suppressed to a limiting value. This probably results in part from the increased rate of reaction 5 with increasing gas concentration, but in addition the rate constant ratio $k_{12}/(k_{13} + k_{14})$ may be greater than $(k_6 + k_7)/k_8$; that is, the propyl radical may be more effective in propagating the chain decomposition of formaldehyde than is the hydrogen atom.

It is evident from the results described here that the photolysis of formaldehyde is a much more complex system than has been expected previously. Some of the details are clear from this work, but obviously further definitive experiments will be necessary to determine the extent of the process III in the creation of the carbon monoxide excess in the products.

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# The $^{13}$C–H Satellite Nuclear Magnetic Resonance Spectrum of Nonequivalent Protons in Acetal

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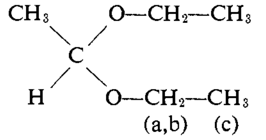
*Received December 22, 1966*

**Abstract:** The nuclear magnetic resonance spectrum of the ethoxy protons in acetaldehyde diethyl acetal (acetal) has been investigated. By using, in addition to the normal proton spectrum, the data provided by the $^{13}$C–H satellite spectrum, a unique set of spectral parameters has been obtained, eliminating the previously reported ambiguity in the solution of this problem. The $^{13}$C–H coupling parameters of the two methylene protons are different, providing a new criterion of nonequivalence in structures of low symmetry.

The proton magnetic resonance spectrum of acetaldehyde diethyl acetal, or simply acetal (I), exhibits a much more complex structure in the methylene region than is to be expected from a simple $A_2B_3$ spin system. Since there is no evidence of coupling through the oxygen atom, this complexity has been attributed to magnetic nonequivalence of the methylene protons.[1-3] Three analyses of the spectrum of acetal have been described, all of which treat the ethoxy group as an $ABC_3$ system, but leading to two markedly different sets of values of the proton–proton couplings. In the first approach Shafer, *et al.*,[1] and Waugh and Cotton[2] assumed $J_{gem}$ to be of the same sign as the vicinal couplings (taken to be positive). Two different values of the vicinal couplings were then required to match the observed spectrum. The coupling values reported in these studies were: $J_{gem} = 9.4$ cps, $J_{vic} = 7.35$, 6.68 cps;[1] and $J_{gem} = 9.2$ cps, $J_{vic} = 7.2$, 6.7 cps.[2] Subsequently, however, Kaplan and Roberts reexamined the problem and reported an acceptable fit using $J_{gem} = -9.30$ cps, in which case the vicinal couplings are identical, $J_{ac} = J_{bc} = +7.03$ cps.[3] Since both sets of values led to acceptable agreement with experiment, the outcome was described as indecisive, following the pattern of some other reported nonunique iterative analyses.[4]



I

In similar situations we have previously demonstrated that the requirement of simultaneously matching $^{13}$C–H satellite patterns and normal proton spectra can yield unique sets of parameters.[5] Several factors suggested the desirability of attempting to resolve the existing ambiguous situation in the case of acetal. Obviously, the occurrence of multiple solutions of the spectroscopic problem is, in general, a deterrent to efforts directed toward the interpretation of nmr parameters. There is, in addition, considerable intrinsic importance and interest in the origin and magnitude of the effects produced by nonequivalent environments such as those existing in acetal. Finally, successful analysis of the satellite patterns would provide still another and different kind of criterion of nonequivalence.

This communication describes the results obtained from such a simultaneous study of the proton and $^{13}$C–H satellite spectra of the ethoxy region of acetal. The proton–proton couplings so obtained are in close agreement with the results of the last analysis cited above ($J_{gem}$ and $J_{vic}$ of opposite sign), and the alternative solution was found to be unacceptable. A small (~1.4 cps) but real difference in the $^{13}$C–H couplings was observed for the two geminal protons. These results are discussed in relation to the other relevant nmr data and to the structural situation in acetal.

## Experimental Section

The acetal used was the commercially available material, purified by fractional distillation over a range of ~0.5°. All spectra were observed with a Varian Associates A-60-A spectrometer operating at 60 Mc/sec. Calibrations were performed by the side-band technique using a Hewlett–Packard Model 200J oscillator monitored with a Hewlett–Packard Model 5512A counter. All reported frequencies represent the average of at least four forward and four reverse sweeps. The neat liquid acetal was used throughout with

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[1] P. R. Shafer, D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, 47, 49 (1961).

[2] J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

[3] F. Kaplan and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961).

[4] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

[5] R. T. Hobgood, Jr., R. E. Mayo, and J. H. Goldstein, *ibid.*, **39**, 2501 (1963).

a small amount of TMS (or benzene in one case) added to serve as the internal reference. Some difficulty was experienced because of the presence of two impurity lines in the satellite region. Since these lines diminished appreciably in relative intensity with purification, they were omitted from further consideration. Only nine lines of the low-field methylene satellite pattern were observable, as the other fifteen were masked by the quartet of the single hydrogen on the central carbon atom.

