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The Effect of Hyperconjugation on the Geminal Spin-Spin Coupling Constant

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The π -electron effect on the geminal proton spin-spin coupling constant can be treated theoretically with a calculation based on the treatment for long range π -electron coupling constants in unsaturated molecules. This treatment relates the σ - π exchange terms used in calculating spin-spin coupling constants to experimental e.s.r. hyperfine constants. The π -electron contribution, on this basis, for a methylene group adjacent to a single π -bond is estimated to be -1.5 c.p.s. Experimental evidence is presented showing that the π -electron contribution to the geminal coupling constant is additive with a contribution of approximately $|1.9|$ c.p.s. per adjacent π -electron bond. It is predicted from theory, and experimentally observed, that there is an enhancement of the π -contribution to the coupled methylene protons if these are symmetrically oriented with respect to the adjacent double bond in certain cyclic compounds. Based on these conclusions, it is reasoned that hyperconjugative effects of the type discussed here are proportional to the number of adjacent π -bonds and are significantly affected by the molecular conformation.

Introduction

Theoretical calculations of electron-coupled nuclear spin-spin coupling constants, although necessarily semiquantitative in nature, have met with a definite degree of success in the correlation of a wide range of experimental data. The use of Heitler-London product wave functions by Ramsey and Purcell¹ and by Gutowsky, McCall and Slichter² in the study of electron correlated nuclear spin-spin interactions for directly bonded nuclei was extended by Karplus and co-workers³⁻⁷ and McConnell⁸ to a method of calculating the contact contribution in the electron-coupled interactions between non-bonded nuclei. These calculations use the standard valence-bond (VB) formalism^{9,10} and show, for example, the qualitatively correct dependence of vicinal H-H coupling constants on the dihedral angle,⁴ the alternation in sign of H-H coupling constants with the number of bonds in even-alternate aromatic hydrocarbons⁸ and in unsaturated molecular systems,⁷ and the relationships of orbital hybridization and charge distribution to C¹³-H coupling constants.⁶ The effects of C-H bond polarity on the geminal and vicinal couplings were studied by Hiroike¹¹ and Ranft,¹² and the effect of substituents on the vicinal coupling constants was discussed.¹² Furthermore, the dependence of geminal H-H coupling constants on the H-C-H angle⁵ and the substituent groups¹³⁻¹⁶ was examined.

The recent findings, however, by a number of workers¹⁷ indicating that geminal H-H coupling constants are, in many cases, opposite in sign to the vicinal coupling constants appears to contradict the theoretical results which predict that the absolute signs of both geminal and vicinal coupling constants are positive.³⁻⁵ Furthermore, the observations of Anet¹⁸ and of Lauterbur,¹⁹ who used double resonance techniques to show, respectively, that the geminal H-H coupling constant in methanol is *opposite* in sign to the directly bonded C¹³-H coupling constant and that the vicinal H-H coupling constant in 1,2-dichloroethane is of the *same* sign as the directly bonded C¹³-H coupling constant, are cited. Collectively, these findings indicate that geminal coupling constants in these compounds are probably negative, while the corresponding vicinal couplings are probably positive.

By treating a CH₂ fragment as a model for a four-electron VB calculation, Gutowsky, *et al.*,⁵ showed by a simple perturbation calculation that the geminal H-H coupling constant could be written in the form

$$J_{\text{HH}}^{\text{gem}} = \lambda[2K(\text{C}_2, \text{H}_1) - K(\text{H}_1, \text{H}_2) - K(\text{C}_1, \text{C}_2)] \quad (1)$$

where $\lambda \cong 30$ c.p.s./e.v. and $K(\text{A}, \text{B})$ is the empirical exchange integral between atomic orbitals A and B. Karplus²⁰ has pointed out that a cancellation of terms occurs in eq. 1 between exchange integrals which are of the same order of magnitude, so that small differences in these values can significantly alter the signs and magnitudes of coupling constants. In the particular case of tetrahedral carbon orbitals for which $K(\text{H}_1, \text{H}_2)$

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$\cong -K(C_1, C_2)$, the geminal coupling constant will be nearly proportional to $2K(C_2, H_1)$. Since this integral is evaluated from crude empirical exchange integrals,²¹ it appears that even approximate VB calculations will not be possible until better methods to estimate it are available.

A more feasible semi-empirical calculation of the contribution to the geminal coupling constant by an adjacent π -electron bond is presented in this paper to show that at least certain features of the geminal coupling constant might still receive theoretical consideration. Using the theory developed by McConnell⁸ and Karplus⁷ for the π -electron contribution to the H-H coupling constants in unsaturated and aromatic molecules, this π -electron substituent effect on the geminal coupling constant is related to the hyperfine constant for the interaction between an unpaired π -electron and the hydrogen α to the multiple bond. Satisfactory agreement of these two experimental quantities suggests that the theoretical VB formulation has some validity, and that the magnitudes of the particular exchange integrals used to obtain this agreement might in fact be the best empirical values available for these integrals.

