# The Effect of Substituents on Proton–Proton Coupling Constants in N-Substituted Pyridines and on the *cis* Coupling Constants in the Vinyl Group of 2-Substituted 1,3-Butadienes

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*Received August 7, 1967*

**Abstract:** The proton nmr spectrum of pyridine N-oxide, recorded while irradiating the $^{14}N$ nucleus, has been completely analyzed in terms of the fundamental nmr parameters. The coupling constants of several N-substituted pyridines are compared, and it is shown that their dependence on the nature of the N substituent shows the same trends as observed for the corresponding parameters in the series of monosubstituted benzenes. The *cis* coupling constants of the vinyl group of 2-substituted 1,3-butadienes are compared with those of the corresponding substituted ethylenes, and it is shown that the effect of the substituent is opposite in the two series of compounds. New spectral parameters of 3,3-dimethylbutene are presented.

The general trends in the variations of the proton–proton spin coupling constants with the nature of the substituent in the series of monosubstituted benzenes have been reported in a recent communication[1] by S. C. In particular, it was pointed out that the changes in the *ortho–meta* coupling constants[2] were opposite to those expected on the basis of the experimental results obtained in the series of monosubstituted ethanes[3,4] and ethylenes;[5–7] whereas in the latter series of compounds the vicinal coupling constants *decrease* as the electronegativity of the substituent increases, in the monosubstituted benzenes $J(1,2)$ shows a reverse trend and *increases* with the electronegativity of the substituent.

Since the variations of the vicinal coupling constants with the nature of the substituent are thought to occur through an inductive effect,[8] the alternating nature of the phenomenon observed may prove to be very valuable in clarifying the mechanism through which the latter is transmitted along the molecular framework. The results obtained in the series of the monosubstituted benzenes prompted us, therefore, to check whether the same anomalous behavior of the vicinal coupling constants could also be found in other series of compounds whose nmr parameters have been published earlier, but not examined critically from this particular point of view. It is the aim of this paper to show that this alternating effect of the substituent on the vicinal coupling constants is very well documented for the series of N-substituted pyridines and 2-substituted 1,3-butadienes. In order to complement the data in the literature for the first series of compounds, we report here the results of a complete analysis of the nmr spectrum of pyridine N-oxide. Also presented in this paper are the results of a new determination of the spectral parameters of *t*-butylethylene.

## Experimental Section

All chemicals were of commercial origin (Aldrich Chemicals, Eastman Organic Chemicals, Baker Chemicals) and were usually used as received. Pyridine N-oxide was recrystallized twice from acetone. The samples were degassed on a vacuum line and sealed in 5-mm nmr tubes. Tetramethylsilane (TMS, 2%, v/v) was included to serve as an internal reference. The proton spectra were recorded using a Varian A-60 spectrometer equipped with an NMR Specialties heteronuclear decoupler (Model SD-60B). To perform decoupling experiments, the variable-temperature equipment was used in order to keep constant the temperature of the samples. In all cases, thermal equilibrium was reached after about 2 hr. For all samples, two spectra were recorded for each sweep direction of the magnetic field using a 50-cps full sweep width. The spectra were calibrated using the side-band technique with the aid of a General Radio frequency synthesizer (Model 1161-A).

**Analyses of the Spectra.** The proton spectra of pyridine N-oxide in solutions in acetone and in trifluoroacetic acid were recorded and analyzed. According to standard nmr nomenclature, the spectrum of the solution in acetone is of the AA′BB′CX type, where the label X refers to the $^{14}N$ nucleus, which appears to be coupled to all protons of the aromatic ring. The proton part of the spectrum consists of two well-separated multiplets corresponding to the resonances of the *ortho* (lower field) and *meta* and *para* hydrogens (higher field); the latter protons give rise to a very strongly coupled system. The coupling of the nitrogen with the protons is partially removed by virtue of the short relaxation time of the $^{14}N$ nucleus and only a broadening of all the lines of the proton part of the spectrum attests to the existence of the coupling with the heteroatom. No precise spectral measurements are possible under these circumstances and it was, therefore, necessary to remove the coupling of the nitrogen with the protons by recording the spectrum while irradiating the sample at a frequency corresponding to the resonance of the $^{14}N$ nucleus. The AA′BB′C spectrum obtained in this way consisted of a well-resolved pattern which allowed a complete determination of all the proton spectral parameters. The analysis was performed with a CDC 1604-A computer and the LAOCN3 program which is a more recent and efficient version of the LAOCOON II program described elsewhere.[9] Two sets of spectra were recorded at 30 and 40°. These spectra were analyzed independently and gave rise to the spectral parameters reported in Table I. In both cases 59 lines were assigned and the rms errors were 0.036

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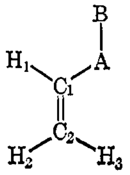
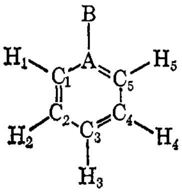
[1] S. Castellano and C. Sun, *J. Am. Chem. Soc.*, **88**, 4741 (1966).

[2] Throughout this paper the vinyl and aromatic protons will be labeled as follows





Whenever confusion may arise between this notation and the usual chemical nomenclature that would otherwise be employed, the position of atoms A and B will be referred to as positions a and b.

[3] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **1**, 165 (1963).

[4] S. Ebersole, S. Castellano, and A. A. Bothner-By, *J. Phys. Chem.*, 68, 3430 (1964).

[5] C. M. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

[6] T. Schaefer, *Can. J. Chem.*, 40, 1 (1962).

