

tion. It is noteworthy that this factor is expressed entirely in the enthalpy of activation; see Table IV.<sup>32</sup>

(32) It is not clear why the entropy of activation for 3,6-dimethyl-2-(hydroxymethyl)benzoic acid lactonization is about 5 e.u. lower than for the other hydroxy acids studied.<sup>29</sup> Restriction of initial state freedom of rotation should tend to increase, not decrease,  $\Delta S^\ddagger$ . A possibility is that solvation of the initial state but not of the transition state is diminished by 3,6-disubstitution, either by direct steric interference with solvation or by obliging the hydroxy and carboxy groups to hydrogen bond with each other with consequent reduction of opportunity to form hydrogen bonds to water molecules.

Bunnett and Okamoto<sup>33</sup> observed huge steric acceleration of the Smiles rearrangement of 2-hydroxy-2'-nitrodiphenyl sulfones by 6-substituents. It also was judged to stem from steric regulation of initial state conformation, and it also appeared to be expressed entirely in a decreased enthalpy of activation.

(33) J. F. Bunnett and T. Okamoto, *J. Am. Chem. Soc.*, 78, 5363 (1956).

## The Relative Signs of the Nuclear Magnetic Resonance Proton-Proton Coupling Constants in Styrene Sulfide and Styrenimine<sup>1</sup>

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Contribution from the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, and Esso Research and Engineering Company, Linden, New Jersey. Received December 28, 1964

From n.m.r. double resonance experiments in which a weak perturbing radiofrequency field was applied to certain spectral lines, it was found that the 1.37-c.p.s. geminal proton-proton coupling in styrene sulfide (III) is a different sign (presumably negative) than the two vicinal couplings of 5.55 and 6.60 c.p.s. between protons in the thiirane ring. Similar experiments on styrenimine (II) showed that the 0.87-c.p.s. geminal coupling in this molecule is the same sign as the 3.29- and 6.12-c.p.s. vicinal couplings in the aziridine ring. These results are discussed in relation to the magnitudes and relative signs of other geminal and vicinal proton-proton coupling constants and their correlation with substituent electronegativities. It is concluded that the linear correlations of geminal and vicinal couplings with substituent electronegativities may be better than previously expected, provided the substituents involved do not possess electronic effects which contribute to the coupling and which are not measured by thermochemical data.

### Introduction

Recently it has been conclusively demonstrated by high-resolution analyses,<sup>4</sup> double resonance experiments,<sup>5</sup> and double quantum transition spectra<sup>6</sup> that

(1) This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

(2) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif.

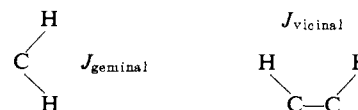
(3) Esso Research and Engineering Co., Linden, N. J.

(4) (a) R. R. Fraser, R. V. Lemieux, and J. D. Stevens, *J. Am. Chem. Soc.*, 83, 3901 (1961); (b) F. Kaplan and J. D. Roberts, *ibid.*, 83, 4474 (1961); C. A. Reilly and J. D. Swalen, *J. Chem. Phys.*, 35, 1522 (1961); H. Finegold, *Proc. Chem. Soc.*, 213 (1962).

(5) (a) R. Freeman, K. A. McLaughlan, J. I. Musher, and K. G. R. Pachler, *Mol. Phys.*, 5, 321 (1962); (b) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 37, 2053 (1963); (c) R. Freeman and N. S. Bhacca, *ibid.*, 38, 1088 (1963).

(6) K. A. McLaughlan and D. H. Whiffen, *Proc. Chem. Soc.*, 144 (1962).

the relative sign of the geminal proton-proton n.m.r. coupling constant is different from the relative sign of the vicinal proton-proton coupling constant in saturated



organic molecules where the carbon hybridization is close to  $sp^3$ . Recently we found by double resonance studies that the relative signs of the coupling constants between the three protons of the oxirane ring of styrene oxide (I) are all the same.<sup>7</sup> This rather striking contrast in the relative signs of geminal coupling constants between those in nearly  $sp^3$ -hybridized systems and that in I which contains a three-membered ring suggested to us that a study of the proton n.m.r. spectra of the nitrogen and sulfur analogs of I should provide some additional information relative to the factors dictating the signs and magnitudes of geminal proton-proton coupling constants. This study is herein described.

