Nuclear Magnetic Resonance Spectroscopy. Analysis of the Proton Spectrum of Cyclobutene[1]
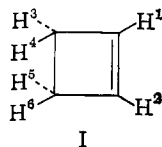
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Contribution No. 3156 from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California. Received September 17, 1964

A complete analysis of the proton n.m.r. spectrum of cyclobutene (I) has been made which shows that the couplings between the allylic and vinylic protons, while small, are by no means negligible; $J_{13} = -0.80$ c.p.s. and $J_{15} = +1.55$ c.p.s. The analysis which involved ^{13}C satellite spectra of ordinary and specifically deuterated cyclobutene gave spin coupling and chemical shift parameters which predict that cyclobutene should show just two quite sharp peaks in its high-resolution n.m.r. spectrum in agreement with experiment.

The proton magnetic spectra of cyclobutene and of its derivatives[2-4] are exceptionally interesting in that no spin–spin splitting is observed between the vinylic and allylic hydrogens. Thus, the spectrum of cyclobutene (Figure 1) consists of two quite sharp singlet resonance peaks. The lack of splitting has led to the assertion that the coupling between the allylic and vinylic protons is in fact equal to zero.[5] In any case, it is clear that the Karplus[6] equation which correlates coupling constants and dihedral angles is not applicable to small, strained-ring systems,[3,5,7-12] the values calculated being rather too large.

To account for the lack of observable splitting with cyclobutene, Wiberg and Nist[3] have suggested that $(J_{13} + J_{15})$ (for numbering convention see I) is likely to be a good approximation for the apparent coupling constant. If J_{13} and J_{15} are small and, as usual, of

I

opposite signs, then the splitting might well be unobservable. Magnitudes of J_{13} (1.5 c.p.s.) and of J_{15} (−1.5 c.p.s.) may be estimated by extrapolation from data for other cycloolefins.[11]

Although a featureless spectrum such as that of

cyclobutene might seem to offer a barren field of investigation, the actual values of coupling constants of cyclobutene are of considerable theoretical interest and, therefore, we have undertaken a complete analysis with the aid of the ^{13}C satellite spectra using ^{13}C of natural abundance.[13] The latter were recorded through time integration for liquid cyclobutene with a Varian A-60 n.m.r. spectrometer adapted for use of a Mnemotron Computer of Average Transients (CAT). The resulting spectra of allylic and vinylic protons are shown in Figures 2 and 3. Direct analysis of these patterns proved to be difficult and deuterium substitution was resorted to for the purpose of reducing the magnitudes of some of the couplings.[14] Cyclobutene-1,2-d_2 (II) was prepared by the following route.

II
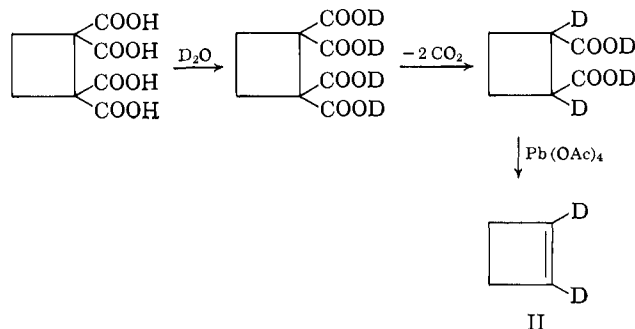
The n.m.r. spectrum of ^{13}C–H satellites of II could be analyzed rather accurately as an approximation to the AA'XX' type. The observed and the computed spectra are shown in Figure 4. The values for J_{34}, J_{35}, and J_{36} thus obtained (Table I) were then used in the analysis of the undeuterated materials. The separations between the two main peaks in the vinylic part of the spectrum (Figure 3) depends only upon the magnitude of J_{12} and could thus be measured directly.[12] The magnitudes of the remaining coupling constants, J_{13} and J_{15}, were found by a trial-and-error method using the Bothner-By–Wiberg–Nist program[15] adapted to an IBM 7090 computer equipped with a XY plotter. The evaluation was complicated by the considerable sensitivity of the computed spectra to small changes in J_{13} and J_{15}. The best fit was obtained with values given in Table I. The computed spectra obtained with these parameters are compared with those observed in Figures 2 and 3.

The calculated spectra are insensitive to changes in sign or magnitude of the *gem* coupling constant over a

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) J. D. Roberts, "Nuclear Magnetic Resonance, Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp. 54, 103.

(3) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

(4) W. G. Dauben and R. L. Cargill, *Tetrahedron*, **12**, 186 (1961).

(5) L. M. Jackmann, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, pp. 85, 86.

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

(7) S. Alexander, *ibid.*, **28**, 358 (1958).

(8) H. S. Gutowsky, M. Karplus, and D. M. Grant, *ibid.*, **31**, 1278 (1959).

(9) A. A. Bothner-By, C. Naar-Colin, and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(10) O. L. Chapman, *ibid.*, **85**, 2014 (1963).

(11) G. V. Smith and H. Kriloff, *ibid.*, **85**, 2016 (1963).

(12) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

(13) A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

(14) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectroscopy," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 9.

(15) K. B. Wiberg and B. J. Nist, "Interpretation of NMR Spectra," W. A. Benjamin, Inc., 1962.
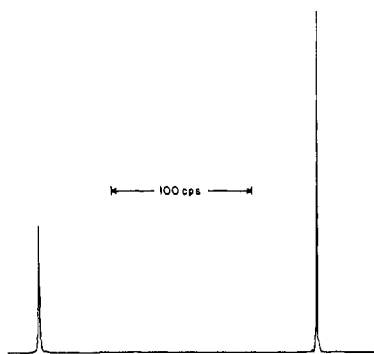
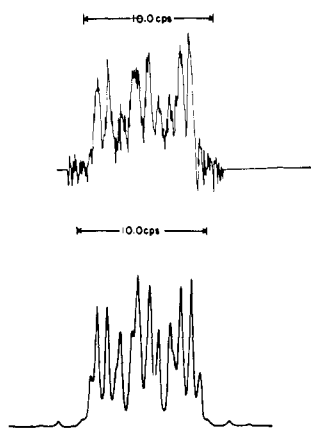Figure 1. N.m.r. spectrum of cyclobutene at 60 Mc.p.s.