[7] J. S. Waugh and S. Castellano, *J. Chem. Phys.*, **35**, 1900 (1961).

[8] M. Karplus, *J. Am. Chem. Soc.*, **85**, 2780 (1963).

[9] S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

Table I. Proton Nmr Spectral Parameters[a] of Pyridine N-Oxide and of 3,3-Dimethylbutene-1

| Compd | Solvent | Chemical shifts W(1) | W(2) | W(3) | Coupling constants J(1,2) | J(1,3) | J(1,4) | J(1,5) | J(2,3) | J(2,4) |
|---|---|---|---|---|---|---|---|---|---|---|
| $C_5H_5NO$ | $(CH_3)_2CO$ (30°) | 491.65 | 444.03 | 439.08 | 6.47 | 1.12 | 0.63 | 1.88 | 7.65 | 2.13 |
| $C_5H_5NO$ | $(CH_3)_2CO$ (40°) | 491.98 | 443.87 | 438.93 | 6.50 | 1.11 | 0.69 | 1.91 | 7.66 | 2.14 |
| $C_5H_5NO$ | $CF_3COOH$ | 530.21 | 483.96 | 505.74 | 6.65 | 1.10 | 0.52 | 2.05 | 7.83 | 1.81 |
| $C_6H_{12}$ | Neat | 347.82 | 287.37 | 293.35 | 10.71 | 17.49 | | | 1.33 | |
| $C_6H_{12}$ | $CCl_4$ | 346.76 | 286.83 | 292.18 | 10.71 | 17.45 | | | 1.37 | |

[a] Unless otherwise indicated, all data were obtained at 36°. Concentration of the solutions, 10% w/w. Chemical shifts referred to TMS as internal standard. All data in cps; $\nu_0 = 60$ Mcps.

and 0.037 cps, respectively; no absolute error larger than 0.08 cps occurred in the fit of the individual lines. The differences between the values of corresponding coupling constants derived from the two sets of spectra are well contained within the limits of the calculated probable errors; the larger differences between corresponding chemical shifts are very likely due to the different temperatures at which the spectra were recorded. The experimental undecoupled (uppermost trace) and $^{14}N$-decoupled (middle trace) spectra of pyridine N-oxide in acetone solution (10% w/w) at 30° are reproduced in Figure 1 (*ortho* protons) and Figure 2 (*meta* and *para* protons). In both figures the lowermost traces represent the calculated spectrum as plotted directly from the output of the computer.

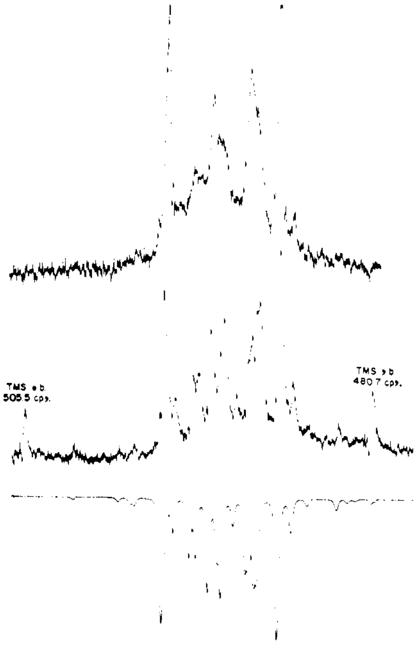


Figure 1. Experimental $^{14}N$-undecoupled (uppermost trace), $^{14}N$-decoupled (middle trace), and calculated (lowermost trace) proton spectra (*ortho* protons) of pyridine N-oxide (10% w/w solution in acetone). Frequencies (cps) referred to TMS as internal standard; $\nu_0 = 60$ Mcps; temperature, 30°.

The proton spectrum of pyridine N-oxide in solution in trifluoroacetic acid also belongs to the AA'BB'C type if no coupling of the protons with the nitrogen nucleus is considered. The pattern of the spectrum is, however, very different from that of the spectrum of the acetone solution because of the much larger relative chemical shifts of the *ortho*, *meta*, and *para* protons caused by the protonation occurring in the acid medium. The spectral lines still appear broadened, but to a much lesser extent than those in the spectrum of the acetone solution; all attempts to reduce the broadening of the proton resonances by irradiation of the $^{14}N$ nucleus were unsuccessful. This suggests that the broadening of the spectra in acid solution may not be due to a residual coupling of the protons with the nitrogen but to other effects such as, for example, a slow rate of exchange of the acidic proton between the trifluoroacetic anion and the pyridine N-oxide molecule. Notwithstanding the unexplained broadening, the pattern of the proton resonances of pyridine N-oxide in trifluoroacetic acid is sufficiently well resolved to allow the accurate measurements of the line frequencies necessary for a complete analysis. Analysis furnished the spectral parameters reported in Table I; 56 lines were assigned and the final fit was achieved with an rms error of 0.050 cps. However, because of the broadening of the peaks we believe that the parameters obtained in this case are reliable only to ±0.15 cps.