### Experimental

The styrenimine (II) was prepared as described elsewhere.<sup>8</sup> The styrene sulfide (III) was prepared by the reaction of styrene oxide and potassium thiocyanate in an aqueous ethanol solution similar to the procedures described by Snyder, Stewart, and Ziegler.<sup>9</sup>

The spectra were obtained with Varian HR-56.4-60 and A-60 spectrometers. The HR spectrometer had a field-frequency lock system similar to that described by Anderson and Freeman.<sup>5b,10</sup> Spectra were recorded by sweeping the frequency of a second audio oscillator with a synchronous motor. In the double resonance experiments a third modulation of an index sufficiently

(7) D. D. Elleman and S. L. Manatt, *J. Mol. Spectry.*, 9, 477 (1962).

(8) S. J. Brois, *J. Org. Chem.*, 27, 3532 (1962).

(9) H. R. Snyder, J. M. Stewart, and J. B. Ziegler, *J. Am. Chem. Soc.*, 69, 2674 (1947).

(10) W. A. Anderson and R. Freeman, *J. Chem. Phys.*, 38, 85 (1962).

large to cause the desired amount of perturbation was applied at a particular transition line. A complete description of this particular apparatus is given elsewhere.<sup>11</sup> The A-60 sweep widths were calibrated by the usual side-band method.<sup>12</sup> The spectra of II were obtained on 15–25% solutions in benzene and D<sub>2</sub>O to which a trace of hydrogen chloride gas had been added. Without addition of a small amount of hydrogen chloride the resonance lines of II were exchange broadened to the extent of being several cycles wide. The spectra of III were obtained on the neat liquid. A small amount (about 1%) of tetramethylsilane (TMS) was added in some cases. Spectra taken with the field-lock system required the addition of about 10% TMS as an internal standard.

### Theory

A theory describing the effect of weak perturbing radiofrequency fields applied to individual lines in an n.m.r. spectrum has been described, and its agreement with experiment has been demonstrated by Freeman and Anderson.<sup>5b</sup> Only the essential conclusions need be mentioned here.

If a perturbing radiofrequency field is set at the frequency of a particular resonance line and the magnitude of this field,  $\gamma H_2/2\pi$ , is about that of the line width in c.p.s. or mgauss then rather simple double resonance spectra result. In this case only transitions which share a common energy level with the irradiated line will be split into doublets. The positions of the members of the doublets are given by

$$\omega_i = \omega_{rp} \pm \gamma H_2 \lambda_{rs}$$

where  $\omega_{rp}$  is the position of the unperturbed line,  $H_2$  is the irradiating field, and  $\lambda_{rs}$  is the matrix element  $|\langle \psi_s | I^+ | \psi_r \rangle|$  which is proportional to the square root of the intensity of the irradiated line  $\omega_{rs}$ . From detailed consideration of line-shape profiles for the two possible arrangements of three n.m.r. energy levels, p, r, and s, in the case where s and p have the same spin quantum number the doublets will be well resolved, and when s and p differ by two units the doublets will be broadened.

The results from the application of weak perturbing fields to individual resonance lines thus enables the energy level diagram of a nuclear spin system to be traced out. Most applications so far reported have been to spectra which are first order or nearly so. In this situation it is possible to identify which line belongs to which nucleus. With the assumption that all the coupling constant signs are positive the spin states of each transition can be assigned. The results from irradiating in turn several lines in the spectrum will determine what changes, if any, need be made in the initial spectral assignment. At this point if the spectrum is truly first order the relative signs of all the couplings will have been determined. However, if the nuclear spin system contains coupling constants which vary in magnitude by a factor of 5–10 then what appears to be a first-order spectrum may be deceptively simple.<sup>13</sup> It is best practice to use the results from double resonance experiments to relate the energy levels of a nuclear spin system and then use computer programs

(11) D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, **42**, 650 (1965).

(12) J. T. Arnold and M. E. Packard, *ibid.*, **19**, 1608 (1951).

(13) The spectrum of indene oxide is such a case. See ref. 11.

such as Swalen and Reilly's NMRT and NMREN programs<sup>14</sup> to obtain a final set of parameters.

### Results

Figures 1 and 2 show the normal and double resonance spectra of II and III recorded with the field-frequency lock spectrometer used in this work. The double resonance results are most readily discussed by referring to a table of transition nuclear spin states for the ABC spin system as shown in Table I. Usually it is simplest to start with a table for all coupling constants the same relative sign and positive and then make any changes which experimental results suggest.