It is the further purpose of this study to show that the experimentally observed π -electron contribution to the geminal coupling constant is additive for a class of compounds having tetrahedral or nearly tetrahedral H-C-H angles, and that there is a conformational effect of this contribution as shown by an enhancement of the coupling in certain cyclic compounds.

Theoretical Considerations

In our previous work¹⁴ it was shown by the use of a six-electron VB model, consisting of a methylene group to which an adjacent π -electron pair was added, that there is a π -electron effect on the geminal H-H coupling which is of the same order of magnitude as those observed experimentally. Since these calculations were based, for the most part, on the exchange integrals which were used by Karplus and Anderson for methane³ and theoretical estimates for σ - π exchange terms, the calculations predict the wrong sign for the π -electron effect on the geminal coupling constant.

The π -electron contribution to the geminal coupling constant can be evaluated, however, without recourse to poor empirical exchange integrals by applying the theory developed by Karplus⁷ and McConnell⁸ for the π -electron contributions to the H-H coupling constants in unsaturated and aromatic molecules. This method recognizes the correspondence between hyperfine constants in the e.s.r. spectra of free radicals and the σ - π exchange terms in the energy matrix, the solution of which gives a molecular wave function to be used in the calculation of the coupling constants, thereby permitting the calculation of the π -electron effect to be based upon experimentally determined quantities. As the π -electrons do not form a connective link in the coupling of geminal protons in the same manner as proposed by Karplus⁷ and McConnell,⁸ it is necessary to base the calculation on the modified approach as used by Holmes and Kivelson²² in determining the indirect π -electron contribution to the long range H-H coupling constant in acetone. Since the geminal protons in a molecular fragment of the type $-\text{CH}_2-\text{C}=\text{X}$

are coupled through only the nearest π -orbital in a manner analogous to the acetone case, the protons are ex-

pected to have parallel spin orientations, as was shown by Holmes and Kivelson,²² and the π -contribution to the geminal coupling constants is negative relative to the one reported by Karplus⁷

$$J_{\text{HH}}^{\pi}(\varphi) = -2.1 \times 10^{-16} (a_{\text{H}} a_{\text{H}}' / \Delta_{\pi}) \quad (2)$$

where Δ_{π} is the average singlet- π to triplet- π excitation energy, a_{H} is the hyperfine constant for the $\text{CH}_3\text{-C}\cdot$ radical, and $J_{\text{HH}}^{\pi}(\varphi)$ is the π -contribution to the geminal coupling constant.

Hyperfine constants, a_{H} , in radicals of the type $\text{CH}_3\text{-C}\cdot$ have been investigated both experimentally^{23,24} and theoretically²⁵ and are shown to be positive and of the form^{23,26}

$$a_{\text{H}} = A_0 + A_1 \cos^2 \varphi \quad (3)$$

where φ is the dihedral angle between the H-C-C plane and the axis of the unpaired π -electron. Using this approach estimates of the value of A_1 based on electron spin resonance data range from 112×10^6 c.p.s. to 150×10^6 c.p.s.^{23,26} while A_0 was taken to be zero, an assumption requiring a negligible hyperfine coupling at $\varphi = 90^\circ$. Furthermore, McLachlan²⁵ showed by a VB perturbation calculation that a_{H} for this type of fragment is directly proportional to the exchange integral $K(C_1, P_1)$ between a carbon hybrid orbital and an adjacent $2p_{\pi}$ electron. As it is this same $K(C_1, P_1)$ integral which most significantly affects the six electron VB calculation of the π -electron contribution to the geminal coupling constant, it is instructive to analyze the results of the two methods. In the standard VB treatment Barfield and Grant¹⁴ used an expression for $K(C_1, P_1)$ having the same angular dependence as shown in eq. 3, but based on existing theoretical integral tables they obtained a value for the angular independent term corresponding to A_0 which was equal to about $-(1/2)$ of the angular dependent term corresponding to A_1 . It is now evident to the authors that their previous value for the A_0 type term is too large and that the approximation of a negligible A_0 term based on e.s.r. hyperfine data is considerably better. Furthermore, only the approximation of $A_0 = 0$ predicts what, at present, seems to be the correct negative sign¹⁷⁻¹⁹ for the adjacent π -electron effect upon the geminal coupling constant and gives the right dependence of this coupling on molecular conformation. When these results are considered in light of the successes of Karplus,⁷ McConnell,⁸ and Holmes and Kivelson,²² it must be concluded that the approximation of $A_0 = 0$ is the better of the two extremes for all practical purposes.