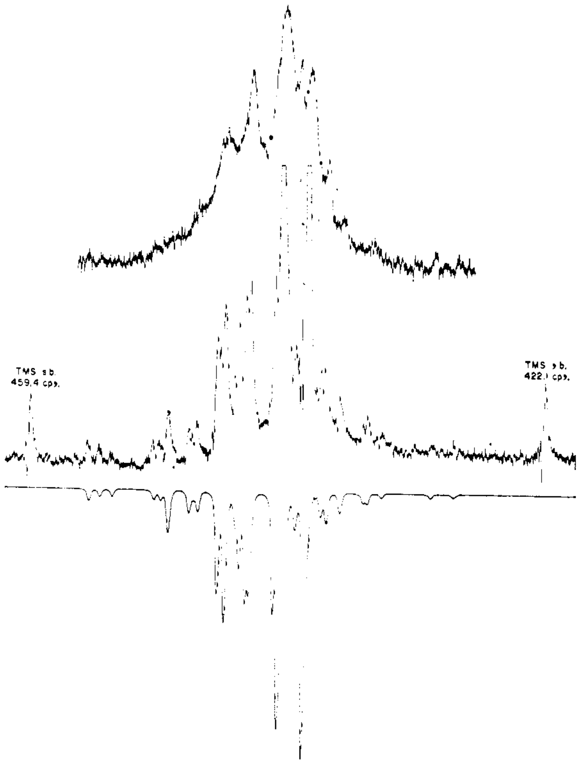


Figure 2. Experimental $^{14}N$-undecoupled (uppermost trace), $^{14}N$-decoupled (middle trace), and calculated (lowermost trace) proton spectra (*meta* and *para* protons) of pyridine N-oxide (10% w/w solution in acetone). Frequencies (cps) referred to TMS as internal standard; $\nu_0 = 60$ Mcps; temperature, 30°.

The analysis of the spectra, neat and 10% w/w solution in $CCl_4$, of the vinyl protons of *t*-butylethylene offered no particular difficultly and was performed with the aid of the EXAN II[10] and LAOCN3 programs. The probable errors of the final parameters, shown in Table I, were always smaller than 0.05 cps. Our data are in good agreement with those previously determined by Alexander[11] but are presumably more accurate.

## Discussion

In Figures 3–5 we have plotted the coupling constants of pyridinium ion[12] and of pyridine N-oxide *vs.*

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[10] A. A. Bothner-By, S. Castellano, and H. Günther, *J. Am. Chem. Soc.*, **87**, 2439 (1965).

[11] S. Alexander, *J. Chem. Phys.*, **28**, 358 (1958).

[12] J. B. Merry and J. H. Goldstein, *J. Am. Chem. Soc.*, **88**, 5560 (1966).

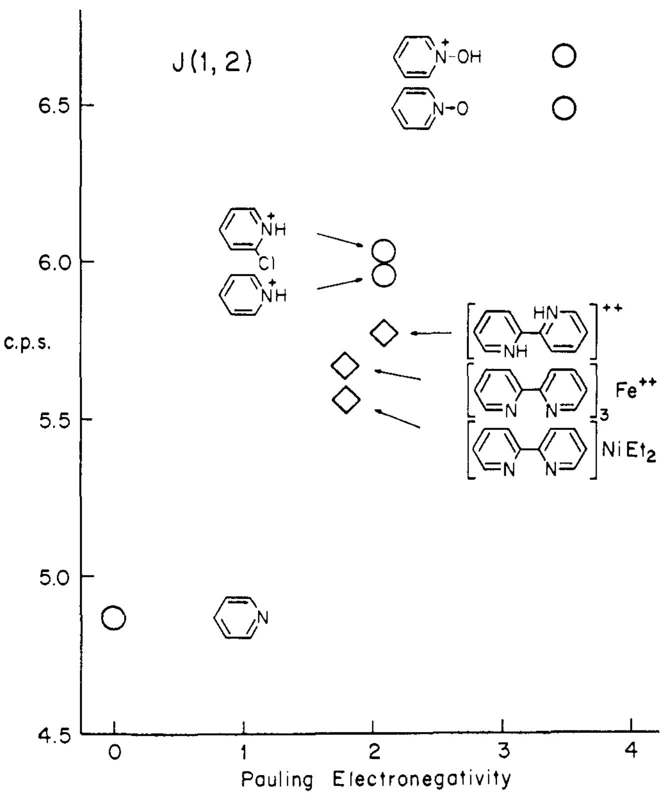

Figure 3. Plot of $J(1,2)$ *vs.* Pauling electronegativity of the first atom of the substituent in N-substituted pyridines.

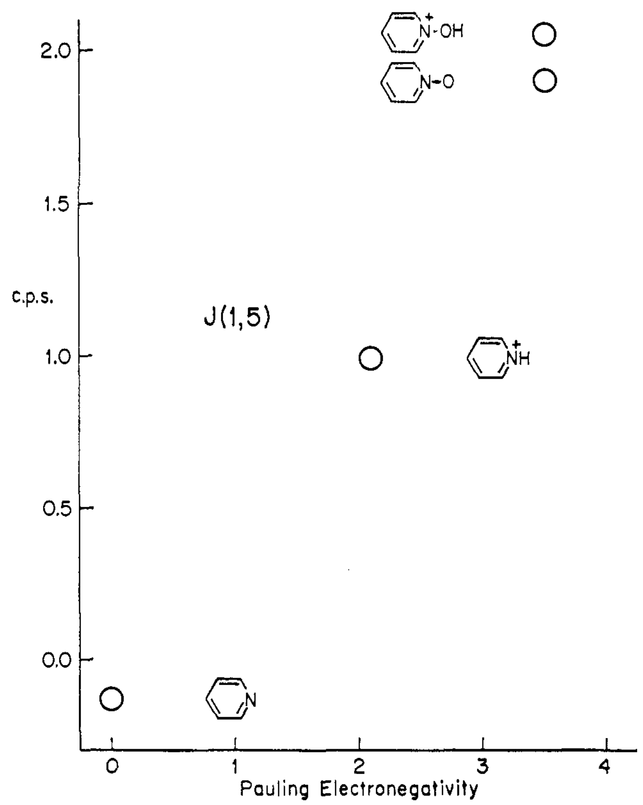

Figure 4. Plot of $J(1,5)$ *vs.* Pauling electronegativity of the first atom of the substituent in N-substituted pyridines.