**Table I.** Nuclear Spin States for the Weakly Coupled ABC Systems of II and III for Coupling Constants of All the Same Relative Sign (Changes for  $J_{BC}$  a Different Sign Than  $J_{AB}$  and  $J_{AC}$  Shown in Parentheses)

Spin states	Transitions											
	A				B				C			
	1	2	3	4	5	6	7	8	9	10	11	12
A					$\alpha$	$\alpha$	$\beta$	$\beta$	$\alpha$	$\alpha$	$\beta$	$\beta$
B	$\alpha$	$\alpha$	$\beta$	$\beta$					$\alpha$	$\beta$	$\alpha$	$\beta$
C	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$(\beta)$	$(\alpha)$	$(\beta)$	$(\alpha)$

An experiment where line 1 of styrenimine (II) was irradiated is shown in Figure 1b. The changes in the B-proton region show that lines 5 and 7 have the same C-spin state as line 1, and the changes in the C-region show that lines 9 and 11 have the same B-spin state as line 1. If the spectrum of II is first order then according to Table I these results indicate that  $J_{AC}$  and  $J_{BC}$  are the same sign, and  $J_{AB}$  and  $J_{BC}$  are the same sign, respectively. Thus in one experiment it is possible to determine all the relative signs for this ABC system. The fact that lines 5 and 9 are sharp doublets and lines 7 and 11 in Figure 1b are broadened identifies the former pair of transitions as those whose energy levels not common to line 1 have the same spin magnetic quantum number as one of the energy levels of line 1.<sup>5b</sup> The latter pair are those whose corresponding energy levels differ in magnetic quantum number from one of the energy levels of line 1 by two units.<sup>5b</sup> Figure 1c shows an additional experiment which serves as a check on our previous conclusion.

Figures 2b and 2c show similar double resonance experiments on styrene sulfide (III). In Figure 2b irradiation of line 1 perturbed lines 6 and 8 in the B-portion and lines 10 and 12 in the C-portion. These results do not agree with Table I which is for all positive signs. The changes indicated in parentheses in Table I agree with the experimental results and are for  $J_{BC}$  a different sign than  $J_{AB}$  and  $J_{AC}$ . The fact that the separate members of the doublets observed in Figure 2b are not of equal intensity means that the perturbing radiofrequency field is slightly off resonance from line 1.<sup>5b</sup> In Figure 2c it is interesting that irradiation of line 5 causes doubling of lines 2 and 9, but no appreciable broadening of lines 4 and 11 at this power level. However, this result is still consistent with the conclusions reached above.

(14) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

**Table II.** Coupling Constants in Styrenimine and Styrene Sulfide

II, X = NH; III, X = S

	$J_{AB}$	$J_{AC}$	$J_{BC}$	$\delta_A^a$	$\delta_B^a$	$\delta_C^a$	Av. dev. <sup>b</sup>
II <sup>c</sup>	$6.120 \pm 0.016$	$3.293 \pm 0.016$	$0.871 \pm 0.016$	$156.99 \pm 0.05$	$105.72 \pm 0.05$	$85.96 \pm 0.05$	0.009
III	$6.605 \pm 0.039$	$5.554 \pm 0.039$	$-1.373 \pm 0.039$	$213.41 \pm 0.05$	$148.40 \pm 0.05$	$137.86 \pm 0.05$	0.023

<sup>a</sup> C.p.s. downfield from tetramethylsilane. <sup>b</sup> Observed minus calculated line position. <sup>c</sup> Results from 15–25% solution in benzene with trace of HCl.

From the magnitudes of the first-order coupling constants and chemical shifts obtained from several A-60 spectra of II and III, energy level assignments were determined with NMRIT.<sup>14</sup> From these assignments, the observed line positions and NMREN and NMRIT, values for the coupling constants and chemical shifts were obtained. These (in c.p.s.) are given in Table II.

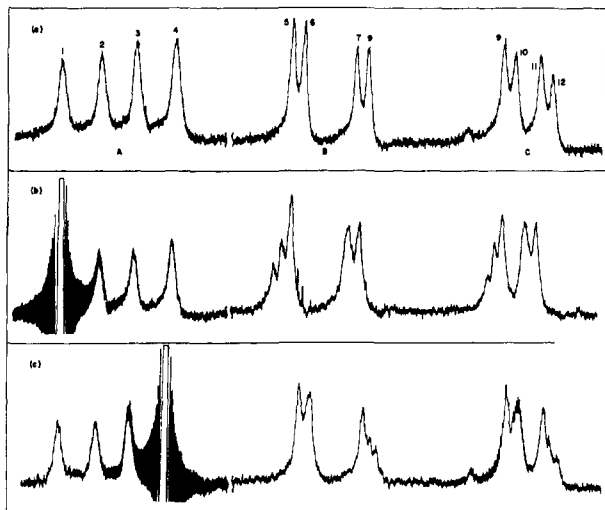


Figure 1. Frequency sweep 60-Mc. n.m.r. spectrum of styrenimine (20% in  $C_6H_6$  with added HCl gas): (a) normal spectrum, (b) line 1 irradiated, and (c) line 4 irradiated.