The equivalence of the two methods, the six-electron VB approach and the method based on eq. 2 and 3, used in calculating the π -electron contribution to $J_{\text{HH}}^{\text{gem}}(\varphi)$, represented by $J_{\text{HH}}^{\pi}(\varphi)$, can be seen from a plot of $J_{\text{HH}}^{\pi}(\varphi)$ vs. φ in Fig. 1. The dashed line corresponds to results obtained from eq. 2 and 3 using 150×10^6 c.p.s. for A_1 , zero for A_0 and 6.0 e.v.⁷ for Δ_{π} . The solid line gives the values obtained from the six-electron VB calculation using zero once again for the angular independent term and -1.159 e.v. for the angular dependent coefficient in the expression for $K(C_1, P_1)$. While this value is slightly larger than the one used by McLachlan²⁵ to calculate an a_{H} of 140×10^6 c.p.s., still it is based on acceptable values¹⁵ for the several terms comprising this integral and in part compensates for the larger 9.0 e.v. used for ΔE in the six-electron VB calculation as compared with 6.0 e.v. for Δ_{π} . To compare the more complete six-electron VB calcula-

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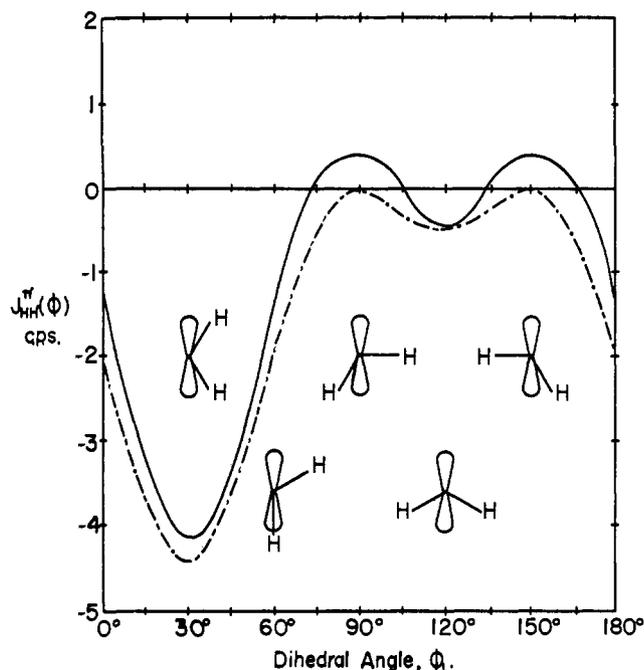


Fig. 1.—The calculated π -contribution to the geminal coupling constant is exhibited as a function of the dihedral angle between the methylene group and the adjacent π -bond. This angle is graphically illustrated by the small drawings which show the projection of the methylene group on the π -bond. The solid line is obtained from the six-electron VB method and the dashed line is based on values obtained from eq. 2 and 3. As this curve has a periodicity of 180° , only the range 0 to 180° is shown.

tion with the hyperfine coupling approach, the results were corrected by subtracting the value obtained from the corresponding four-electron VB calculation⁵ which neglects $K(C_1, P_1)$ and $K(P_1, P_2)$. While the value of $K(C_2H_1)$ dominates the σ -electron term in the geminal coupling constant, it was found that it has no effect upon the π -electron contribution as obtained for Fig. 1. The serious inaccuracies inherent in $K(C_2H_1)$, which limit the validity of the four-electron treatment,²⁰ therefore do not affect this work as the σ - and π -contributions are separable. The agreement between the two methods of calculating the π -electron contribution is remarkable, and one can assume that the simplifying assumptions used in the theory linking hyperfine constants with spin-spin coupling constants have not been more hazardous than those inherent in the general VB treatment.

To predict the π -electron enhancement of an adjacent geminal coupling constant in a rotating methyl or methylene group, it is necessary to average $J_{HH}^{\pi}(\varphi)$ for all possible conformations, weighted with respect to the potential barrier hindering internal rotation. A good rotational averaging of $J_{HH}^{\pi}(\varphi)$ would require a relation of the form

$$\langle J_{HH}^{\pi}(\varphi) \rangle_{av} = \frac{\int J_{HH}^{\pi}(\varphi) \exp \{-(V_0/2RT)(1 - \cos 3[\varphi - \pi/2])\} d\varphi}{\int \exp \{-(V_0/2RT)(1 - \cos 3[\varphi - \pi/2])\} d\varphi} \quad (4)$$

where V_0 is the height of the assumed threefold barrier. If V_0 is significantly greater than RT it is sufficient merely to sum over the couplings for conformations of minimum energy. Information on the conformations of greatest stability for a tetrahedral carbon relative to an adjacent trigonal carbon has been supplied by microwave work on propylene²⁷ and on molecules of the type CH_3COX ,²⁸ wherein it was exhibited that the stable

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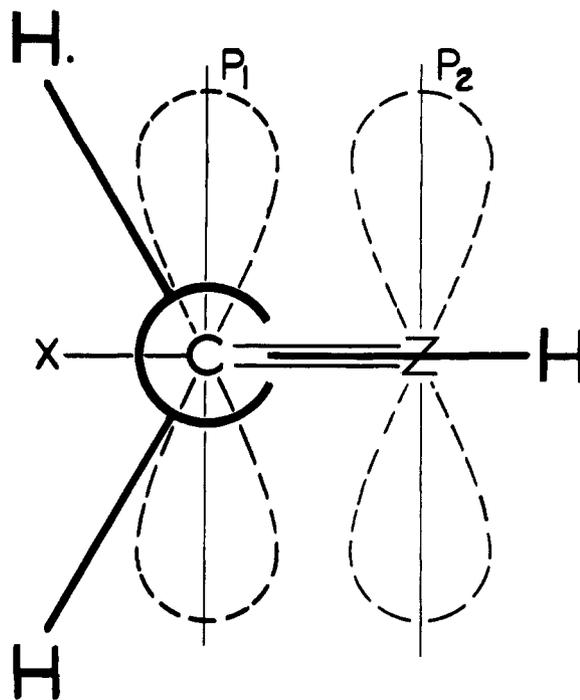