the electronegativity of the N substituent. As additional data, we have reported in Figure 3 the coupling constants between $\alpha$ and $\beta$ protons of 2-chloropyridinium ion[13] and of some N,N'-disubstituted $\alpha,\alpha'$-bipyridyls. The parameters were obtained from the analysis of the nmr spectra of $\alpha$-chloropyridine and $\alpha,\alpha'$-bipyridyl[14] in trifluoroacetic acid solutions, of diethyldipyridylnickel,[15] and of the iron complex,[14] $[Fe^{II}(C_{10}H_8N_2)_3]Cl_2$. Use of these data, in the context of this paper, is fully justified since the effect of an $\alpha$ substituent on $J(1,2)$ is exceedingly small as shown by the direct comparison of the values (in cps) of this coupling constant in pyridine[16] (4.88), $\alpha,\alpha'$-bipyridyl[14] (4.76), $\alpha$-phenylpyridine[17] (4.80), $\alpha$-benzoylpyridine[9] (4.84), $\alpha,$-$\alpha'$-bipyridil[18] (4.80), $\alpha$-chloropyridine[18] (4.83), and $\alpha$-methoxypyridine[18] (5.01). Throughout Figures 3–5 we have also reported the values of the corresponding coupling constants of pyridine;[16] in plotting the latter parameters we have followed Bent's suggestion[19] of considering the lone pair electrons of the nitrogen as the shared pair of an hypothetical bond with a substituent, corresponding to the zero of the electronegativity scale. In all cases the experimental values of the coupling constants of pyridine match perfectly the values extrapolated from the plots of Figures 3–5, giving strong experimental support to the above, otherwise somewhat arbitrary, suggestion.

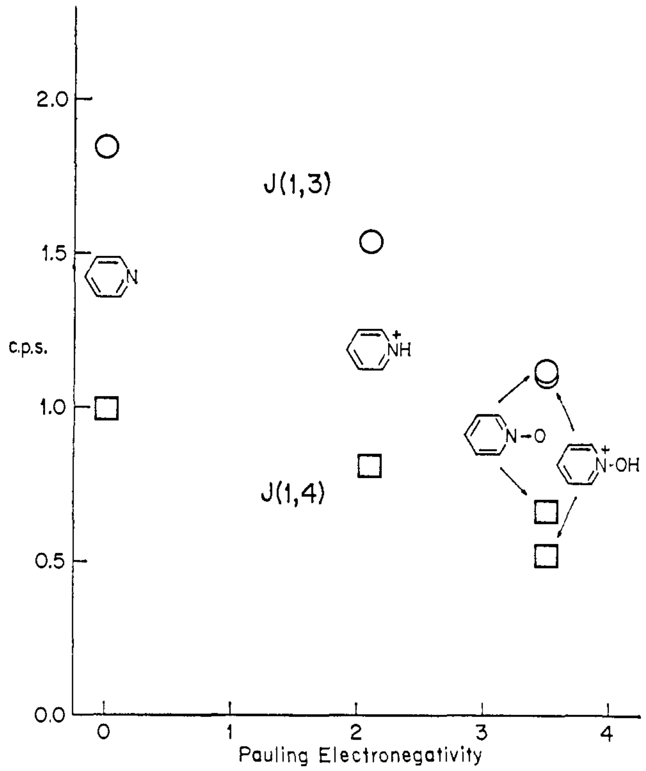

Figure 5. Plots of $J(1,3)$ and $J(1,4)$ *vs.* Pauling electronegativity of the first atom of the substituent in N-substituted pyridines.

For all the parameters reported in Figures 3–5 the trends of the variations produced by the substituents are identical with those observed for the corresponding

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(13) R. H. Cox, private communication.

(14) S. Castellano, H. Günther, and S. Ebersole, *J. Phys. Chem.*, **69**, 4166 (1965).

(15) H. Günther and S. Castellano, unpublished results.

(16) S. Castellano, C. Sun, and R. Kostelnik, *J. Chem. Phys.*, **46**, 327 (1967).

(17) H. Günther and S. Castellano, *Ber. Bunsenges. Physik. Chem.*, 70, 913 (1966).

(18) S. Castellano and R. Kostelnik, unpublished results.

