

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY:  
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MOLECULAR ASYMMETRY, III

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GEORGE M. WHITESIDES, FRED KAPLAN, K. NAGARAJAN, AND  
JOHN D. ROBERTS

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology*

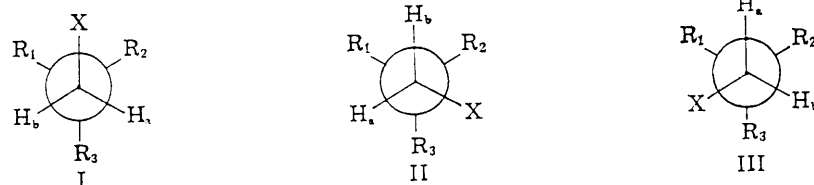
NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: ABNORMAL  
 SPLITTING OF ETHYL GROUPS DUE TO MOLECULAR  
 ASYMMETRY, III\*

BY GEORGE M. WHITESIDES, FRED KAPLAN, K. NAGARAJAN, AND JOHN D.  
 ROBERTS

GATES AND CRELLIN LABORATORIES OF CHEMISTRY, † CALIFORNIA INSTITUTE OF TECHNOLOGY

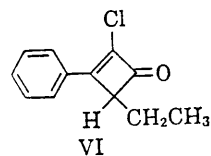
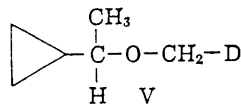
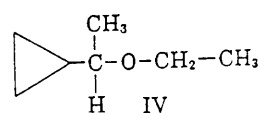
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The protons of a methylene group removed by one or more bonds from a center of molecular asymmetry may be magnetically nonequivalent and display AB-type nuclear magnetic resonance (n.m.r.) spectra.<sup>1-4</sup> It has been suggested that the chemical shift between the two methylene protons arises from unequal populations of the possible rotational conformations.<sup>2</sup> However, even assuming equal populations and rapid interconversion of the three conformers I, II, and III, H<sub>a</sub> and H<sub>b</sub> are always distinct and identifiable, since no two conformers are identical except



for interchange of H<sub>a</sub> and H<sub>b</sub>.<sup>5, 6</sup> This "intrinsic asymmetry" of the methylene group might also be the cause of the observed magnetic nonequivalence of the methylene protons.

The n.m.r. spectrum of the —O—CH<sub>2</sub>— protons of cyclopropylmethylcarbonyl ethyl ether IV (Fig. 1) is of the AB type (split by the methyl protons) and results from proximity of a center of molecular asymmetry to the methylene protons. To investigate the possibility that the difference in chemical shift between these methyl-



ene protons arises from an intrinsic asymmetry depending *only* on the symmetry characteristics of the molecule, we have examined the n.m.r. spectrum of cyclopropylmethylcarbonyl methyl-d<sub>1</sub> ether (V).<sup>7</sup> Substitution of a deuteromethyl group for the ethyl group of IV would be expected to eliminate any conformational

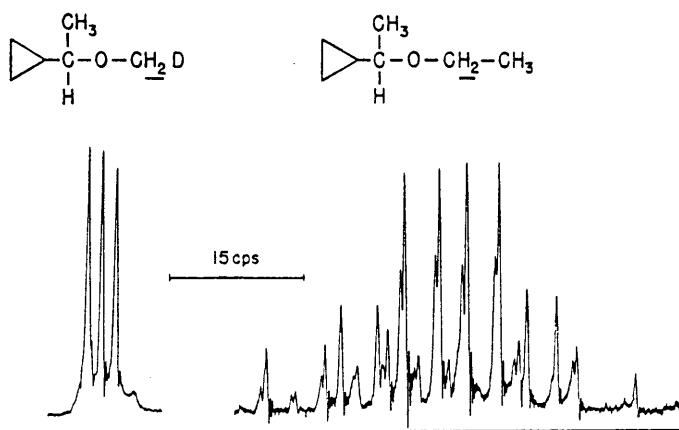


FIG. 1.—Nuclear magnetic resonance spectra of the methylene protons of cyclopropylmethylcarbonyl methyl-d<sub>1</sub> ether and cyclopropylmethylcarbonyl ethyl ether at 60 Mc/sec.

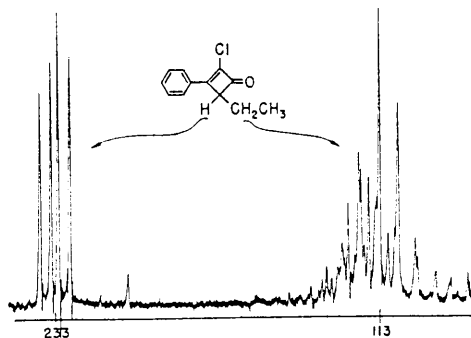


FIG. 2.—Methine and methylene proton resonances of 2-chloro-4-ethyl-3-phenylcyclobut-2-enone in carbon tetrachloride at 60 Mc/sec with tetramethylsilane (0 cps) as external standard. The values of coupling constants to the methine proton at the 4-position are  $|J_{AX}| = 6.9$  cps and  $|J_{BX}| = 4.3$  cps.

preference of the methylene protons with respect to the asymmetric center; hence, observation of an AB-type methylene spectrum for V would be evidence for an observable chemical shift arising from intrinsic asymmetry in the molecule.

After account is taken of coupling between the protons and deuterium, which has a nuclear spin of 1, the methylene resonance of V is clearly A<sub>2</sub> (Fig. 1). The magnetic equivalence of these methylene protons of V appears to us as strongly sug-

gestive that conformational preference is the factor responsible for the magnetic nonequivalence of the methylene protons of IV.

Further support for this conclusion is provided by the n.m.r. spectrum of the substituted cyclobutenone VI (Fig. 2). The resonance centered on 113 cps is of the methylene protons of the ethyl group of this compound and is the rather complicated AB part of an ABC<sub>3</sub>X system. The resonance of the methine proton at the 4-position of the cyclobutene ring is centered on 233 cps and is split into two equally intense doublets, rather than a 1:2:1 triplet. This splitting is most simply explained as the result of unequal coupling between the methine proton and the two adjacent methylene protons, arising from a preference for a conformation for the molecule in which the methine proton is *trans* to one methylene proton and *gauche* to the other.

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<sup>1</sup> Pople, J. A., W. G. Schneider, and H. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (New York: McGraw-Hill Book Co., 1959), pp. 88, 119-123.

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

<sup>3</sup> Shafer, P. R., D. R. Davis, M. Vogel, K. Nagarajan, and J. D. Roberts, these PROCEEDINGS, **47**, 49 (1961).

<sup>4</sup> Kaplan, F., and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 4666 (1961).

<sup>5</sup> Pople, J. A., *Mol. Phys.*, **1**, 1 (1958).

<sup>6</sup> Waugh, J. S., and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961).

<sup>7</sup> Prepared by reaction of methyl bromide-*d*<sub>1</sub> with sodium 1-cyclopropylethoxide.