Acrylonitrile-α,β,β-d_3 was prepared by adding D_2 to propargylnitrile-β-d (98% D) which was obtained from nitrile-d_0 by repeating (eight times) H-D exchange with D_2O. The exchange was performed by shaking the mixture vigorously at room temperature for 8 hr without using any additives. Preparation of the oligomers and purification were performed by methods similar to those described previously.[1]

Tsuneo Yoshino, Hikaru Iwanaga, Kiyoshi Kuno
Basic Research Laboratories, Toyo Rayon Company
Kamakura, Kanagawa, Japan

Received September 18, 1967

The Effect of Polar Substituents upon $^{13}C-^{13}C$ Coupling Constants

Sir:

It is generally accepted that bond hybridization[1-8] plays an important role in the directly bonded $^{13}C-H$ spin-spin coupling constant. Nevertheless, charge polarization features[9] and variations in the carbon-hydrogen bond distance[10] have also been shown to alter the hyperfine contact interaction term important in the $^{13}C-H$ coupling mechanism. Thus, hybridizational arguments based on $J_{^{13}C-H}$ values may be used only with care on systems in which other electronic features remain essentially constant.

While the work of Frei and Bernstein[11] and of Lynden-Bell and Sheppard[12] has exhibited the importance of hybridizational variations in the $^{13}C-^{13}C$ coupling constant, the relative influence of polarizing groups has not been explored systematically for this particular coupling constant in a class of related compounds. Table I contains $J_{^{13}C-^{13}C}$ values[13] for a set of compounds having very similar structures (*i.e.*, neopentane and related *t*-butyl derivatives), along with values of $J_{^{13}C-H}$ obtained in the corresponding methyl compounds. It is to be noted from Figure 1 that both coupling constants increase in a directly proportional manner, although it should be stressed that the relative increase (25 : 125) in $J_{^{13}C-H}$ is more than twice that (3 : 37) noted in $J_{^{13}C-^{13}C}$. As both of these couplings have the same relative sign[14] and are affected in a similar manner by hybridizational and charge polarization features, it is reasonable to conclude that the important coupling mechanism must be similar in both instances. It is interesting, therefore, to speculate on the reason for the relative increases being different in the two cases. One is led to conclude that the electronic structure of both nuclei involved in the coupling is affected by the electronegative substituent and not merely the carbon atom which is directly bonded to the polar group. Otherwise, the two couplings would be expected to increase by the same relative amount. This conclusion suggests that the relatively simple calculations of $J_{^{13}C-H}$ values by Grant and Litchman[15] should be extended to include possible polarization changes in the effective nuclear charge of the directly bonded hydrogen atom. As a hydrogen is a terminal atom, inductive effects cannot be transferred onto additional atoms as they can in a methyl group. Thus, polarization effects due to an electronegative group can be expected to be less severe in an adjacent C-C bond when compared with an adjacent C-H bond, and $J_{^{13}C-^{13}C}$ can reasonably be expected to be less sensitive to directly attached polar substituents than is $J_{^{13}C-H}$.

Table I. The Effect of Polar Groups on Directly Bonded Coupling Constants

X	$J_{^{13}C-^{13}C}$, cps, in $XC(CH_3)_3$	$J_{^{13}C-H}$, cps, in XCH_3[a]
CH_3	36.9	126
NH_2	37.1	133
OH	39.5	141
Cl	40.0	150
Br	40.2	152

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

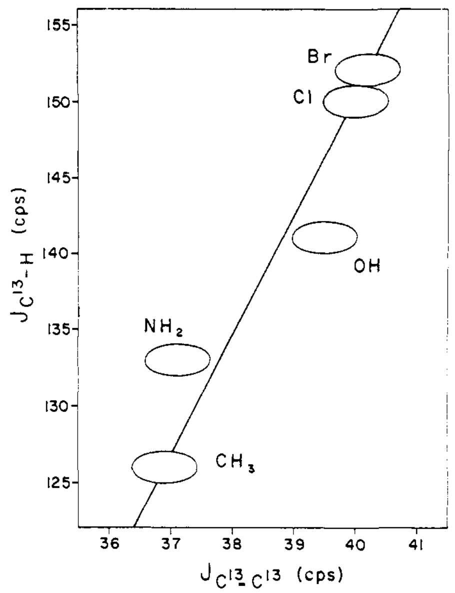

Figure 1. The values of $J_{C^{13}-H}$ in $X-CH_3$ are plotted *vs.* $J_{C^{13}-C^{13}}$ in the similar $X-C(CH)_3$ compounds for X equal to CH_3, NH_2, OH, Cl, and Br.