(19) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

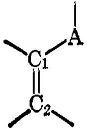
coupling constants in the monosubstituted benzenes:[1] $J(1,2)$ and $J(1,5)$ present the larger changes and increase with increasing electronegativity of the N substituent; on the other hand, $J(1,3)$ and $J(1,4)$ show decreasing trends—their variations are relatively smaller. This parallel behavior of the coupling constants in the two series of compounds is further underlined by the observation that in the N-substituted pyridines $J(2,3)$ remains about constant and $J(2,4)$ presents a less definite and more scattered behavior, precisely as found for the corresponding parameters of monosubstituted benzenes.[1] For both series of compounds all the experimental results indicate that, as far as the magnitude of the coupling constants is concerned, the perturbation introduced by the substituent is mainly localized around the atom to which the substituent is bonded and attenuates rapidly along the molecular framework. A perturbative mechanism of this type, which is almost quenched beyond the *ortho* position, is usually associated with an inductive effect. The strongest evidence concerning the nature of the effect discussed here, comes from the observation that, in the monosubstituent benzene series, the smallest and largest values (in cps) of $J(1,2)$ and $J(1,5)$ are found respectively in phenyllithium[1] (6.73; 0.74) and trimethylanilinium ion[18] (8.55; 3.10) in which the interaction between the substituent groups and the phenyl ring occurs primarily through an inductive mechanism.[20] Further evidence in support of the above conclusion is also gained from the comparison of the plots of $J(1,2)$ *vs.* the electronegativity of the substituent for monosubstituted benzenes (Figure 1 in ref 1) and N-substituted pyridines (Figure 3). The two plots run almost parallel and the values in the pyridine series are always smaller than those in the benzene series; corresponding values in the two plots differ, on the average, by 1.5 cps. This difference is consistent with the variations observed in the values of the *cis* coupling constant of monosubstituted ethylenes when the electronegativity of the substituent is increased.[5] For the ethylene series, Banwell and Sheppard[5] found that the straight line, which best correlates the experimental values of *J cis vs.* the electronegativity ($\chi$) of the substituent, has the slope

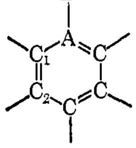
$$\frac{\partial J(1,2)}{\partial \chi_{\mathrm{A}}} = \frac{J_{\mathrm{C_2H_3A}} - J_{\mathrm{C_2H_3A'}}}{\chi_{\mathrm{A}} - \chi_{\mathrm{A'}}} = -3.98$$

Using the same linear relationship with the experimental values of $J(1,2)$ of monosubstituted benzenes and N-substituted pyridines, we find, in good qualitative agreement

$$\frac{\partial J(1,\ 2)}{\partial \chi_{\mathrm{A}}} = \frac{J_{\mathrm{C_5H_5CB}} - J_{\mathrm{C_5H_5NB}}}{\chi_{\mathrm{C}} - \chi_{\mathrm{N}}} = \frac{1.5}{-0.5} = -3.00$$

This result shows very clearly that for both classes of compounds





the variations of the vicinal proton–proton coupling constants *vs.* the electronegativity of atom A have the same trends, $\partial J(1,2)/\partial \chi_{\mathrm{A}} < 0$, and that therefore the same perturbative mechanism may be operative in both cases, at least, for that part of the molecular skeleton connecting atoms A, $C_1$, and $C_2$.

According to current theory on the inductive effect,[19,21] the substituent B should induce along the bonds of the molecular framework a rapidly decreasing monotomic polarization as shown schematically in I and II

$$\underset{\mathrm{I}}{\overset{\delta\delta\delta^+}{\mathrm{C}_2} \longrightarrow \overset{\delta\delta^+}{\mathrm{C}_1} \longrightarrow \overset{\delta^+}{\mathrm{A}} \longrightarrow \overset{\delta^-}{\mathrm{B}_x}} \qquad \underset{\mathrm{II}}{\overset{\delta\delta\delta^-}{\mathrm{C}_2} \longleftarrow \overset{\delta\delta^-}{\mathrm{C}_1} \longleftarrow \overset{\delta^-}{\mathrm{A}} \longleftarrow \overset{\delta^+}{\mathrm{B}_y}}$$

whose direction would depend on the electron-withdrawing ($B_x$) or electron-releasing ($B_y$) characteristics of the substituent. It follows that the electron-withdrawing power of atom A with respect to $C_1$ should increase or decrease correspondingly,[19] and that these changes should be manifested in well-defined trends of $J(1,2)$ with the electronegativity of B, $\partial J(1,2)/\partial \chi_{\mathrm{B}} < 0$. The experimental values of $J(1,2)$ in the series of monosubstituted benzenes and N-substituted pyridines do indeed show very specific trends, but they are *opposite* to those predicted by this theory and, in fact, *the greater the electronegativity of B, the larger the value of J(1,2).* The average value of the slopes of the plots of Figure 3 in this paper, and of Figure 1 in ref 1, is $\partial J(1,2)/\partial \chi_{\mathrm{B}} = 0.55$. From the values of the partial derivative of $J(1,2)$ with respect to $\chi_{\mathrm{A}}$ and $\chi_{\mathrm{B}}$, one obtains the damping factor

$$k = \frac{\partial J(1,2)/\partial \chi_{\mathrm{B}}}{\partial J(1,2)/\partial \chi_{\mathrm{A}}} \simeq \frac{1}{6}$$

which illustrates very well both the change of sign and the decrease of the effect of a substituent on passing from an a to a b position. A careful examination of the experimental data of the other vicinal coupling constant, $J(2,3)$, further reinforces the previous conclusions. In both series of compounds this parameter shows very little dependence on electronegativity, with average values[22] of 7.73 cps (N-substituted pyridines) and 7.46 cps (monosubstituted benzenes). From these data one obtains

$$\frac{\partial J(2,3)}{\partial \chi_{\mathrm{A}}} = \frac{J_{\mathrm{C_5H_5CB}} - J_{\mathrm{C_5H_5NB}}}{\chi_{\mathrm{C}} - \chi_{\mathrm{N}}} = \frac{-0.27}{-0.50} = 0.54$$

The good agreement between the values of $\partial J(2,3)/\partial \chi_{\mathrm{A}}$ and $\partial J(1,2)/\partial \chi_{\mathrm{B}}$ is surely somewhat accidental, nevertheless, very satisfactory. Using the value of $k$, defined above, one finally obtains

$$\frac{\partial J(2,3)}{\partial \chi_{\mathrm{B}}} = k\frac{\partial J(2,\ 3)}{\partial \chi_{\mathrm{A}}} = -0.09$$

which gives the slope expected in the plots of $J(2,3)$ *vs.* the electronegativity of the substituent B, if the perturbation is propagated by a mechanism of the inductive type. There are indications[18] that trends with variations of this order of magnitude are recognizable in the series of monosubstituted benzenes, although experimental errors and possibly small secondary effects obscure the over-all pattern. It is, however, very likely

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(20) C. K. Ingold "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 252.

