

Fig. 1.—Optical rotation, ultraviolet absorption, and titration of poly-L-glutamic acid, 0.5 g./dl. in 0.2 *M* NaCl. (O), Molar (residue) extinction coefficient at 200 *mμ*, ϵ_{200} . (●), Specific rotation at 589 *mμ*, $[\alpha]_{589}$. Degree of dissociation of carboxyl groups is shown by titration curve. Ordinate scales are adjusted to make the ranges of the various measurements approximately coincide.

In the absorption measurements reported here no attempt has been made to separate the changes in carboxyl absorption with pH from the changes in amide absorption. A rough experiment on acetic acid under conditions similar to those used for PGA showed $\epsilon_{200} = 260$ at pH 9 and $\epsilon_{200} = 130$ at pH 4. These values are relatively small, and an attempt to correct for carboxyl absorption would not be expected to affect our conclusions.

It will be noted that our curve showing absorption *vs.* pH is markedly different from that observed by Imahori and Tanaka under the conditions of their measurements (unspecified). They found ϵ_{190} to change gradually from pH 4 to 8, with an intermediate plateau from about pH 4.5 to 6. No such plateau is evident from our data, and the transition is sharper. It is unlikely that the difference is due to the choice of wave length, as we find similar transition curves at all wave lengths in the portion of the band accessible to accurate measurements. It will also be noted that the optical rotation reaches a constant value at the low pH side in our data, whereas other experimenters^{2,7} have observed a maximum in the rotation at about pH 4.5. This difference may be due to unknown factors in the particular samples or handling techniques. Solutions at about pH 4 are, for example, known to be metastable, and precipitation sometimes produces irreproducible results. No precipitation was evident above pH 4 in our experiments.

Acknowledgment.—This investigation was supported by a Public Health Service research grant (GM-10882-03) from the Division of General Medical Sciences, Public Health Service.

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RECEIVED JULY 8, 1963

Vicinal Proton Coupling in Nuclear Magnetic Resonance¹

Sir:

Considerable attention has focused recently on the utilization of the dihedral-angle dependence of vicinal proton coupling constants for structural studies of

(1) Most of the calculations reported in this paper were made on ILLIAC at the University of Illinois during the year 1959–1960 and reported at the American Chemical Society Symposium on High Resolution n.m.r. held at Boulder, Colorado, July 2–4, 1962.

organic molecules.² Since most of the investigations have been experimental in character, it is helpful to recall the theoretical foundations of the subject. This seems to be of particular relevance at the present time because of published statements³ (*e.g.*, the implication that the vicinal coupling constants are expected theoretically to depend *only* on the dihedral angle) that indicate some confusion concerning the predictions and the limitations of the theory. In this communication we outline the theoretical results for vicinal proton couplings in ethanic, ethylenic, and related systems. Special emphasis is placed on the factors that are expected to alter the behavior from that determined for the unperturbed model used in the original calculations.⁴

The valence-bond σ -electron calculation,^{4,5} which utilizes a nonionic six-electron, six-orbital fragment (HCC'H') to determine the contact interaction, yields results that can be approximated by the equation⁶

$$J_{\text{HH}'} = A + B \cos \phi + C \cos 2\phi \quad (1)$$

where ϕ is the dihedral angle. For a C–C bond length of 1.543 Å., sp^3 hybridized carbon atoms, and an average energy (ΔE) equal to 9 e.v., the constants are $A = 4.22$, $B = -0.5$, and $C = 4.5$ c.p.s. A fragment with sp^2 hybridization, a C–C bond length of 1.353 Å., and the same ΔE value gives $J_{\text{HH}'}(\text{cis}) = 6.1$ c.p.s. and $J_{\text{HH}'}(\text{trans}) = 11.9$ c.p.s. These results appear to be in qualitative agreement with some of the salient features of the measured couplings (*e.g.*, the dihedral-angle dependence in ethanic compounds, the *cis/trans* ratio in ethylenic compounds.^{7,8} However, the numerical values obtained from the calculations are to be regarded as only "zero-order" approximations. As pointed out originally,⁹ "the variability of the observed coupling constants is not predicted by the simple model considered in this paper. Refinements, such as the inclusion of electron orbital and dipolar electron spin terms, a more careful choice of integral values, and the consideration of ionic and other perturbations, should be introduced. Also, a determination of the θ dependence [HCC' angle] and the C–C bond-length dependence of the coupling constant, which are only hinted at here by the differences between ethane and ethylene, would be of value for the interpretation of various ring-system spectra." In what follows we provide estimates of some of these effects. As in our previous work, this is done primarily to suggest the trends that are expected on theoretical grounds.