Fig. 2.—Equilibrium conformation for a series of compounds $Z-CH_2CX$. With the methyl carbon projected on the α -carbon, one of the methyl hydrogens will eclipse the substituent Z , which forms a double bond with the α -carbon.

conformations are those with one of the methyl hydrogens eclipsing the double bond as shown in Fig. 2. Using this structural information and the assumption that V_0 is much greater than RT as a basis for simplifying eq. 4, we obtain the following expression for calculating $\langle J_{HH}^{\pi}(\varphi) \rangle_{av}$

$$\langle J_{HH}^{\pi}(\varphi) \rangle_{av} = \frac{1}{3} [J_{HH}^{\pi}(90^\circ, 210^\circ) + J_{HH}^{\pi}(210^\circ, 330^\circ) + J_{HH}^{\pi}(330^\circ, 90^\circ)] \quad (5)$$

This simplified expression is acceptable whenever the threefold minima are of comparable energy and separated by a rotational barrier significantly exceeding the value of RT . A value of -1.5 c.p.s. for $\langle J_{HH}^{\pi}(\varphi) \rangle_{av}$ is obtained if the dashed line of Fig. 1 is treated with eq. 5.

The following more generalized expression is required if the threefold symmetry is destroyed with a substituent on the methyl group

$$\langle J_{HH}^{\pi}(\varphi) \rangle_{av} = p_I J_{HH}^{\pi}(210^\circ, 330^\circ) + p_{II} [J_{HH}^{\pi}(90^\circ, 210^\circ) + J_{HH}^{\pi}(330^\circ, 90^\circ)] \quad (6)$$

where p_I and p_{II} are population factors ($p_I + 2p_{II} = 1$) for the distinguishable conformers in which either the substituent or a hydrogen respectively eclipse the double bond. Equation 5 is the special case where each of these statistical factors is $1/3$. Considering the feature of eq. 6 and the results of Fig. 1 it is evident that $\langle J_{HH}^{\pi}(\varphi) \rangle_{av}$ will be enhanced when p_I increases at the expense of p_{II} while a decrease in the π -electron contribution will result when p_I approaches zero.

Expression 5 or 6 cannot properly be applied to the contribution of a π -electron pair in a triple bond due to the cylindrical symmetry of the four π -electrons. This condition will render V_0 equal to zero, and the expression for $\langle J_{HH}^{\pi}(\varphi) \rangle_{av}$ per π -electron pair becomes

$$\langle J_{HH}^{\pi}(\varphi) \rangle_{av} = \frac{1}{2} \pi \int_0^{2\pi} J_{HH}^{\pi}(\varphi) d\varphi \quad (7)$$

Integration of eq. 7 using eq. 2 and 3 gives a value of

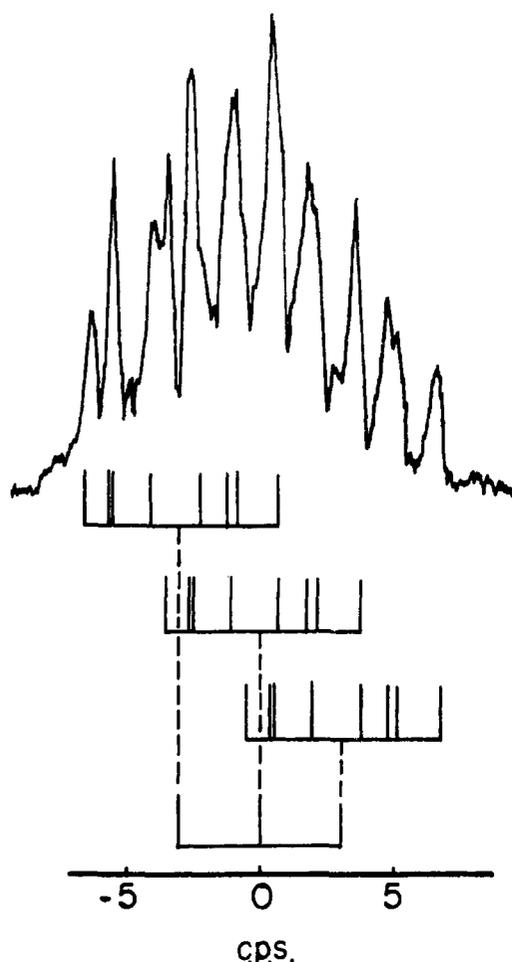


Fig. 3.—The proton magnetic resonance spectrum of the CHD group of vinylmonodeuterioacetonitrile.