(21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 128, and literature quoted therein.

(22) The largest deviations (cps) from the averages are: (+0.25, −0.20) in the benzene series and (+0.25, −0.10) in the pyridine series,

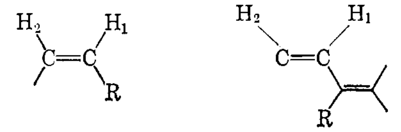
that more definite experimental trends of $J(2,3)$ with the electronegativity of a b substituent may be found in other systems. Experimentally, it is found that the values of $\partial J(1,2)/\partial \chi_A$ are roughly proportional to the values of $J(1,2)$ in the parent hydrocarbon as shown by the ratios[23]

$$\frac{\partial J(1,2)/\partial \chi_A}{J(1,2)}$$

for the ethylene series ($-0.347$) and the aromatic series ($-0.394$). It follows that, if the mechanism of the vicinal H–F coupling is the same as that governing the H–H coupling, larger variations of $J(2,3)$ are to be expected in monosubstituted *p*-fluorobenzenes because of the greater values of vicinal $J$(H,F) coupling constants.

It could be argued that the alternating effect of the electronegativity of the substituent on the magnitude of the vicinal coupling constant is a peculiarity of aromatic systems. However, several other examples have been reported in the literature[1,26] indicating the widespread occurrence of the phenomenon in both saturated and unsaturated hydrocarbons. Unfortunately, in many instances the effect is either too small to be observed or masked by errors affecting the parameters so that it can be only qualitatively inferred from the experimental data.[26] It is therefore of great interest to find other systems in which the same effect can be reliably documented. In Table II we have reported the values of the *cis* coupling constants in the vinyl groups of monosubstituted ethylenes[24] and 2-substituted 1,3-butadienes[27–30] bearing the same substituent. The alternating effect of the substituent on $J^{cis}$ is immediately apparent from the comparison of the values and of the signs of the differences.

**Table II.** Effect of the Substituent on the *cis* Proton–Proton Coupling Constants (cps) of Monosubstituted Ethylenes and 2-Substituted 1,3-Butadienes



| R | $J(1,2)$ | $\Delta_{\text{ethylenes}}$ | $J(1,2)$ | $\Delta_{\text{butadienes}}$ |
|---|---|---|---|---|
| H | 11.50[a] | 0.00 | 10.17[c] | 0.00 |
| $C(CH_3)_3$ | 10.71 | −0.79 | 10.80[c] | +0.63 |
| $CH_3$ | 10.02[a] | −1.48 | 10.50[d] | +0.33 |
| I | 7.91[b] | −3.59 | 10.17[e] | 0.00 |
| Br | 7.30[a] | −4.20 | 10.41[e] | +0.24 |
| Cl | 7.10[a] | −4.40 | 10.51[e] | +0.34 |
| $OCH_3$ | 6.60[a] | −4.90 | 10.83[c] | +0.66 |
| F | 4.65[a] | −6.85 | 11.14[e] | +0.97 |

[a] Reference 24. [b] Reference 27. [c] Reference 28. [d] Reference 29. [e] Reference 30.

$$\Delta_{\text{ethylenes}} = J^{cis}{}_{C_2H_3R} - J^{cis}{}_{C_2H_4}$$

$$\Delta_{\text{butadienes}} = J^{cis}{}_{C_4H_5R} - J^{cis}{}_{C_4H_6}$$

are reported in Table II for each substituent. The 1,3-butadienes here considered, with the exception of the *t*-butyl compound, are all predominantly in an *s-trans* conformation,[28–30] and the vinyl group and the substituents are in a relative *cis* orientation. In the monosubstituted benzenes or N-substituted pyridines the $C_1$–$C_2$ bond has, on the other hand, a *trans* orientation to the substituent. Hence, the effect here considered cannot be highly dependent on these geometrical factors. The presence of the same effect in 2-*t*-butyl-1,3-butadiene, which is in a skew conformation,[28–31] further supports that conclusion and indicates that the coplanarity of the $C_1$–$C_2$ and A–B bonds is not an essential feature of the phenomenon observed. It must be pointed out also that in the 2-halo-1,3-butadienes, the *trans* coupling constants of the unsubstituted vinyl group increase with the electronegativity of the substituent[30] and that this trend, too, is opposite to that observed in the monosubstituted ethylenes.[5]

## Conclusions

All this experimental evidence, gathered from the behavior of the vicinal proton–proton coupling constants as a function of the electronegativity of b substituents, does not agree with the predictions based on the models I and II of the inductive effect. The impasse may be overcome if it is assumed that the polarization of the bonds and the transmission of charges alternate along the molecular framework as shown[32] in III and IV.

$$\underset{\text{III}}{\overset{\delta\delta\delta^+}{C_2} \longrightarrow \overset{\delta\delta^-}{C_1} \longleftarrow \overset{\delta^+}{A} \longrightarrow \overset{\delta^-}{B_x}} \qquad \underset{\text{IV}}{\overset{\delta\delta\delta^-}{C_2} \longleftarrow \overset{\delta\delta^+}{C_1} \longrightarrow \overset{\delta^-}{A} \longleftarrow \overset{\delta^+}{B_y}}$$