Ionic Substitution Perturbations.—If a substituent is introduced whose electronegativity (X) is different from hydrogen (X_{H}), significant deviations from the

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(3) See, for example, (a) K. L. Williamson, *ibid.*, **85**, 516 (1963); (b) O. L. Chapman, *ibid.*, **85**, 2014 (1963); G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963); P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2018 (1963).

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

(5) H. Conroy, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 265, gives a molecular orbital treatment.

(6) Equation 1 is similar to, but slightly more accurate than, the original equation (eq. 11, ref. 4). Corresponding expressions have recently been suggested by J. Powles, *Discussions Faraday Soc.*, **34**, 30 (1962); M. Barfield and D. M. Grant (private communication); and O. Jardetsky (private communication).

(7) For a recent review, see C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

(8) The theoretical positive sign for most vicinal couplings is probably confirmed by the measurement of K. L. McLauchlan and A. D. Buckingham (private communication) of $J_{\text{HH}'}(\text{ortho})$ in *p*-nitrotoluene, though additional relative sign determinations are needed [*e.g.*, $J_{\text{HH}'}(\text{ethyl})$ vs. $J_{\text{HH}'}(\text{ortho})$].

(9) Ref. 4, p. 15.

unperturbed fragment results are to be expected (even if the structure of the molecule remains unaltered). There is a "direct" inductive effect on the polarity of the CH and C'H' bonds involved in the coupling that has been considered by Hiroike¹⁰ and by Ranft.¹¹ Introduction of reasonable inductive parameters into their treatment indicates that the "direct" term is relatively small. However, there is an additional effect that arises through the substituent-induced changes in hybridization¹² of the HCC'H' fragment carbon atoms. If the structure of the molecule is assumed constant, an estimate of the carbon atom hybridization can be obtained from J_{CH} coupling measurements¹³ and an appropriately modified fragment calculation can be performed. The values found can be written $J_{\text{HH}}(\text{cis}) \cong J_{\text{HH}}^{\text{u}}(\text{cis})(1 - 0.60\Delta X)$, $J_{\text{HH}}(\text{trans}) \cong J_{\text{HH}}^{\text{u}}(\text{trans})(1 - 0.25\Delta X)$ for CH_2CHX , and $J_{\text{HH}}(\text{av}) \cong J_{\text{HH}}^{\text{u}}(\text{av})(1 - 0.07\Delta X)$ for $\text{CH}_3\text{CH}_2\text{X}$, where J_{HH}^{u} refers to the unperturbed fragment and $\Delta X = X - X_{\text{H}}$. These results for the substituent effects are in qualitative agreement with the available experimental data.^{3a,7,14}

Bond Angle Dependence.—The vicinal couplings are expected to depend significantly on the angles θ and θ' [$\theta = \angle \text{HCC}'$, $\theta' = \angle \text{CCH}'$] of the HCC'H' fragment, even when the orbitals point along the bond direction and the bond lengths remain unchanged. Fragment-model calculations show that J_{HH} should decrease for most dihedral angles as θ and θ' increase. For $105^\circ \leq \theta, \theta' \leq 115^\circ$, we find that A , B , and C of eq. 1 are given approximately by $A \cong 4.2 - 0.1(\Delta\theta + \Delta\theta')$, $B = -0.5 - 0.05(\Delta\theta + \Delta\theta')$, and $C = 4.4 - 0.12(\Delta\theta + \Delta\theta')$, where $\Delta\theta = \theta - 110^\circ$, $\Delta\theta' = \theta' - 110^\circ$. Corresponding results for the ethylenic system are $J_{\text{HH}}(\text{cis})$ equals 16, 6.1, 2.1 for ($\theta = \theta'$) angles of 110° , 120° , 130° , respectively.¹⁵ Bond angle changes of J_{HH} in the calculated direction were noted some years ago by Pople, Bernstein, and Schneider¹⁶ and have been emphasized recently by a number of workers.^{3b}

