

¹¹ Sargent, J. A., and F. Skoog, "Effects of indoleacetic acid and kinetin on scopoletin-scopolin levels in relation to growth of tobacco tissue *in vitro*," *Plant Physiol.* (in press, 1960).

¹² Goodwin, R. H., and C. Taves, "The effect of coumarin derivatives on the growth of *Avena* roots," *Amer. J. Bot.*, **37**, 224-231 (1950).

¹³ Avers, C., and R. H. Goodwin, "Studies on roots, IV. Effect of coumarin and scopoletin on the standard root pattern of *Phleum pratense*," *Am. J. Bot.*, **43**, 612-620 (1956).

¹⁴ Fults, J. H., and G. A. Johnson, "A cumulative fluorescent chemical found in certain plants treated with 2,4-D identified as scopoletin (6-methoxy-7-hydroxycoumarin)," *Proc. Western Weed Control Conference, Denver, 1950*, p. 108.

¹⁵ Best, R. J., "Studies on a fluorescent substance present in plants, III. The distributions of scopoletin in tobacco plants and some hypotheses on its part in metabolism," *Aust. J. Exp. Biol. Med.*, **26**, 223-230 (1948).

¹⁶ Wells, P. V., "A study of free nucleotides and other compounds absorbing ultraviolet light in the acid-soluble fracture of plant tissues," M.S. Thesis, University of Wisconsin, 1955.

¹⁷ Tryon, K., "Scopoletin in differentiating and non-differentiating cultured tobacco tissue," *Science*, **123**, 590 (1956).

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: ABNORMAL SPLITTING OF ETHYL GROUPS DUE TO MOLECULAR ASYMMETRY*†

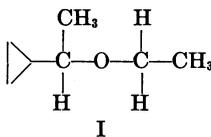
BY PAUL R. SHAFER, DONALD R. DAVIS, MARTIN VOGEL, K. NAGARAJAN, AND JOHN D. ROBERTS

GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY

Communicated November 10, 1960

Nuclear magnetic resonance (n. m. r.) spectroscopy provides an excellent means for qualitative identification of ethyl groups by use of the familiar three-four pattern of spin-spin splitting.¹ It has been observed previously² that the methylene protons of systems of the type R—CH₂—CR₁R₂R₃ (where R₁ can be the same as R or different) may be magnetically nonequivalent and display AB rather than A₂-type spectra.³ We now wish to report several examples of this type of behavior with ethyl groups, particularly ethoxy groups, knowledge of which could be important to anyone using n. m. r. for organic qualitative analysis.

A typical example is cyclopropylmethylcarbonyl ethyl ether (I). The spectrum of the ethyl CH₂ group of I is nearly identical to that of the CH₂ groups acetaldehyde diethyl acetal (II) shown in Figure 1 and appears not as a simple quartet



but as the very complicated AB part of an ABX₃-type spectrum with $\nu_A - \nu_B = 9.0$ cps and $J_{AB} = 9.4$ cps. The nonequivalence of the CH₂ hydrogens is due to the asymmetric center at the carbonyl group of the cyclopropylmethylcarbonyl moiety, which acts to favor one of the possible rotational conformations about the C—O bonds over the others.² Similar behavior has been noted with acetaldehyde