According to these schemes, the same substituent would produce changes of a different sign in the vicinal coupling constant according to whether it is in an a, $\partial J(1,2)/\partial \chi_A < 0$, or b position, $\partial J(1,2)/\partial \chi_B > 0$, in complete agreement with the experimental results. Furthermore, an inductive mechanism of this kind would rationalize the otherwise unexpected result that an electropositive substituent in the monosubstituted benzene series causes a shift of $J(1,2)$ toward values characteristic of pyridine, and an electronegative N-substituent in the pyridine series produces a shift of the same coupling constant toward values characteristic of benzene. It is encouraging and reassuring that alternance of charges as schematized in III and IV has been deduced[33] also from theoretical quantum mechanical calculations of the effects of substituents on the dipole moments of saturated and unsaturated molecules.

Because of the alternating character, the schemes III and IV bear a close resemblance to the mesomeric effect associated with the migration of charges in the $\pi$ systems ($p_z$ electrons) of conjugated hydrocarbons. The mechanism proposed here, however, would act primarily through the polarization of the $\sigma$ (s, $p_x$, $p_y$)

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(23) The values of $\partial J(1,2)/\partial \chi_A$ used in the calculations are those previously determined. The values of the coupling constant (cps) are: ethylene,[24] 11.50; benzene,[25] 7.56.

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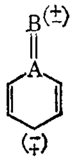
(32) The model here proposed is to be used in the context of this paper, namely as a description of the polarization induced by a substituent B along the bonds of the chain $-C_3-C_2-C_1-A-$, where A can be either carbon or nitrogen. It is not meant to be used in connection with the evaluation, on the basis of a structural formula, of the electron-withdrawing or -releasing characteristic of a substituent.

(33) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

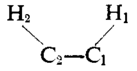
electrons since (a) the substituents most effective in altering the values of $J(1,2)$ are those for which it is harder to write mesomeric structures in conjugation with the aromatic or vinyl groups [$-Li$, $-N^+(CH_3)_3$]; (b) the alternating effect is still present in compounds in which the vinyl group and the bond between the $\alpha$-carbon and the $\beta$ substituent are not coplanar and therefore in an unfavorable conformation for the stabilization of any mesomeric structure [2-*t*-butyl-1,3-butadiene]; (c) the $\pi$ electrons have nodes in the plane of the molecule and do not contribute significantly to the coupling between vicinal protons.[8]

Several papers in recent years have dealt with correlations between the magnitudes of the vicinal coupling constants, $J(1,2)$, and the $\pi$ bond order of the $C_1$–$C_2$ fragment in polynuclear aromatic hydrocarbons[34,35a] and conjugated cyclic diolefins.[35b] These correlations do not imply, however, that the changes in the vicinal coupling constants occur through a mechanism involving the $\pi$ electrons. They give experimental support only to the theoretical result that the coupling between vicinal protons is directly related, given the constancy of other factors, to the $C_1$–$C_2$ distance,[8] which is in turn proportional to the $\pi$ bond order between the carbon atoms.[36] Within the same series of compounds, however, it is very unlikely that the substituents affect the magnitude of the vicinal coupling constant exclusively through changes in the carbon–carbon bond distance. In passing from ethylene to vinyl fluoride (or vinyllithium) unrealistic increases (or decreases) of 9% (or 10%) of the bond length would be required if direct proportionality between $J^{cis}$ and carbon–carbon bond length is demanded.[37] Microwave determinations of the carbon–carbon distances in vinyl fluoride[38] and other monosubstituted[39,40] ethylenes do not support such an hypothesis. It is also doubtful whether a large contribution of quinoid forms to the molecular electronic hybrid structure such as



would result in a sufficient shortening[36,41] of the $C_1$–$C_2$ bond. Furthermore stabilization of such structures would require, for internal consistency, variations of $J(2,3)$ of the same order of magnitude as those observed in the values of $J(1,2)$. Such large variations are not observed experimentally. On the other hand, current theories of the effect of $\alpha$ substituents on the proton–proton coupling constants in vinyl compounds rely quite heavily on the variations of the $C_2C_1H_1$ angle caused by the changes of hybridization of the carbon ($C_1$) bonded to the substituent.[8,42,43] Estimates of the amount of s character of the carbon orbital in the $C_1$–$H_1$ bond are obtained from the values of $J(^{13}C_1,H_1)$ in monosubstituted methanes ($CH_3R$) and then transferred to the vinyl series ($CH_2{=}CHR$) after multiplication by a factor of $^4/_3$ to take into account the different state of hybridization of the carbon atom in the parent hydrocarbons[43] ($CH_4$ and $CH_2{=}CH_2$). This theory seems to account satisfactorily for the trends of the proton–proton coupling constants in monosubstituted ethylenes[8] but unfortunately fails to reproduce the values of $J(^{13}C_1,H_1)$ determined experimentally for the vinyl halides.[27] If the theory is extended to monosubstituted benzenes, it predicts a linear correlation between the values of $J(1,2)$ and $J(^{13}C_1,H_1)$. From the data on $J(1,2)$ and $J(^{13}C_1,H_1)$ (in cps and in the same order) available in the literature[1,44–48] for monosubstituted benzenes ($C_6H_5R$) [(R = H) 7.6, 159.0; (OH) 8.2, 161.0; ($OCH_3$) 8.3, 156.0; ($NO_2$) 8.3, 170.0; (I) 7.9, 168.0; ($NH_2$) 8.1, 151.0], no correlation whatsoever can be found. Furthermore, this model, in which the effect of a substituent is manifested mainly through a change in the hybridization of the atom to which it is bonded, is identical with the one used by Bent[19] to rationalize the propagation of the inductive effect according to the schemes I and II; these schemes, however, predict trends of $J(1,2)$ opposite to those found experimentally.