In both II and III the resonance lines of the proton in the three-membered ring which is closest to the aromatic ring (proton A in both cases) are considerably broader than those of the other two protons. This is caused by small, long-range couplings with one or more protons on the aromatic ring. In the case of II the proton on nitrogen was observed as a broadened single line 47 c.p.s. downfield from TMS. The area of this line determined by electronic integration was that for one proton.

### Discussion

We have based the assignment of  $J_{AB}$  as the *cis*-vicinal coupling and  $J_{AC}$  as the *trans*-vicinal coupling in II and III on analogy with the experimental results in the oxirane<sup>11</sup> and cyclopropane series.<sup>15,16</sup> Karplus' theoretical work on the dependence of vicinal coupling constants on dihedral angle<sup>17</sup> also supports the same assignment. In addition the relative chemical shifts of the B and C protons in these two molecules are

(15) D. J. Potel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(16) K. B. Wiberg and B. J. Nist, *ibid.*, **85**, 2788 (1963).

(17) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

explicable in terms of slightly different local field contributions from the magnetic anisotropy of the C–C bond to the phenyl group.<sup>18</sup> The small, long-range coupling of the phenyl ring protons cause the A proton lines in both II and III to be rather broader than those of the B- and C-protons (see Figures 1 and 2).

Absolute signs of the spin–spin couplings have been

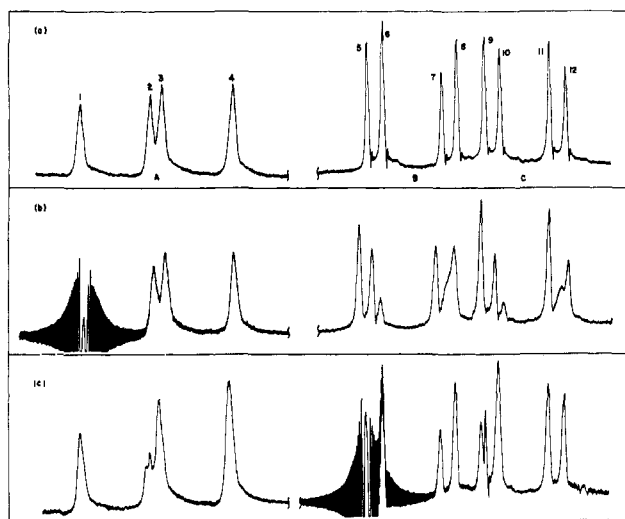


Figure 2. Frequency sweep 60-Mc. n.m.r. spectrum of styrene sulfide (neat liquid): (a) normal spectrum, (b) line 1 irradiated, and (c) line 5 irradiated.

given in Table II based on the recent work which has related <sup>13</sup>C–H couplings, which are believed to be positive absolute, to the vicinal H–C–C–H coupling.<sup>19–21</sup>

There is presently considerable interest in what electronic and structural factors determine the magnitudes and relative signs of geminal proton–proton couplings. The initial theoretical attempts to describe this coupling by Karplus and co-workers<sup>22</sup> have been shown experimentally to be insufficient in several respects. First, the effects of the adjacency to a methylene group of substituents containing  $\pi$ -electron centers was not accounted for, although subsequently Grant has proposed a semiempirical theory which has remedied this.<sup>23</sup> Also the effect on the geminal coupling

(18) (a) J. I. Musher, *ibid.*, **35**, 1159 (1961); (b) J. I. Musher and R. G. Gordon, *ibid.*, **36**, 3097 (1962).

(19) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962).

(20) P. C. Lauterbur and R. J. Kurland, *ibid.*, **84**, 3405 (1962).

(21) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **39**, 806 (1963).

(22) (a) M. Karplus and D. H. Anderson, *ibid.*, **30**, 6 (1959); (b) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(23) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

due to electron withdrawal by electronegative substituents was not accounted for. Probably the most dramatic failing is the fact that the theory predicted a positive sign for the geminal coupling in an  $sp^3$ -hybridized methylene group whereas there is overwhelming evidence that this coupling is negative.<sup>4-6</sup>

We chose to study the signs and magnitudes of the coupling constants in styrene oxide (I) (results reported previously<sup>7</sup>), styrenimine (II), and styrene sulfide (III) for several reasons. First structural information from other methods<sup>24</sup> suggest that the H-C-H angles in these three molecules are about the same (approximately  $116^\circ$ ); thus perhaps any differences in the geminal couplings could be attributed to substituent effects. The H<sub>2</sub>-C-C angles in I and II are very similar and that in III is only slightly less,<sup>25</sup> and the changes of the vicinal couplings in at least I and II may reflect mainly electronic rather than steric substituent effects.