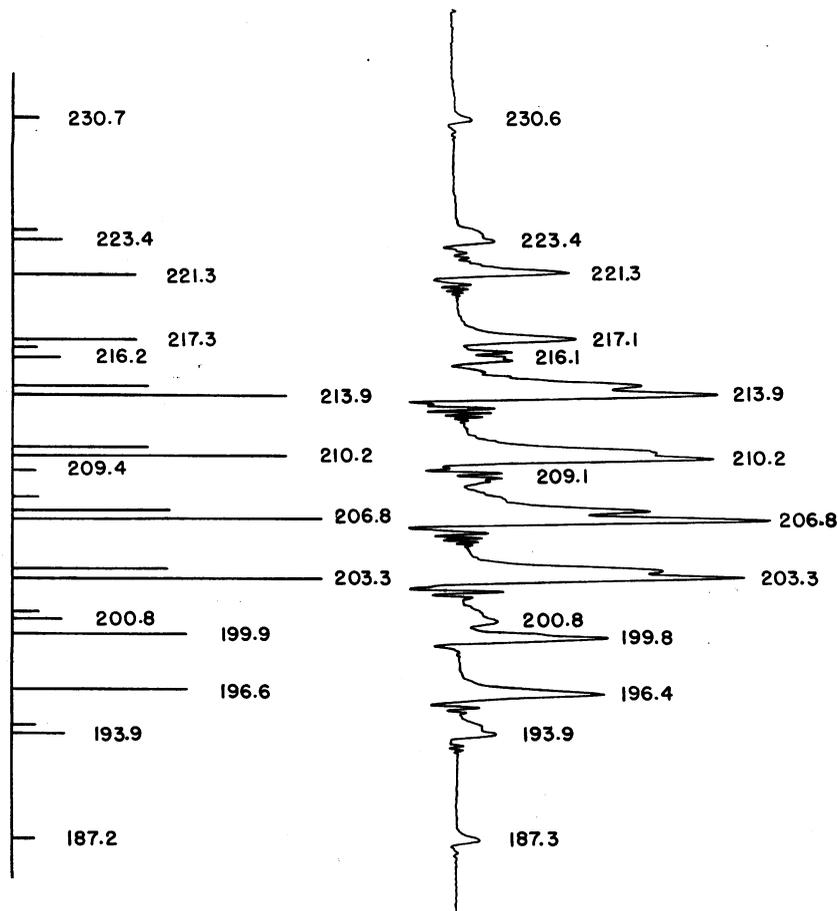
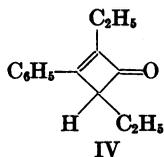


FIG. 1.—Observed and calculated nuclear magnetic resonance spectra of acetaldehyde diethyl acetal at 60 Mc with tetramethylsilane as internal reference. The calculated spectrum was based on an ABC_2 model with $\nu_A = 0.0$ cps, $\nu_B = 9.0$ cps, $\nu_C = 146.3$ cps, $J_{AB} = 9.4$ cps, $J_{AC} = 7.35$ cps, and $J_{BC} = 6.68$ cps.

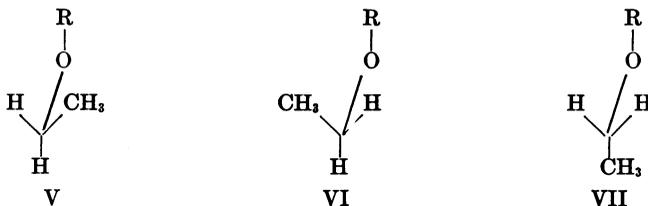
diethyl acetal (II) and acetophenone diethyl ketal (III) and with ethyl-substituted cyclobutenones such as IV:



With IV, the effect is observed with the CH_2 of the ethyl located directly at the asymmetric 4 position and is further complicated of course by spin-spin interaction involving the 4 hydrogen.

The spectra of I, II, and III show a very interesting effect in that the methylene hydrogens of their ethyl groups are not equally coupled to the methyl hydrogens. Assignment of the respective couplings to be 7.35 cps and 6.68 cps for I and II

gives excellent agreement between calculated and observed line positions and intensities (see Fig. 1). Since the splittings result from electron coupling of nuclear spins, this speaks for induction of asymmetry in the bonding of the methylene protons to their carbon. Such would be expected to be the case if the effect of R were to make either V or VI a more favorable conformation about the C—O bond



than VII. Predominance of either V or VI would fit well of course with the considerable chemical shift difference between the methylene hydrogens. One of these conformations must be quite favored, since no significant change in the spectrum of II was noted at temperatures as low as -80° .

It seems possible that the asymmetry of the ethyl groups recently noted by Finegold⁴ in the n. m. r. spectrum of diethyl sulfite is derived from the same causes as discussed above. We have noted that admixture of carbon tetrachloride with III results in changes of the methylene resonances in a manner analogous to that observed by Finegold for diethyl sulfite. Some other observations bearing on the relation of the present research to Finegold's results will be published later.

We are much indebted to Dr. Stanley L. Manatt and the Computing Center of the Jet Propulsion Laboratory for IBM 704 calculations of comparison spectra to check the chemical shift and spin-coupling parameters.

* Contribution No. 2640.

† Supported in part by the Office of Naval Research.

¹ Roberts, J. D., *Nuclear Magnetic Resonance Spectroscopy* (New York: McGraw-Hill Book Co., 1959), chap. III.

² Nair, P. M., and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957).

³ Pople, J. A., W. G. Schneider, and H. Bernstein, *High-resolution Nuclear Magnetic Resonance* (New York: McGraw-Hill Book Co., 1959), pp. 98, 119-123.

⁴ Finegold, H., *Proc. Chem. Soc.*, 283 (1960).