum calculated for  $K = -15.5$  cps, and very poor agreement for  $K = 15.5$  cps. As a check, spectra not shown were also calculated for  $K = +9.1$  and  $M = 15.5$  cps, and they too do not agree with experiment.

Therefore, we conclude that the parameters which apply to the  $-CH_2CH_2-$  group are:

$$\begin{array}{ll} K = -15.5 \text{ cps} & N = 8.0 \text{ cps} \\ M = 9.1 & L = 16.0 \end{array} \quad (3)$$

Upon combining these results with the definitions in Eq. (2) we find from N and L that  $J_g$  and  $J_{gem}$  are 12.0 and 4.0 or 4.0 and 12.0 cps. Moreover, they are of opposite signs because  $N < L$ . From K and M,  $J_t$  and  $J_g'$  are 12.3 and 3.2 or 3.2 and 12.3 cps. Also, they are of the same sign because  $K > M$ . (Here, both K and M must be treated as positive quantities.) Furthermore, since K and N actually have opposite signs, the largest constant of the K,M pair (12.3 cps) is of opposite sign to the largest constant of the N,L pair (12.0 cps). The assignment is completed by introducing the inequality  $|J_t| > |J_g'|$  which is known with certainty from the nmr studies of substituted ethanes,<sup>4,6</sup> and the inequality  $|J_{gem}| > |J_g|$  which is equally certain from the experimental results<sup>4,6</sup> for substituted ethanes in combination with those on  $J_{gem}$  in methane<sup>2</sup>

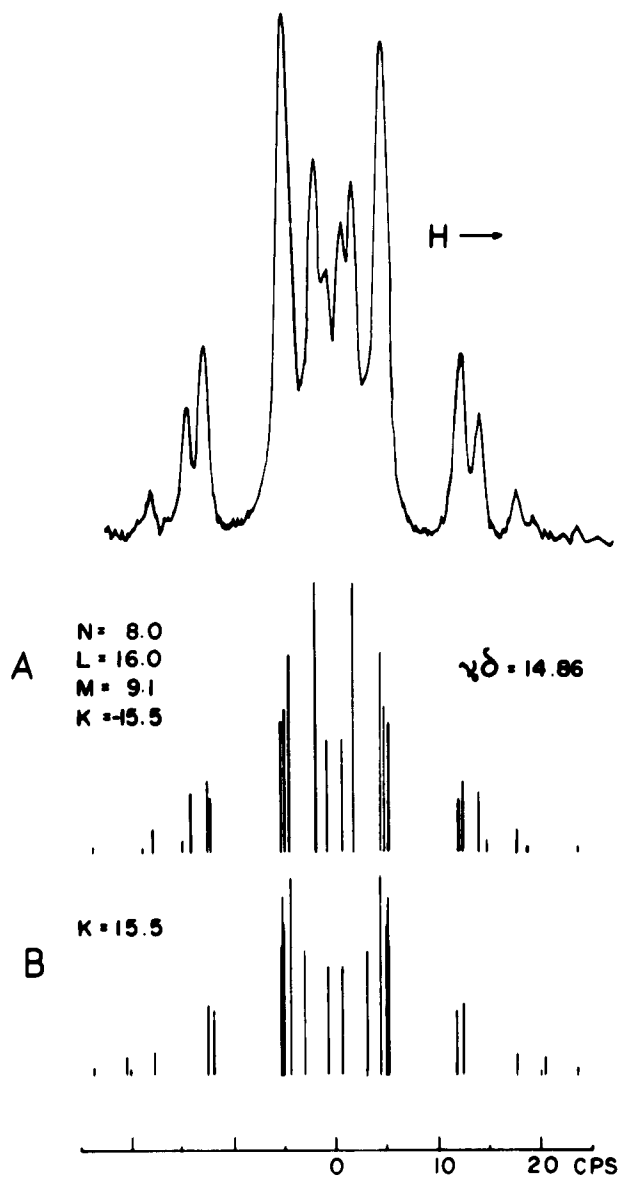


Fig. 3. At the top is the spectrum observed at 15.083 Mcs for the  $-\text{CH}_2\text{CH}_2-$  group protons in (2.2)metacyclophane. The line spectra shown below were calculated for the two remaining sign permutations, i.e. for K positive and negative. The bottom spectrum, for K positive disagrees greatly with the center portion and also the wings of the observed spectrum.

and in substituted methanes having HCH angles near tetrahedral.<sup>5</sup> The final assignment is

$$\begin{aligned} J_t^{HH} &= \pm 12.3 \text{ cps} & J_{gem}^{HH} &= \bar{+}12.0 \text{ cps} \\ J_{g'}^{HH} &= \pm 3.2 & J_{g''}^{HH} &= \pm 4.0 \end{aligned} \quad (4)$$

where the probable errors of the numerical values are about  $\pm 0.1$  cps.

### III. Discussion

Our finding of large values of opposite sign for  $J_t^{HH}$  and  $J_{gem}^{HH}$  leaves little room for manoeuver. The closeness of the  $12.0 \pm 0.1$  cps value for  $J_{gem}^{HH}$  to the  $12.4 \pm 0.6$  cps observed in methane<sup>2</sup> indicates that it is not affected by angular distortion and substituent effects. The small difference between the 3.2 and 4.0 cps values for  $J_{g'}^{HH}$  and  $J_{g''}^{HH}$  is compatible with the C-C-C-C dihedral angle being slightly less than the  $60^\circ$  for a symmetric, staggered C-CH<sub>2</sub>CH<sub>2</sub>-C group, which is suggested by the x-ray data for the solid.<sup>11</sup> Also, this would account for the value of 12.3 cps for  $J_t^{HH}$  being on the small side of values found for substituted ethanes.<sup>6,7</sup> Therefore, our results, as well as the less conclusive earlier studies<sup>6,9</sup> show that either the calculation on CH<sub>4</sub><sup>2</sup> or that on the ethanic (and probably also on the ethylenic) fragment<sup>3</sup> is in error.