Several correlations have been described which attempt to relate magnitudes of couplings to substituent electronegativities.<sup>26-33</sup> All these treatments have used plots of coupling constants vs. electronegativity to derive a linear correlation. These linear relationships have all shown a significant scatter of points. It would seem that a multiplicity of substituent effects influences these couplings and that the most important one appears to be that of electronegativity. It has been pointed out<sup>31</sup> that in systems containing  $\pi$ -electron centers adjacent to a -CH-CH<sub>2</sub>- fragment, two classes of  $\pi$ -electron effects appear to be distinguishable. In addition, in the case of oxiranes much better correlation between substituent electronegativity and coupling constants is arrived at if groups containing  $\pi$ -electrons adjacent to the -CH-CH<sub>2</sub>- fragment are not used to establish the correlation line. The deviations for the latter type of substituents then provide a measure of the magnitude of these special electronic effects which must not contribute significantly to the determination of the electronegativity of a substituent, which itself should be directly related to thermochemical properties. It should be pointed out, as discussed elsewhere,<sup>31</sup> that  $\pi$ -electron effects exist for both vicinal and geminal proton-proton couplings, a fact which has not been noted previously. More detailed discussions of the multiplicity of substituent effects on geminal and vicinal couplings will be deferred at present. The main point we wish to make here is that the linear correlation between vicinal and geminal proton-proton couplings and substituent electronegativities for substituents which do not have the possibilities of bringing into play electronic effects not measured by bond energy quantities may be much better than pre-

(24) See E. Goldish, *J. Chem. Educ.*, **36**, 408 (1959), for structural data on ethylene oxide, ethylenimine, and ethylene sulfide.

(25) Estimated to be  $158.1 \pm 0.5^\circ$ ,  $159.4^\circ$ , and  $151.7^\circ$ , respectively, from data in ref. 24.

(26) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

(27) N. Sheppard and J. J. Farner, *Proc. Roy. Soc. (London)*, **A252**, 506 (1959).

(28) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(29) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

(30) K. L. Williamson, C. A. Lanford, and G. R. Nichol森, *ibid.*, **86**, 762 (1964).

(31) S. L. Manatt, Space Programs Summary No. 37-21, Vol. IV, Jet Propulsion Laboratory, Pasadena, Calif., 1963, pp. 250-253.

(32) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963).

(33) J. Lehn and J. Riehl, *ibid.*, **8**, 33 (1964).

viously thought. Some evidence supporting this viewpoint will now be presented.

Some time ago Muller and Pritchard<sup>34</sup> discussed the correlation of the  $^{13}\text{C}$ -H coupling in substituted methanes with  $s$  character of the carbon orbital and the C-R bond distance in a three-parameter equation. Looking at the same data we feel that perhaps a simpler relation exists, *i.e.*,  $J_{^{13}\text{C-H}} = A + BE_R$  (where  $A$  and  $B$  are positive constants and  $E_R$  is the electronegativity) provided that R is not a group which can participate in special electronic effects not measurable from thermochemical data. Figure 3 shows the  $^{13}\text{C}$ -H data for  $\text{CH}_3\text{CH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_3\text{F}$  plotted against the Huggins electronegativities.<sup>35</sup> An excellent straight line can be drawn through the points for R =  $-\text{CH}_3$ ,  $-\text{NH}_2$ , and  $-\text{OH}$  while the point for R =  $-\text{F}$  appears to deviate very slightly. More careful measurements of these  $^{13}\text{C}$ -H couplings might be worthwhile to establish unequivocally whether the very good line determined by the three points  $-\text{CH}_3$ ,  $-\text{NH}_2$ , and  $-\text{OH}$  is not an artifact and the deviation of the point for  $-\text{F}$  is real. There are several pieces of evidence<sup>36,37</sup> that  $-\text{F}$  should deviate, *i.e.*, have certain capacities for electronic effects not measured by thermochemical properties.

We have found another case where a set of molecules all having similar geometry but differing only in a substituent give a good linear plot between Huggins electronegativities and the  $^{13}\text{C}$ -H coupling. In Figure 3 there is a good linear relation for the case of the three-membered ring compounds cyclopropane, ethylenimine, and ethylene oxide. This linear plot is derived from experimental data reported to be less in error ( $\pm 0.5$  c.p.s.)<sup>15,38</sup> than that for the substituted methanes ( $\pm 1$  c.p.s.).<sup>34</sup> These linear correlations are both excellent for the two sets of three points for the substituents involving C, N, and O atoms. As is shown in Figure 3, the points for styrene sulfide and methyl sulfide fall considerably off the two correlation lines determined by the first-row elements thus indicating contributions to the  $^{13}\text{C}$ -H couplings of about  $+9$  and  $+13$  c.p.s., respectively, in these latter molecules above those predicted by a linear correlation with electronegativity.