The average deviations of the measured frequencies (per peak) were: proton patterns, 0.065 cps; satellite patterns, 0.08 cps.

## Results

The proton spectrum of I is essentially similar to that previously reported and will not be described here in detail. The satellite spectrum is given in Table I.

**Table I.** The $^{13}$C–H Satellite Spectrum of the Ethoxy Protons of Neat Acetal[a]

| | Calculated | | Calculated intensity | |
|---|---|---|---|---|
| Observed | Methyl | Methylene | | |
| Low-Field Methylene | | | | |
| −301.02 | | −300.92 | | |
| −293.72 | | −293.69 | | |
| −291.41 | | −291.50 | | |
| −287.18 | | −287.13 | | |
| −277.12 | | −277.14 | | |
| −270.33 | | −270.15 | | |
| −266.26 | | −266.26 | | |
| −263.56 | | −263.67 | | |
| −256.78 | | −256.85 | | |
| High-Field Methylene and Low-Field Methyl | | | | |
| −160.69 | | −160.61 | | 0.17 |
| −154.07 | | −154.00 | | 0.21 |
| −153.05 | | −153.07 | | 0.44 |
| −151.24 | | −151.26 | | 1.31 |
| −147.27 | | −147.29 | | 1.35 |
| . . . | | −146.80 | | 0.26 |
| −145.78 | | −145.79 | | 0.57 |
| −144.80 | | −144.79 | | 1.52 |
| −143.68 | | −143.68 | | 3.16 |
| −141.04 | | −141.08 | | 1.55 |
| −140.18 | | −140.21 | | 3.19 |
| −138.80 | | −138.83 | | 0.37 |
| −138.11 | | −137.95 | | 0.15 |
| −137.57 | −137.20 | −137.64 | 3.67 | 1.83 |
| −136.62 | −136.61 | | 7.14 | |
| −136.30 | −136.08 | −136.40 | 3.50 | 3.83 |
| −134.36 | | −134.37 | | 1.84 |
| −133.41 | | −133.44 | | 3.80 |
| −132.24 | | −131.87 | | 0.19 |
| −131.16 | | −130.82 | | 0.42 |
| −129.86 | −129.86 | | 11.86 | |
| −129.49 | −129.41 | −129.54 | 11.86 | 2.33 |
| −127.06 | | −127.06 | | 2.25 |
| −125.20 | | −125.21 | | 0.26 |
| −124.06 | | −124.05 | | 0.59 |
| −123.24 | −123.26 | | 2.55 | |
| −122.62 | −122.65 | | 5.00 | |
| −121.97 | −121.91 | | 2.44 | |
| −117.55 | | −117.78 | | 0.42 |
| High-Field Methyl | | | | |
| . . . | −11.23 | | | |
| −10.96 | −10.98 | | | |
| . . . | −10.77 | | | |
| −3.96 | −4.05<br>−3.87 | | | |
| . . . | +2.83 | | | |
| +3.05 | +3.06 | | | |
| . . . | +3.33 | | | |

[a] All frequencies are in cps at 60 Mc/sec, relative to TMS.

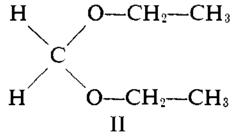
Each proton gives rise to two patterns displaced by $\pm 0.5J_{^{13}\text{C-H}}$ from its proton resonance position (except for a negligible isotopic effect on the proton shift). The upper pattern of the methyl group and the lower methylene pattern are well isolated, but the two remaining patterns overlap very badly, as indicated in Table I. This complicated the assignments, and it was necessary in the analysis of the spectrum to proceed on a trial-and-error basis in this region until a consistent set of assignments was obtained for all the spectral lines in Table I.

The final predicted frequencies and intensities are listed in the appropriate columns of Table I. Excluding overlapping lines, the predicted and observed frequencies agree to within ~0.05 cps. (The corresponding agreement for the proton pattern is ~0.02 cps.)

The above results were obtained using the final values for the nmr parameters shown in Table II. (The uncertainties shown in this table are those derived from the least-squares procedure used.) On the other hand, the couplings first reported by Shafer, *et al.*, clearly failed to reproduce the satellite spectra, and no reasonable variation of these values were found to improve the results. The isotope effect for the methylene proton shifts (not listed) were ~0.05 cps and were not considered to be significant; that for the methyl group is also quite small, but probably outside experimental error.

## Discussion

The results described above establish that, to a very high degree of probability, the parameters of Table II constitute a unique set of values for the ethoxy group of acetal. Accordingly, the ambiguity in the solution referred to by Kaplan and Roberts can be considered as essentially resolved. The proton–proton couplings determined here do not vary significantly from those reported by Kaplan and Roberts, the differences being ~0.13 and ~0.01 cps for $J_{gem}$ and $J_{vic}$, respectively. The difference in shifts for the methylene protons also agrees nicely in the two studies, 9.23 cps as against the value of 9.02 cps obtained here.