—1.5 c.p.s. for $\langle J_{HH'}(\varphi) \rangle_{av}$ which is the same as found from eq. 5 for a large barrier.

Based on the above considerations, the theoretical conclusions are summarized in the following statements. First, a π -electron pair in either a double or triple bond adjacent to a "freely rotating" methylene group makes a contribution to the geminal coupling constant of about -1.5 c.p.s. In addition, the nature of this treatment would suggest at least for "freely rotating" systems that an equal and additive contribution is expected for each adjacent π -electron pair. Second, for systems locked into a particular conformation or for a system in which one conformer is more prevalent, the theory indicates that the π -electron contribution can range between a value close to zero to a value of around -4.5 c.p.s., depending upon the dihedral angles between the methylene carbon hydrogen bonds and the orientation of the π -electron orbitals. While it is to be expected that the approximate theoretical values will not agree perfectly with the experimental ones, it will be essential that the proper dependence on conformation be observed.

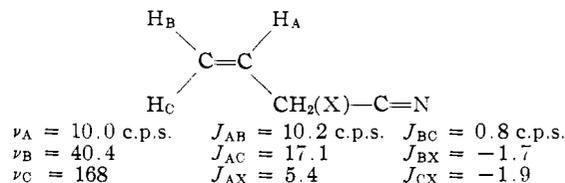
Experimental

Equipment.—The proton magnetic resonance spectra were obtained with a Varian Associates A-60 analytical spectrometer console in conjunction with a Varian Associates 12-in. electromagnet system. Varian precision 5-mm. sample tubes were used in this system, and the samples were degassed prior to analysis. Coupling constants are average values obtained from at least ten separate measurements.

Vinylmonodeuterioacetonitrile.—The deuterated compound was prepared by the exchange of 0.8 ml. of vinylacetonitrile with 2 ml. of a solution of NaOD in deuterium oxide. No attempt was made to separate the product from the parent compound or

the corresponding dideuterio compound, which was undoubtedly formed in much greater quantity.

The CHD group of the vinylmonodeuterioacetonitrile in the methylene region of the proton magnetic resonance spectrum is depicted in Fig. 3. The eight asymmetric lines of nearly unit intensity which are expected in the X portion of the ABCX proton spectrum²⁹ are split into first-order triplets by the deuterium. The X-portion of the spectrum was calculated on the basis of the following parameters for the ABCX₂ spectrum of the parent compound which was analyzed by Hirst³⁰



The spectrum of the methylene group of vinylmonodeuterioacetonitrile, therefore, as given in Fig. 3, is the superposition of three X groups, with a geminal H-D coupling of 2.96 ± 0.04 c.p.s.

Phenylmonodeuterioacetonitrile.—The deuterated compound was prepared by refluxing phenylacetonitrile with an equal volume of heavy water and a small quantity of sodium carbonate to catalyze the exchange. The resulting triplet in the methylene group was broadened due to small splittings from the phenyl protons. The H-D coupling constant was found to be 2.82 ± 0.06 c.p.s.

Mono- and Dideuterio-2,5-hexanedione.—The deuterium was introduced into the parent compound by exchange with a solution of NaOD in D₂O. Although the exchange took place in both the methylene and methyl groups, it was not possible to determine the H-D splitting in the former since the spectrum was complicated by the superposition of the large number of "isotopic" species. The H-D coupling constant in the deuterio-methyl group was 2.19 ± 0.04 c.p.s.

Mono- and dideuterioacetic acids were prepared by the thermal decarboxylation of malonic acid which had been exchanged with deuterium oxide.¹³ The more precise value of $J_{HD} = 2.22 \pm 0.04$ c.p.s. was obtained under the conditions of greater sweep stability obtainable on the A-60 spectrometer.

Sodium mono- and dideuterioacetates were prepared by titrating the above mixture of mono- and dideuterioacetic acids with NaOD in D₂O. The spectrum of these compounds shows clearly the singlet of the parent compound, the 1:1:1 deuterium coupled triplet shifted upfield of the singlet, and the 1:2:3:2:1 quintet shifted even further upfield of the singlet. The H-D coupling constant, obtained for these compounds, was 2.16 ± 0.05 c.p.s.

α -Monodeuteriotoluene was prepared according to the method described by Choppin and Smith.³¹ The Grignard reagent was decomposed by the addition of D₂O. The H-D coupling constant was 2.21 ± 0.03 c.p.s. In addition, fine splitting of about 0.2 c.p.s. due to coupling with the ring protons was detected.