It would seem reasonable that for systems with substituents whose spin coupling contributions are derived only from electronic effects measured by electronegativity it should be possible from measured  $^{13}\text{C}$ -H couplings to derive an appropriate group electronegativity. *A priori* we would expect this to be possible for alkyl groups and substituents which do not contain  $\pi$ -electrons. We have taken the recent  $^{13}\text{C}$ -H data<sup>15</sup> for 1,1-dimethylcyclopropane and spiro-pentane and derived an electronegativity for the  $>\text{C}(\text{CH}_3)_2$  and  $>\text{C}-\text{CH}_2-\text{CH}_2$  substituents in a three-membered ring as indicated in Figure 3.

As was discussed above, linear correlations between substituent electronegativity and geminal and vicinal couplings have been suggested. In Figure 4 we have taken the data for the vicinal (*cis* and *trans*) couplings

(34) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 1471 (1959).

(35) M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

(36) N. Muller and P. I. Rose, *ibid.*, **84**, 3973 (1962).

(37) C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

(38) F. S. Mortimer, *Mol. Spectry.*, **5**, 199 (1960).

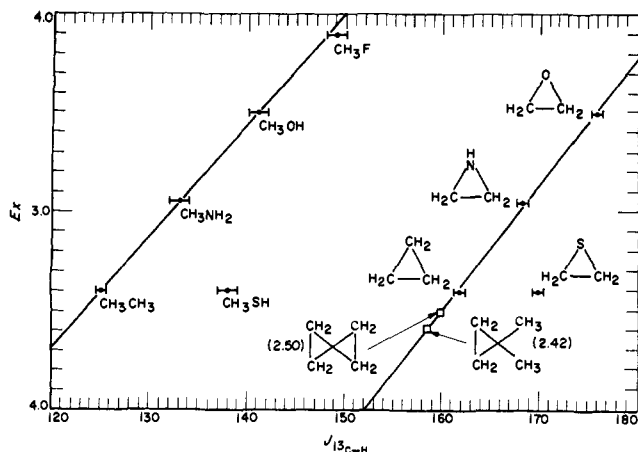


Figure 3. Plot of  $J_{^{13}\text{C}-\text{H}}$  vs.  $E_x$ , the Huggins' electronegativity, for some substituted methanes and some three-membered ring compounds;  $\square$ , predicted electronegativities based on  $J_{^{13}\text{C}-\text{H}}$  for the substituents  $\text{CH}_2-\text{CH}_2-\text{C} < \text{ and } > \text{C}(\text{CH}_3)_2$

for the cyclopropanes mentioned above, ethylene imine,<sup>38</sup> and ethylene oxide<sup>38</sup> and plotted them vs. the Huggins electronegativity.<sup>35</sup> For the former two compounds this electronegativity was determined from Figure 3. A rather satisfactory linear relation is evident. The points for ethylene sulfide are also shown in Figure 4. As in the case of the  $^{13}\text{C}-\text{H}$  coupling the points for the vicinal couplings in this molecule deviate significantly from the linear correlation. Also shown in Figure 4 are the data for the styrene oxide, styrenimine, and styrene sulfide. The data for the former two would appear to determine lines parallel to but slightly displaced from those determined for the unsubstituted molecules. The points for the sulfur analog III again deviate.

In the case of the geminal coupling, values for ethylene oxide,<sup>39</sup> 1,1-dimethylcyclopropane,<sup>15</sup> and spiropentane<sup>15</sup> are available. The difference between the geminal couplings in ethylene oxide and styrene oxide is very small. We have plotted the five points for ethylene oxide, the two cyclopropanes mentioned above, styrene oxide, and styrenimine and as is evident they determine a rather satisfactory straight line. Again the sulfur analog's geminal coupling deviates from this linear relation.