II

Waugh and Cotton were the first to correctly identify the origins of the nonequivalence of the methylene protons in structures such as acetal.[2] They pointed out that, although nonequivalence could arise from rotational isomers of different stability, it would still persist in the case of free internal rotation because of the low degree of symmetry of the acetal molecule. These workers also commented that the pmr spectrum of ethylal (II) exhibited an uncomplicated pattern indicative of equivalent methylene protons. We have confirmed this observation by examining the $^{13}$C–H satellite patterns of II, which turns out to correspond qualitatively to an $A_2B_3$ ethoxy system. Frankiss has also reported values of 140.5 ± 1.0 and 126.0 ± 0.3 cps for the two $^{13}$C–H couplings of the ethoxy system in ethylal.[6] These results were quite similar to those obtained here for acetal. More recently, Elvidge and Foster, in their nmr studies of various acetals, have restated the conclusions of Waugh and Cotton regard-

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(6) S. G. Frankiss, *J. Phys. Chem.*, **67**, 752 (1963).

**Table II.** Nmr Parameters for the Ethoxy Protons in Neat Acetal[a]

| | Methylene | | Methyl |
|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ |
| $\nu$ | $-212.88 \pm 0.03$ | $-203.855 \pm 0.03$ | $-67.165 \pm 0.03$ |
| $J_{^{13}\text{C-H}}$ | $141.01 \pm 0.06$ | $139.64 \pm 0.08$ | $125.86 \pm 0.07$ |
| $J_{vic}$ | $+7.043 \pm 0.018$ | | |
| $J_{gem}$ | $-9.427 \pm 0.034$ | | |
| Isotope shift | | | $+0.155$ |

[a] All values are in cps. The shifts are relative to internal TMS, at 60 Mc/sec.

ing the source of nonequivalence.[7] The present evidence does not permit an assignment of the relative importance of inherent asymmetry and restricted rotation, and it is likely that detailed temperature studies will be required to clarify the problem. (Shafer, *et al.*, reported the proton pattern of acetal is not significantly changed at temperatures as low as −80°.)

Whatever the origin of the environmental nonequivalence may be, any interpretation of the chemical shift difference, $\nu_b - \nu_a$, is complicated by the difficulty of separating magnetic and inductive contributions. Conceivably, a significant fraction of the 9 cps difference could be attributed, for example, to neighboring-group anisotropy effects. Hence, it is problematical whether, on the basis of the shift data, a significant difference in the character of the two methylene C–H bonds can be inferred.

The $^{13}$C–H coupling values, again, reflect very decisively the nonequivalence of the two methylene protons. The difference of ~1.3 cps, while small, is nevertheless approximately 10% of the total substituent effect produced by an oxygen atom.[8] (It is worthwhile to point out this difference could not possibly be determined by the simple procedure of calibrating the centers of the satellite patterns, if for no other reason, because of the overlapping of the two systems of peaks.) The occurrence of two distinct $^{13}$C–H couplings in the methylene group means that the nonequivalence can actually be localized in the two corresponding C–H bonds. By contrast in the case of the shifts, it is possible, as pointed out above, that part or all of the difference resides in the environment and is of largely magnetic origin.

It has been established that $^{13}$C–H couplings are, in at least some cases, affected by the medium.[9,10] However, such affects do not appear to be of magnetic origin, but rather to arise from factors, either specific or general, which influence the charge distribution in the C–H bonds. For chloroform[9] and for several dihaloethylenes and halomethanes[10] it has been found that increasing $J_{^{13}\text{C-H}}$ was associated with the displacement of the shifts to the lower field. In the latter compounds, in fact, a plot of $J$ *vs.* $\nu$ (as concentration is varied) turns out to be quite linear. Any interaction which displaces charge from the proton to its bonded C atom would be expected to produce at least the observed trend, and it can be tentatively assumed that in acetal also the methylene C–H bonds have been polarized in this manner. (It is observed that in acetal the larger $J_{^{13}\text{C-H}}$ is associated with the lower shift value.) However, the factors responsible for this polarization cannot be reliably assigned on the basis of the presently available evidence.

To the extent that these arguments are valid and applicable here, it seems likely that the $^{13}$C–H coupling parameter provides a new criterion of nonequivalence, which has the advantage of not being significantly affected by the magnetic contributions which complicate the interpretation of chemical shifts. Further, use of this criterion in similar stereochemical situations appears to be warranted.

**Acknowledgments.** This research was supported by grants from the National Institutes of Health and the Corn Industries Research Foundation. One of us (L. S. R.) is the recipient of a National Science Foundation Predoctoral Traineeship. We wish to acknowledge several helpful discussions with Dr. D. J. Goldsmith.

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[7] J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 981 (1964).

[8] N. Muller and P. I. Rose, *J. Am. Chem. Soc.*, **84**, 3973 (1962).

[9] D. F. Evans, *J. Chem. Soc.*, 5575 (1963).

[10] V. S. Watts, J. E. Loemker, and J. H. Goldstein, *J. Mol. Spectry.*, **17**, 348 (1965); V. S. Watts and J. H. Goldstein, *J. Phys. Chem.*, **70**, 3887 (1966).