Results and Discussion

Geminal H-H coupling constants reported for the first time in this study are entered in Table I along with pertinent values which were previously obtained. The entries in this table are for only those compounds in which the methylene or methyl groups can assume all the normal rotational conformations relative to the π -electron bonds. Each of these coupling constants was obtained from J_{HD} of the corresponding deuterated compound and the relation $J_{HH'} = (\gamma_{HH'}/\gamma_{HD})J_{HD} = 6.55J_{HD}$. These experimental coupling constants excluding that for nitromethane, plotted in Fig. 4 as a function of the number of adjacent π -electron bonds which are able to conjugate with the methyl or methylene group, show the linear relationship which exists between these values and the number of adjacent π -electron pairs. An examination of the slope of the line drawn through the circles in this figure indicates that the contribution is about $|1.9|$ c.p.s. per adjacent π -electron bond. Furthermore the excellent linearity of the plot supports the postulate that the π -electron contribution is additive, and therefore, the effect of each

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TABLE I

GEMINAL H-H COUPLING CONSTANTS IN SUBSTITUTED METHANES

Compound	$ J_{\text{HH}}^{\text{gem}} $, c.p.s.
1 Malononitrile	20.3 ± 0.3^a
2 Allyl cyanide	$19.4 \pm .3$
3 Ethyl cyanoacetate	$18.7 \pm .6^b$
4 Phenylacetoneitrile	$18.5 \pm .4$
5 Acetonitrile	$16.9 \pm .3^b$
6 Acetone	$14.9 \pm .3^a$
7 Acetic acid	$14.5 \pm .3$
8 Toluene	$14.5 \pm .2$
9 2,5-Hexanedione	$14.3 \pm .2$
10 Sodium acetate	$14.2 \pm .3$
11 Nitromethane	$13.2 \pm .2^b$
12 1,1,1-Trichloroethane	$13.0 \pm .4^c$
13 Methane	$12.4 \pm .6^d$

^a H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959). ^b M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **83**, 4726 (1961). ^c H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962). ^d M. Karplus, D. H. Anderson, T. C. Farrar and H. S. Gutowsky, *ibid.*, **27**, 597 (1957).

π -bond upon the geminal coupling constant is independent for all practical purposes of other adjacent π -electron pairs in the molecule. As the magnitude of this enhancement in the geminal coupling constant is added upon what is generally considered¹⁷⁻¹⁹ to be a negative quantity, it is probably safe to assume that the contribution of an adjacent π -electron substituent is -1.9 c.p.s., a value which compares very favorably with the -1.5 c.p.s. predicted from the theory based on hyperfine couplings.

It is interesting to note that an adjacent triple bond containing two π -electron pairs has twice the effect on the geminal coupling constant as an adjacent double bond with one π -electron pair. This indicates for "freely rotating" systems that the orthogonal nature of the two π -electron pairs in a triple bond does not inhibit both pairs from making an equal contribution to the enhancement of the coupling constant in question. Furthermore, π -bonds in several different types of groups (carbonyls, carboxyls, carboxylates, phenyls, cyanides and vinyls) seem to affect an adjacent geminal coupling to the same extent. The difference in polarity of these bonds and the possible resonance stabilization in the case of the aromatic phenyl group might have been expected to lead to differing substituent effects. As no major differences were noted, with the possible exception of allyl cyanide, the data seem to suggest that bond polarity and aromaticity do not greatly affect the contribution of a given carbon $2p_\pi$ -orbital in a molecular π -electron system.

An explanation for the measurable deviation of the geminal coupling constant in allyl cyanide is suggested by the work of Bothner-By³² on the vicinal coupling between the methylene hydrogens and the α -vinyl hydrogen. The experimental value found for this vicinal coupling when compared with a large body of data from other allyl compounds indicates that $p_I = 0.56$ instead of 0.33 . This larger value for p_I when used in eq. 6 will give a value of -2.5 c.p.s. for $\langle J_{\text{HH}}^{\pi}(\varphi) \rangle_{\text{av}}$ to be compared with -1.5 c.p.s. for $p_I = 0.33$. The additional -1.0 c.p.s. adequately accounts for the deviation noted in Fig. 3 for allyl cyanide and, while the geminal coupling constant data are not as refined as those used by Bothner-By to determine p_I , the qualitative conclusions are the same.

The low value for nitromethane can be reconciled with the recently measured value of 11.4 gauss³³ for

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(33) This value was reported by E. W. Stone and A. H. Maki in *J. Chem. Phys.*, **37**, 1326 (1962), on work carried out by Prof. Ralph N. Adams.