The reduced sensitivity of $J_{^{13}C-^{13}C}$ to charge polarization effects is fortunate in one respect as even greater confidence can be placed in the use of $J_{^{13}C-^{13}C}$ values as a criterion for bond hybridization.[11,12] This conclusion is especially significant in the recent $J_{^{13}C-^{13}C}$ work of

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(1) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(2) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

(3) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **45**, 1269 (1959).

(4) N. Muller, *J. Chem. Phys.*, **36**, 359 (1962); **42**, 4309 (1965).

(5) H. S. Gutowsky and C. S. Juan, *J. Am. Chem. Soc.*, **84**, 307 (1962).

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

(7) H. Dreeskamp and E. Sackmann, *Z. Physik. Chem.* (Frankfurt), **34**, 273 (1962).

(8) J. H. Goldstein and R. T. Hobgood, Jr., *J. Chem. Phys.*, **40**, 3592 (1964).

(9) D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965).

(10) D. S. Bartow and J. W. Richardson, *J. Chem. Phys.*, **42**, 4018 (1965).

(11) K. Frei and H. J. Bernstein, *ibid.*, **38**, 1216 (1963).

(12) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).

(13) The measurement of these values was first reported in *Chem. Eng. News*, **45**, 46 (March 27, 1967).

(14) D. M. Grant, *J. Am. Chem. Soc.*, **89**, 2228 (1967).

(15) See ref 9. While this extension in the previous calculation may yield different numerical results, the central concept of ref 9, that the effective nuclear charge of the carbon is altered by polar groups, is merely extended to include both the carbon and hydrogen atoms.

Weigert and Roberts[16] on some halogenated cyclopropanes in which they characterized for the first time the nature of hybridization in a three-member ring system. Although the paucity of $J_{^{13}C-^{13}C}$ data still prevents any final conclusions, all available evidence suggests that the major factor of $J_{^{13}C-^{13}C}$ is a hybridizational one and that measurable polarization effects are less significant than they are in the related $J_{^{13}C-H}$ couplings.

The values given in Table I were obtained on a Varian AFS-60 spectrometer utilizing proton decoupling and time-averaging techniques. The spectrometer was operated in the external lock mode, allowing proton decoupling power to be introduced to the sample through the internal lock circuitry. Operation in this configuration capitalizes on the advantages of the proton-decoupling technique[17] (*i.e.*, signal enhancement through multiplet collapse and a favorable nuclear Overhauser enhancement). This mode of operation, however, does suffer from certain magnetic field inhomogeneities which limit the accuracy of our measurements to a value approaching 1 cps. In the external lock mode, long-term magnetic field drifts between the reference and analytical samples along the *x*-axis limit our accuracy in defining the position of the carbon-13 satellite peaks. The signal width is also broadened by decay in the homogeneity of the field along the *y* axis as the Autoshim circuitry provided in the AFS-60 operates only in the internal lock mode. Even with these difficulties, ^{13}C–^{13}C splittings can be readily observed on the C-1024 TAD after several hundred sweeps. As an indication of the sensitivity of the method it is noted that only 0.04 and 0.03%, respectively, of the neopentane and *t*-butyl molecules have two adjacent ^{13}C isotopes due to the relatively low abundance (1.1%) of this carbon isotope.

Acknowledgment. This work was supported by the National Institutes of Health under grant GM-08521. A frequency synthesizer used to stabilize the proton decoupler was obtained with support from National Institutes of Health Biomedical Scientific Support Grant No. FR7092-01.