The discussion and coupling constant data above indicate that the linear correlation between geminal and vicinal proton-proton couplings in rigid systems and Huggins electronegativities<sup>35</sup> is rather better than previously indicated.<sup>29,30</sup> It is then possible to predict with some reasonable confidence the values for certain couplings heretofore unobserved or undetermined. Previously Mortimer in his analysis of the  $^{13}\text{C}$  satellite spectrum of ethylenimine could not determine the proton-proton geminal coupling<sup>38</sup>; from Figure 4 this coupling is estimated to be about +1 c.p.s. Similarly, for cyclopropane itself the geminal and the two vicinal couplings are predicted to be -3.0, +8.5 (*cis*), and +5.0 c.p.s. (*trans*), respectively. Assuming that the points for the vicinal couplings for styrene oxide and styrenimine determine lines parallel to those of the unsubstituted molecules, the vicinal

(39) Derived from the observation of certain weak transitions in a sample of  $^{13}\text{C}$ -enriched material; S. L. Manatt, unpublished work.

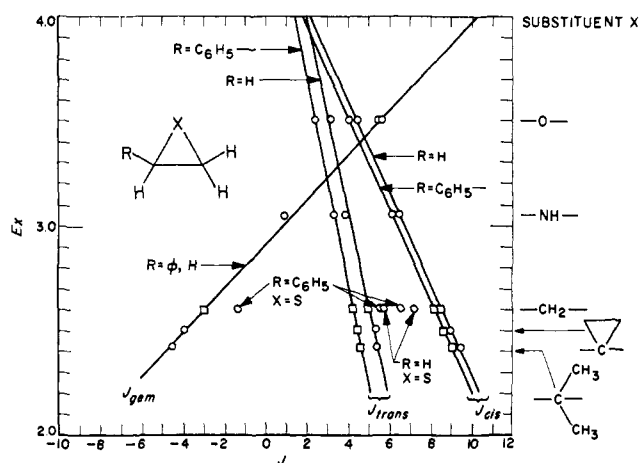


Figure 4. Plot of vicinal couplings and the geminal coupling vs.  $E_x$ , the Huggins' electronegativity, for a series of three-membered ring compounds;  $\square$ , certain predicted couplings.

couplings for phenylcyclopropane are predicted to be +4.3 (*trans*) and +8.2 c.p.s. (*cis*). The geminal coupling is estimated to be about -2.7 c.p.s. There are still two more vicinal couplings in this molecule whose values may be estimated from other data<sup>15,16</sup> to be +10.5 and +7.5 c.p.s. Table III summarizes predictions from Figure 4 for this latter molecule and several other molecules whose n.m.r. spectra have not been analyzed.

Table III. Summary of Couplings Constants Predicted from Figure 4

R	X	$J_{AB}^a$	$J_{AC}^a$	$J_{BC}^a$
H	-CH <sub>2</sub> -	+8.5	+5.0	-3.0
C <sub>6</sub> H <sub>5</sub> -	-CH <sub>2</sub> -	+8.2	+4.3	-3.0
C <sub>6</sub> H <sub>5</sub> -	>C-CH <sub>2</sub> -CH <sub>2</sub>	+8.6	+4.5	-4.1
C <sub>6</sub> H <sub>5</sub> -	>C(CH <sub>3</sub> ) <sub>2</sub>	+9.1	+4.6	-4.5

<sup>a</sup>  $J$  values in c.p.s.

Figure 3 shows that the  $^{13}\text{C}-\text{H}$  coupling in the substituted methanes is only slightly more strongly dependent on substituent electronegativity than the  $^{13}\text{C}-\text{H}$  coupling in the three-membered cyclics. Comparing the plots in Figures 3 and 4 it is obvious that of the four types of couplings we have discussed the  $^{13}\text{C}-\text{H}$  coupling is much more strongly dependent on the electronegativity. The *trans*-vicinal couplings are the least strongly dependent on electronegativity, while the *cis*-vicinal couplings are only slightly more dependent than the latter. The geminal coupling is more dependent on substituent electronegativity than the vicinal couplings. Also the dependence is of opposite sense to that for the vicinal couplings. As is evident from these linear correlations with electronegativity both vicinal couplings and the geminal coupling in the simple three-membered cyclics we have discussed are linearly related to the respective  $^{13}\text{C}-\text{H}$  couplings.<sup>40</sup> As the appropriate  $^{13}\text{C}-\text{H}$  couplings become available

(40) Such a correlation has been suggested for the geminal coupling by H. J. Bernstein and N. Shepperd, *J. Chem. Phys.*, 37, 3012 (1962).

for the unsymmetric substituted derivatives, such as styrene oxide, styrenimine, and phenylcyclopropane, it will be interesting to see if any degree of generality exists for this type of relation. There should be different  $^{13}\text{C-H}$  couplings in the three-membered ring of these latter derivatives for each C-H bond.<sup>41</sup>