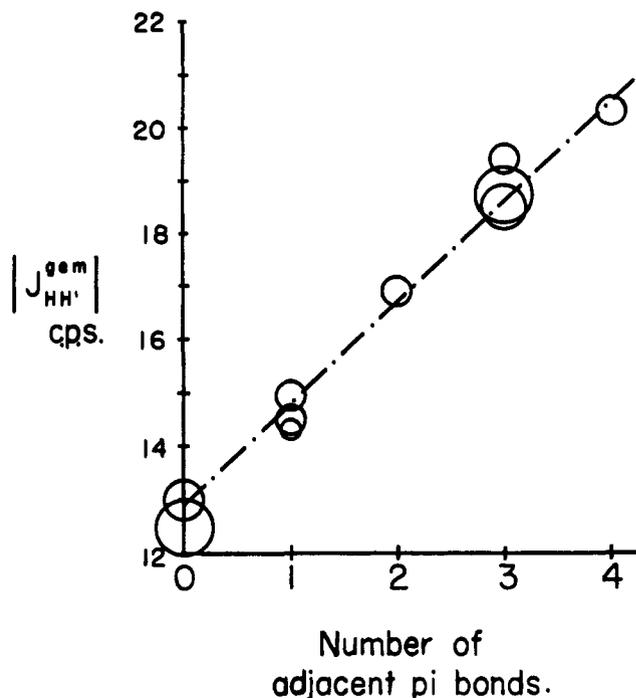


Fig. 4.—Geminal H-H couplings constants plotted as a function of the number of adjacent π -bonds. The corresponding compounds, listed in ascending order, are methane, 1,1,1-trichloroethane, 2,5-hexanedione, acetic acid, acetone, acetonitrile, phenylacetoneitrile, ethyl cyanoacetate, allyl cyanide and malononitrile. The size of the circle indicates the magnitudes of the errors in the determination of the coupling constants.

the hyperfine coupling constant obtained from the electrochemically generated nitromethane anion in aqueous solution. According to Stone and Maki,³³ this hyperfine splitting corresponds to a spin density³⁴ of $\rho_N^\pi = 0.7 \pm 0.1$; hence the hyperfine splitting (free rotation assumed) due to a completely occupied p_π -orbital is given in c.p.s. by $a_H = (27.994 \times 10^5 \text{ c.p.s./gauss})(11.4 \text{ gauss}/0.7) = 45.6 \times 10^6 \text{ c.p.s.}$ Using this value in eq. 2 gives a value of -0.7 c.p.s. for the π -electron contribution to the geminal coupling constant in nitromethane, which when added to the -12.4 value suggested for methane gives a value of -13.1 c.p.s. to be compared with $|J_{\text{HH}}^{\text{gem}}| = 13.2$ c.p.s. Hence, it would seem that σ - π exchange effects in nitromethane are smaller than in the other molecules which were studied. Couplings through a p_π -orbital centered on a nitrogen *vs.* a carbon therefore can be expected to give lower values.

In Table II geminal coupling constant data, which have been reported in the literature, are presented for a number of ring compounds. It is to be noted in the cyclic compounds (items 6 and 7) which do not contain π -electron systems that the geminal coupling constants are within experimental error of the value in methane. On the other hand, cyclic methylene groups (items 2-5) adjacent to a single π -electron pair exhibit geminal coupling constants which exceed the methane value by $|4.2|$ c.p.s. to $|7.4|$ c.p.s. and for cyclopentene-3,4-dione in which the methylene is sandwiched between two carbonyl groups an enhancement of $|9.1|$ c.p.s. above that for methane is noted. In each of these compounds the close to planar conformation of these ring systems restricts the methylene group in an orientation near to the $(30^\circ, 150^\circ)$ conformation which leads to the maximum π -electron enhancement in an adjacent geminal

(34) Reference 33. This calculation was based on one-electron MO and approximate SCF-MO treatments of the NO_2^- fragment. See also M. Katayama, *J. Chem. Phys.*, **37**, 2143 (1962).

TABLE II

Compound	$ J_{HH}^{gem} $, c.p.s.
1 Cyclopentene-3,5-dione	21.5 ± 0.3^a
2 Bromosuccinic anhydride	$19.8 \pm .2^b$
3 Chlorosuccinic anhydride	$19.1 \pm .2^b$
4 Malic anhydride	$18.2 \pm .2^b$
5 β -(<i>p</i> -Nitrophenyl)- β -propiolactone	$16.6 \pm .2^a$
6 1,1,4,4-Tetramethylcyclohexyl- <i>cis</i> -2,6-diacetate	$12.4 \pm .2^c$
7 3,3,4,4,5,5-Hexadeuteriocyclohexanol	$12.2 \pm .1^d$
8 (2.2)Metacyclophane	$12.0 \pm .1^e$

^a H. S. Gutowsky, M. Karplus and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959). ^b L. E. Erickson, Ph.D. Thesis, University of Wisconsin, 1959, and private communication. ^c J. I. Musher, *J. Chem. Phys.*, **34**, 594 (1961). ^d F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 1053 (1962). ^e H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 120 (1962).

coupling constant. Although ring puckering can be expected to decrease the contribution of the most favorable configuration, still the value obtained by averaging over all the puckered conformations should be near to the -4.5 c.p.s. per adjacent electron pair predicted for the (30° , 150°) conformation.