The implications of this finding are unfortunate. For example, comparisons with experiment of theoretical calculations of  $\pi$ -electron contributions to long-range proton-proton coupling constants in unsaturated straight chain compounds were based on the assumption that  $J_{vic}^{HH}$  is positive.<sup>17</sup> This comparison, as well as many others, is now in doubt, and it is essential to clarify the problem. One can speculate as to which of the calculations is most likely to be in error, if not both. In some ways, the calculations for the HCCH fragment

present the best opportunities for error. The calculations are more complex than for  $\text{CH}_4$  (or  $\text{CH}_2$ ), and it is possible for example that the *exchange integrals* non-neighboring-atom<sub>A</sub> should not have been neglected.<sup>3</sup>

A more direct approach to the problem would be to determine  $J_{\text{vic}}^{\text{HH}}$  and/or  $J_{\text{gem}}^{\text{HH}}$  with respect to  $J_{\text{Cis-H}}$ . The calculation of the latter is considerably simpler than for  $J_{\text{HH}}$ , and there is little doubt but that  $J_{\text{CH}}$  is positive.<sup>18,19</sup> At least such relative sign determinations would suggest which of the  $J_{\text{HH}}$  calculations should be redone first. Fortunately, it appears feasible to determine the relative signs of  $J_{\text{CH}}$ ,  $J_{\text{gem}}^{\text{HH}}$ , and  $J_{\text{vic}}^{\text{HH}}$  by the sort of approach used here and also by double resonance methods.

In fact, analysis of the  $\text{P}^{31}$  and proton spectra observed for diphosphine  $\text{H}_2\text{PPH}_2$  has given results,<sup>20</sup> bearing at least indirectly on our problem. For this compound,  $J_{\text{gem}}^{\text{HH}}$  and  $J_{\text{pp}}$  were found to have values of  $108.2 \pm 0.2$  and  $12 \pm 4$  cps, respectively, and to be of the same sign. Moreover,  $J_{\text{vic}}^{\text{HH}}$  (cis and trans) has values of  $10.5 \pm 0.2$  and  $6.8 \pm 0.2$  cps which are of the same sign but opposite to  $J_{\text{gem}}^{\text{HH}}$  and  $J_{\text{pp}}$ . By analogy to the results of the HCCH calculations,<sup>3</sup> it was assumed<sup>20</sup> that  $J_{\text{vic}}^{\text{HH}}$  was positive in diphosphine, which, of course, made  $J_{\text{pp}}$  and  $J_{\text{gem}}^{\text{HH}}$  negative. A negative value for  $J_{\text{pp}}$  is surprising because the coupling between directly bonded atoms due to the usually dominant contact term is positive. In view of the present findings it may be somewhat more plausible to take  $J_{\text{pp}}$  as positive, which leads to  $J_{\text{gem}}^{\text{HH}}$  positive and  $J_{\text{vic}}^{\text{HH}}$  (cis and trans) negative. Moreover, a positive value of  $\sim 12$  cps for  $J_{\text{gem}}^{\text{HH}}$  in diphosphine, and in phosphine,<sup>20</sup> is consistent with the small,  $94^\circ$  HPH bond angle and the valence-bond calculations of positive geminal coupling constants in  $\text{CH}_4$ <sup>2</sup> and in  $\text{SiH}_4$ .<sup>21</sup> But the consistency does not prove that the latter are correct.

\* Acknowledgment is made to donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The work also was supported by the Office of Naval Research.

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<sup>2</sup>M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *J. Chem. Phys.* 27, 597 (1957); M. Karplus and D. H. Anderson, *J. Chem. Phys.* 30, 6 (1959).

<sup>3</sup>M. Karplus, *J. Chem. Phys.* 30, 11 (1959).

<sup>4</sup>H. S. Gutowsky, G. G. Belford and P. E. McMahon, *J. Chem. Phys.* 37, 000 (1962), and prior work cited there for substituted ethanes.

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<sup>10</sup>D. J. Wilson, V. Boekelheide and R. Griffin, *J. Am. Chem. Soc.* 82, 6302 (1960).

<sup>11</sup>C. J. Brown, *J. Chem. Soc.* 3278 (1958).

<sup>12</sup>D. M. Grant, R. C. Hirst and H. S. Gutowsky, *J. Chem. Phys.* 37, 000 (1962). This reference describes in considerable detail the nature and analysis of  $A_2B_2$  and  $A_2X_2$  spectra in general, and serves as a basis for the approach used here on (2.2)metacyclophane.

<sup>13</sup>The x-ray structure of the solid, reported in reference 11, indicates a  $1^\circ$  difference in the C-C-C bond angles at the two ends of the  $-CH_2CH_2-$  groups. This could reduce the symmetry of the 4-spin system from  $A_2X_2$  to ABXY. However, the nmr spectra contain no evidence of such asymmetry, which may be too small for detection or else effectively absent in the liquid phase.

<sup>14</sup>We are indebted to the staff of the Digital Computer Laboratory for their assistance with the calculations.

<sup>15</sup>This program was written by Dr. Geneva G. Belford.

<sup>16</sup>The relation found between the splitting inequality and the relative (absolute) values of K and M holds over the considerable range of parameters for which spectra were calculated. However, the relation is reversed if one takes  $N > L$  instead of  $N < L$  as it must be here; see e.g. the calculated spectra in reference 12.

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