Bond Length Dependence.—For constant bond angles and hybridization, the vicinal σ -bond coupling is expected to be a function of the C-C bond length (R), a decrease of the coupling being produced by an increase in the bond length. For ethylenic systems, for example, the fragment calculations yield an almost linear dependence of the form $J_{\text{HH}}(\text{cis}) \cong J_{\text{HH}}^{\text{u}}(\text{cis}) [1 - 2.9(R - 1.35)]$ for R in the range 1.35–1.55 Å, in qualitative agreement with experiment.¹⁷

In addition to the factors discussed in detail, other molecular properties (e.g., exchange integral variation, molecular vibrations,¹⁸ ΔE variation, changes in π -bonding¹⁹) can influence vicinal coupling constants under appropriate conditions. Also, it is likely that the various perturbations affect the coupling through a

combination of the mechanisms that have been isolated earlier for convenient description.²⁰

Any structural analysis based on the dihedral-angle dependence of vicinal coupling constants must take account of their variation as a function of other aspects of the molecular environment. Until extensive studies have been made to ascertain the quantitative details of these relationships, the most reliable results are to be expected from the comparison of closely related species. The introduction of empirical parameters to adjust the theoretical formulas for a particular series of compounds can be helpful in this regard.² Furthermore, it is best if the solution to the structural problem under consideration depends not on the exact values of coupling constants, but only on the fact that certain couplings are "large" rather than "small," or *vice versa*. Certainly with our present knowledge, the person who attempts to estimate dihedral angles to an accuracy of one or two degrees does so at his own peril.

(20) This means of course, that experimental attempts to test the theoretical results must use care to isolate the variables under consideration.

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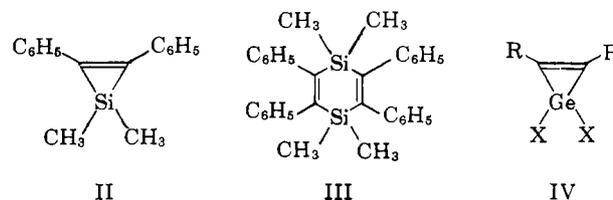
MARTIN KARPLUS

RECEIVED JULY 25, 1963

The Nature of "Silirene" Compounds

Sir:

In 1961 Vol'pin and his co-workers reported the synthesis of a compound with an empirical formula $\text{C}_{16}\text{H}_{16}\text{Si}$ (I), which they supposed to have the novel "silirene" structure (II).¹⁻³ We have found that compound I actually has a molecular weight twice that reported by Vol'pin.⁴ The compound probably has the six-membered ring structure III. The same



workers also reported three-membered ring structures (IV) for the related germanium compounds.^{2,3,5} These compounds have recently been shown to be dimers of this structure, in mass spectrometric studies by Johnson and Gohlke,⁶ who also suggested that the three-ring structures advanced for the silicon compounds might be incorrect. Thus the heterocyclic three-membered ring system containing a metalloid atom, theoretically rationalized by Vol'pin and his co-workers,^{2,7} has yet to be demonstrated.

A modification of the method of synthesis used by the previous workers led to a 10-fold increase in the yield of I. A suspension of 10 g. (0.43 g.-atom) of sodium was prepared in a solution of 27 ml. (0.22 mole) of dimethyldichlorosilane in 500 ml. of xylene. At

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(15) See also, H. S. Gutowsky and A. L. Porte, *ibid.*, **35**, 839 (1961).

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