### Conclusion

In the foregoing analysis we have attempted to demonstrate for one series of molecules containing a three-membered ring that there appears to exist a very simple linear relation between geminal and vicinal proton-proton couplings and the Huggins electronegativity<sup>38</sup> (or a related quantity derived from  $^{13}\text{C-H}$  couplings) and that this relation is better than previous similar correlations would lead one to believe. The reason for the scatter in the previously offered correlations is the fact that certain substituents possess electronic interactions, which we shall term "extra electronic effects," whose presence does not contribute measurably to the determination of bond energies from which electronegativities are derived, but whose presence does provide additional possibilities for the propagation of nuclear spin-spin coupling. This may mean that in many cases the  $^{13}\text{C-H}$  coupling does not directly measure the percentage s character in a carbon bonding orbital when a carbon atom is substituted by one of the type of substituents capable of "extra electronic

(41) See R. M. Lynden-Bell, *Mol. Phys.*, **6**, 537 (1963), for the case of vinyl bromide- $^{13}\text{C}$ .

effects." This same conclusion has also been reached by Karabatsos,<sup>42</sup> who suggests that the breakdown of the simple correlation stems from spin-dipole and/or electron-orbital contributions to the  $^{13}\text{C-H}$  coupling. However, Pople's recent theoretical treatment of the coupling between directly bonded atoms suggests that these two contributions will both be zero if one of two coupled nuclei is hydrogen.<sup>43</sup> On this basis it would seem that the deviations from a simple correlation of  $^{13}\text{C-H}$  coupling with s character observed may well arise through a Fermi contact mechanism involving electrons of substituent atoms or groups. A theoretical consideration of this possibility could be fruitful.

Deviation from a simple correlation can probably *a priori* be expected for substituents with  $\pi$ -electrons, second and higher row elements, and fluorine atoms in close proximity to a set of coupled nuclei. Possibly low-lying excited states and/or d-orbital participation contribute to these effects for second and higher row elements. The nature of these electronic effects in the case of fluorine appears rather obscure.

The manner in which the relation between coupling constants and electronegativity has been discussed here could serve as a basis for making a separation between contributions to spin-spin coupling due to factors depending on bond strength and those derived from several extra electronic effects; these points are being further investigated.

(42) G. J. Karabatsos and C. E. Orzech, *J. Am. Chem. Soc.*, **86**, 3575 (1964).

(43) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

## Carbon-13 Magnetic Resonance. III.<sup>1</sup> Purine

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*Using deuterated compounds of known structure the carbon-13 chemical shift values for the 2, 6, and 8 carbons in purine were assigned unequivocally. The two remaining peaks found at the lowest and highest field positions are assigned to carbons 4 and 5, respectively, on the strength of the theoretical prediction that the highest  $\pi$ -electron density is at C-5. For an increasing magnetic field the resonance pattern for carbon-13 (2, 8, 6) differs from that noted for the corresponding directly bonded hydrogens (6, 2, 8). This disagreement suggests that chemical shift values should be used with care as a means for predicting charge densities. Nevertheless, a gross correlation of carbon-13 chemical shift data with theoretical estimates of the charge distribution in purine does exist.*

### I. Introduction

The recent literature contains several papers<sup>2-6</sup> in which the proton magnetic resonance spectra of

purine and some of its derivatives are discussed. Early assignments of the chemical shifts of the 2, 6, and 8 hydrogens in purine were based upon values obtained for purine derivatives and related heterocyclic compounds. More recent work has shown that these early assignments were in error, and the correct assignment has been obtained from various deuterium-substituted purines of known structure. Comparison of spectra of deuterated and nondeuterated species has made it possible to assign the peaks for an increasing field to the 6, 2, and 8 hydrogens, respectively.

In a series of aromatic compounds, Spiesecke and Schneider<sup>7</sup> have observed a direct relationship between the carbon-13 chemical shift value and the  $\pi$ -electron charge density. Their work has been given a theoretical

(2) C. D. Jardetzky and O. Jardetzky, *ibid.*, **82**, 222 (1960).

(3) S. Matsuura and T. Goto, *Tetrahedron Letters*, 1499 (1963).

(4) M. P. Schweizer, S. I. Chan, G. K. Helmkamp, and P. O. P. Ts'o, *J. Am. Chem. Soc.*, **86**, 696 (1964).

(5) F. J. Bullock and O. Jardetzky, *J. Org. Chem.*, **29**, 1988 (1964).

(6) S. I. Chan, M. P. Schweizer, P. O. P. Ts'o, and G. K. Helmkamp, *J. Am. Chem. Soc.*, **86**, 4182 (1964).

(7) H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, **14**, 468 (1961).

(1) Previous paper in series: D. M. Grant and E. G. Paul, *J. Am. Chem. Soc.*, **86**, 2984 (1964).