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[16] F. J. Weigert and J. D. Roberts, *J. Am. Chem. Soc.*, **89**, 5962 (1967). The authors wish to thank these workers for providing a prepublication manuscript of this very interesting work.

[17] E. G. Paul and D. M. Grant, *ibid.*, **86**, 2977 (1964).

William M. Litchman, David M. Grant
Department of Chemistry, University of Utah
Salt Lake City, Utah 84112

Received October 9, 1967

Ferrocene-Photosensitized *cis–trans* Isomerization of Piperylene

Sir:

A recent study by Dannenberg and Richards indicates that the photostationary state observed in ferrocene-sensitized piperylene isomerization and the product distribution for the ferrocene-sensitized dimerization of isoprene are the same as those reported for high-energy sensitizers.[1,2] They also report that ferrocene accelerates the photoisomerization of *trans*-piperylene by a factor of five. Most of these photoisomerization studies were conducted in benzene as solvent.[3] We have observed that ferrocene behaves as a low-energy photosensitizer in the *cis–trans* isomerization of piperylene in *trans*-1,2-dimethylcyclohexane solvent and that the rate of photoisomerization is low. The mechanism of photosensitization is consistent with that demonstrated in other photoisomerization studies involving triplet–triplet energy transfer from sensitizer to olefin.[4–7] Our preliminary studies in benzene as solvent yielded the same photostationary-state composition that was reported by Dannenberg and Richards.[1,2] This suggests that there is a marked solvent effect in the ferrocene-sensitized isomerization of piperylene.

All experiments were conducted using degassed solutions sealed in quartz cells. Two irradiation systems were employed. The first consisted of a Hanovia 450-w medium-pressure mercury lamp in a cylindrical reactor. The second was a PEK 200-w short-arc mercury lamp mounted on an optical bench with quartz lens and a mirror to provide a collimated beam. Most of the experiments were conducted in Phillips research grade *trans*-1,2-dimethylcyclohexane which was purified with activated silica gel to remove absorbing impurities. Benzene obtained commercially from James A. Hinton (99.99%) was used without further purification. Matheson Coleman and Bell ferrocene was sublimed before use, and Baker *cis*- and *trans*-piperylenes were purified by preparative vapor phase chromatography. All samples were degassed by the freeze–pump–thaw technique.

Our energy-transfer results with *trans*-1,2-dimethylcyclohexane agree with the intramolecular energy partitioning scheme which has been suggested for ferrocene.[8,9] No *cis–trans* conversion was observed upon excitation at 4400 Å using a 4000 Å cut-off filter (Corning C.S. 3-73). Photosensitization occurred, however, after excitation at 3240 Å and/or 2650 Å (Figure 1).[10] The rate of conversion in our ferrocene sample was slower than that in the "blank" (*i.e.*, similar piperylene solutions without ferrocene) for excitation in the 2650-Å region. In a typical experiment a solution containing 0.20 *M* ferrocene and 0.05 *M* *trans*-piperylene in *trans*-1,2-dimethylcyclohexane was irradiated along with the corresponding "blank" using a 0.05 *M* *trans*-piperylene solution as the filter. Table I summarizes conversion rates and light absorption characteristics of the two solutions in the 2500–2800-Å region. No light of wavelengths less than 2500 Å was transmitted by the filter solution.

The data in Table I show that the conversion rate in the ferrocene sample that can be attributed to direct

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[1] J. J. Dannenberg and J. H. Richards, *J. Am. Chem. Soc.*, **87**, 1626 (1965).

[2] J. J. Dannenberg, Ph.D. Thesis, California Institute of Technology, 1967.

[3] J. H. Richards, private communication.

[4] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

[5] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[6] W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

[7] R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966).

[8] D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).

[9] A careful reexamination of the anomalous emission from ferrocene has shown that most of the reported phosphorescence stems from solvent impurities. There still remains some evidence, however, of a weak emission around 5200 Å (R. S. Becker, private communication).

[10] A 3130-Å filter train was used for the 3240-Å excitation which consisted of a Corning C.S. 7-54 glass filter, a 1-mm-thick Corning C.S. 0-53 filter, and 2.0 cm cell of 0.0005 *M* K_2CrO_4.