In the instance of β -(*p*-nitrophenyl)- β -propiolactone and of cyclopentene-3,5-dione, with one and two adjacent π -bonds, respectively, the $|4.2|$ c.p.s. and $|9.1|$ c.p.s. enhancements found experimentally compare well with the -4.5 and -9.0 c.p.s. values predicted from theory, and once again suggest the negative sign for the experimental values. For the three substituted succinic anhydrides, the increase over methane of $|5.8|$ c.p.s. $|6.7|$ c.p.s. and $|7.4|$ c.p.s. for, respectively, the hydroxy, chloro and bromo are all higher than theoretically predicted; but for the hydroxy compound, malic anhydride, the value is not disproportionately higher than was found for the "freely rotating" set of compounds. If the theory is correct in assuming that the maximum π -electron enhancement is threefold greater than the rotationally averaged value, then three times -1.9 c.p.s. or -5.7 c.p.s. might be considered as a reasonable upper limit in the magnitude of this effect. Depending on the validity of this assumption it may be necessary to look for an adjacent chloro and bromo substituent effect to account fully for the couplings found in these corresponding substituted succinic anhydrides.

The effect of the ring in each of these compounds is to lock the orientation of the methylene hydrogens into the same symmetry as the adjacent π -orbitals. It is suggested that this will lead to an increased contribu-

tion of the canonical structure $\begin{array}{c} \text{H} \\ | \\ \text{C}=\text{C}-\text{X} \\ | \\ \text{H} \end{array}$ into the ground state wave function having the principal bond

structure $\begin{array}{c} \text{H} \\ | \\ \text{C}-\text{C}=\text{X} \\ | \\ \text{H} \end{array}$. Any increase in this hypercon-

jugative structure in the molecular wave function directly accounts for an enhancement in the associated geminal spin-spin coupling constant.

Perhaps in the compound (2.2)metacyclophane (item 8 in Table II), the spectrum of which was obtained by Gutowsky and Juan,³⁵ is found one of the best substantiations of the proposed conformational dependence of this π -electron effect. A Dreiding model of this compound indicates that one of the hydrogens of each methylene group lies essentially³⁶ in

(35) H. S. Gutowsky and C. Juan, *J. Chem. Phys.*, **37**, 120 (1962).

(36) If pure trigonal and tetragonal angles are assumed for the sp^2 and sp^3 carbons, respectively, in (2.2)metacyclophane, a geometrical calculation of

the plane of the aromatic ring. In this conformation the methylene hydrogens do not exhibit the same symmetry as the aromatic π -orbitals, and only a small, if not negligible, π -electron enhancement of the adjacent geminal coupling is expected on the basis of Fig. 1. Corroboration of the theoretical formulation is found in the experimental coupling of $|12.0|$ c.p.s., a value very close to that in methane.

Taken as a whole, the data in Table II fit into the theoretical framework relating the molecular conformation and the geminal coupling constant. Even though all the quantitative relationships for this set of compounds are not as clear as those for the "freely rotating" set, complete information on ring puckering in four- and five-member rings is not presently available and detailed information on ring conformations therefore is lacking. Perhaps, with more accurate theoretical assessment and refined experimental values, greater insight might be obtained by this technique on the geometry of certain ring systems.

While it is even more difficult to discuss the data contained in Table III in terms of exact molecular conformations, nevertheless it seems desirable to note that the trend in coupling values is qualitatively in harmony with the theoretical conclusions proposed in this paper. Starting with malic anhydride with a geminal coupling constant of $|18.2|$ c.p.s. one notes a decrease of $|1.1|$ c.p.s. as the anhydride ring is opened to give malic acid. This reduction in coupling is consistent with the supposition that considerably more rotational isomerization is available for malic acid whereas this is not possible for the corresponding anhydride. However, the relatively high value of $|17.1|$ c.p.s. for malic acid suggests that intramolecular hydrogen bond formation is stabilizing those conformations which lead to a larger π -electron contribution in the adjacent geminal coupling constant. As two of the three hydrogens available for hydrogen bond formation are removed successively to give, respectively, the mono- and dibasic malate anions, a reduction in the absolute value of the coupling is again noted. Increased rotational averaging resulting from a decrease in hydrogen bond formation can account for these smaller coupling constants. As little change has been noted in the geminal coupling constants for α -hydrogens in other carboxyl *vs.* carboxylate compounds, substituent inductive effects upon the geminal coupling probably can be ignored. If the inductive effect is negligible, then the conformational effect does, indeed, become important in explaining the change in the observed coupling constants.

TABLE III

Compound	$ J_{HH}^{gem} $, c.p.s.
1 Malic anhydride	18.2^a
2 Malic acid	17.1^b
3 Monopotassium malate	16.4^b
4 Dipotassium malate	15.3^b

^a L. E. Erickson, Ph.D. Thesis, University of Wisconsin, 1959.

^b R. A. Alberty and P. Bender, *J. Am. Chem. Soc.*, **81**, 542 (1959).

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the dihedral angles between the π -orbitals of the aromatic rings and the methylene hydrogens indicates that these values are 85° and 205° . This configuration, according to Fig. 1, should result in a negligible π -electron contribution. X-Ray work on this compound in the solid state by C. J. Brown (*J. Chem. Soc.*, 3278 (1953)) indicates that steric strain distorts the trigonal and tetragonal angles by as much as 3.5° . While the positions of the hydrogen atoms could not be determined with this method, forceful distortion of the carbon atoms of a molecular model into the geometry proposed by Brown compels the two methylene hydrogens to move toward the 90° , 210° configuration.