Without any doubt, geometrical changes will occur in the molecular framework upon introduction of a substituent, but it is doubtful that these changes alone represent the primary mechanism through which a substituent affects the vicinal proton–proton coupling constant. To the extent that the magnitude of $J(1,2)$ in the parent hydrocarbon reflects the particular geometrical situation in the



fragment, the proportionality between $J(1,2)$ and $J(1,2)/\partial\chi_A$ seems to indicate that the effect of a substituent should occur primarily through the variations of an *intensive* physical parameter such as charge density and/or related quantities and not through changes of *extensive* parameters as bond length or bond angles. Hiroike[49] and Ranft[50] have tried to take directly into account the charge polarization caused by a substituent by introducing, in the valence bond formalism, an ionicity parameter of the $C_1$–$H_1$ bond. The results are in qualitative agreement with the experimental trends of the proton–proton coupling constants, but the magnitudes of the variations calculated are too small. Perhaps these calculations should be repeated employing the MO theory of Pople and Santry,[51] which is better suited[52] than the valence bond methods, to take into account polarity effects. In view of the ability of the MO theory to predict alternance of sign in the charge

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distributions,[32] its application to the theoretical calculations of vicinal coupling constants appears very alluring. Because of the strong similarity of behavior of all other coupling constants in the series of N-substituted pyridines and monosubstituted benzenes, the experimental correlations of these parameters with the nature of the substituent will be discussed in a forthcoming paper dealing with the latter series of compounds.

**Acknowledgments.** The authors wish to thank Dr. A. A. Bothner-By and Dr. J. A. Pople for having made available to them preprints of their papers. They are also very grateful to Dr. A. A. Bothner-By for reading the text of the manuscript. This work was performed using in part the nmr facility for biomedical studies supported by National Institutes of Health Grant FR 00292-01.

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# The Nuclear Magnetic Resonance Spectra of Fluorobenzenes. II. The Effect of Substituents on the *meta* and *para* Fluorine–Fluorine Coupling Constants[1a]

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*Received May 15, 1967*

**Abstract:** A breakdown of the *meta* and *para* F–F couplings in fluorobenzenes on the basis of additive substituent contributions enables both the magnitude and sign of any such F–F coupling to be calculated from the substituent contributions given here. The agreement between the calculated and observed couplings is, in general, within the experimental error of the latter and in those cases where the signs are known these are reproduced precisely. These couplings vary from *ca.* +5 to +18 cps for the *para* coupling and from *ca.* −20 to +20 cps for the *meta* coupling. The substituent contributions show a linear dependence on the Hammett $\sigma$ value of the substituent, in contrast to the analogous H–H couplings, and also, more surprisingly, the substituent contributions change sign in going from *ortho–ortho* to *ortho–para* positions. These trends, and the contrast between FF and (FH and H–H) couplings, are shown to be due to the $\pi$ electron contribution to the F–F couplings.

Proton–proton couplings in aromatic systems are known to fall within characteristic ranges depending on the orientation of the coupled protons; *e.g.*, Emsley, *et al.*, quote $J_{ortho}$ = 7.0–9.2 cps, $J_{meta}$ = 1.1–3.1 cps, and $J_{para}$ = 0.0–0.7 cps.[2] These characteristic values have been used extensively in structural determinations for a number of years. The analogous proton–fluorine couplings may also be used in this manner although as the characteristic ranges of the *ortho* and *meta* couplings overlap considerably (Emsley, *et al.*, quote $J_{ortho}$ = 6.2–10.1 cps, $J_{meta}$ = 6.2–8.3 cps, and $J_{para}$ = 2.1–2.3 cps),[3] these only distinguish the *para* couplings.

However, the analogous fluorine–fluorine couplings, for which there are a large amount of data in the literature,[4–6] cannot be used at all to obtain structural information. Previous workers[2,7] in this field have attempted to define characteristic ranges of values of these couplings, but, as more data became available, these "ranges" overlap so considerably as to be of little use to the structural chemist.

The *ortho* F–F couplings are virtually constant (*ca.* −19 to −21 cps)[3,7] and independent of the substituents and we will not consider them further. However, this small range of values means that the determination of the negative sign of this coupling in a few compounds[1,8] may be safely extrapolated to all *ortho* F–F couplings. We use this assumption and adjust all the relative sign data reported to agree with this. In contrast, the *para* and particularly the *meta* F–F couplings show amazingly large variations. We shall show that it is possible to obtain *para* F–F couplings ranging from +5 to +18 cps and *meta* couplings from −20 to +24 cps. The range of values for the *meta* coupling overlaps those of both the *ortho* and *para* couplings and is so large that the concept of characteristic values becomes too vague to be meaningful. We shall show that it is possible to interpret all the existing data on the basis of a simple scheme which considers the effects of substituents on these couplings explicitly. Furthermore, in many compounds, the sign of the *meta* coupling has not been determined. The scheme presented here predicts the signs of these couplings. In the cases subsequently reported,[9,10] these predictions were confirmed. Pre-

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