Figure 2. Proton n.m.r. spectrum of ^{13}C satellites of cyclobutene of methylene hydrogens. Observed spectrum, above; computed spectrum, below.

wide range and therefore the value in Table I for J_{34} is arbitrary and was actually assigned to accord reasonably with values obtained in an earlier investigation.[16]

Table I. N.m.r. Parameters of Cyclobutene, C.p.s.

1,2-Protons[a] δ = 5.95 p.p.m.; $J^{13}C_{-H}$ = 170	
3,4,5,6-Protons[a] δ = 2.57 p.p.m.; $J^{13}C_{-H}$ = 140	
J_{12} = (− ?)2.70[b]	J_{34} = −12.00
J_{13} = −0.80	J_{35} = +1.65
J_{15} = +1.55	J_{36} = +4.35

[a] For numbering convention see I. [b] See text for discussion of the problem of the sign of this coupling constant.

The fit in the methylene part of the spectrum is excellent, in the vinylic part only good which may actually reflect no more than the difficulty of obtaining good spectra by the experimental procedure used. Reversing the sign of J_{12} leaves the methylene part of the spectrum unchanged while slightly improving the fit in the vinylic part as shown in Figure 3. The calculated n.m.r. spectrum of cyclobutene which corresponds to the parameters given in Table I (Figure 1) is identical with the experimental spectrum.

Although the evidence is not conclusive, the vinylic coupling constant J_{12} may have a negative value. This may not actually be unreasonable because there is a strong decreasing trend of (cis) vinylic coupling constants with ring size 11.8 c.p.s. for cyclooctatetraene,

(16) K. L. Servis and J. D. Roberts, *J. Phys. Chem.*, **67**, 2885 (1963).
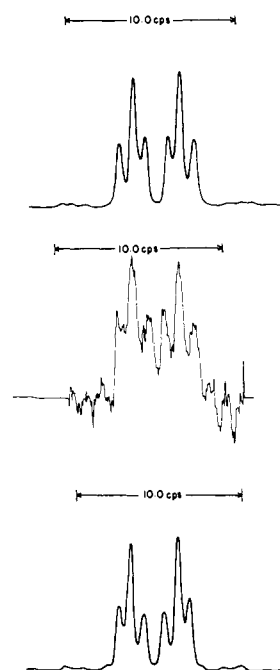

Figure 3. Proton n.m.r. spectrum of cyclobutene showing ^{13}C satellites of vinyl hydrogens. Observed spectrum, middle, and computed spectra with J_{12} = +2.70 c.p.s. (above) and J_{12} = −2.70 c.p.s. (below).
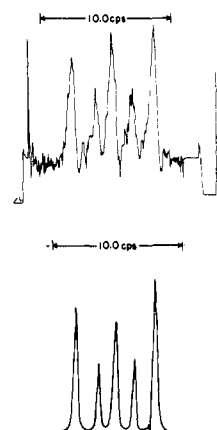

Figure 4. Proton n.m.r. spectrum of cyclobutene-1,2-d_2 showing ^{13}C satellites of methylene protons. Observed spectrum, above; computed spectrum, below.

9.6 c.p.s. for cyclohexene,[17] and 5.4 c.p.s. for cyclopentene.[12] This trend has been attributed to the increasing ring strain and, more importantly, to the changing geometry around the double bond, i.e., to the increasing distance between the olefinic protons.[10-12] It is, of course, quite possible that a further, sharp, decrease occurs on going to cyclobutene so that the value of J_{12} passes zero and becomes negative. Cyclopropene is particularly interesting in this connection. It was recently reported[13] that J_{12} in 3,3-dimethylcyclopropene fell between 0.5 and 1.5 c.p.s. The sign was not determined but is of obvious interest.

Experimental

Cyclobutane-1,1,2,2-tetracarboxylic Acid. Tetraethyl cyclobutane-1,1,2,2-tetracarboxylate[18] (50.0 g.)

(17) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).
(18) W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 572 (1894).

was refluxed for 5 hr. with potassium hydroxide (40.0 g.) in water (180 ml.). The solution was then diluted to 500 ml. and passed through a column of Amberlite IR-120 ion-exchange resin (500 ml.). The acid was eluted with 500 ml. of water and the combined eluates were evaporated to dryness under reduced pressure. The residue was dried at 60° under reduced pressure; the yield of the acid was 31 g. (92%).

Cyclobutane-1,1,2,2-tetracarboxylic Acid-d_4. The undeuterated acid (30 g.) was dissolved in deuterium oxide (25 ml., 99.7% D) and the solution was evaporated to dryness under reduced pressure. The residue was dried under reduced pressure at 60°. This procedure was repeated four times.

Cyclobutane-1,2-d_2-1,2-dicarboxylic Acid-d_2. The deuterated tetracarboxylic acid was heated to 200° until the evolution of carbon dioxide ceased. The residue was recrystallized from benzene–ligroin yielding 10 g.

(53%) of a mixture of cis- and trans-cyclobutane-1,2-d_2-dicarboxylic acid-d_2.

Cyclobutene-1,2-d_2. The mixture of cis- and trans-cyclobutane-1,2-d_2-dicarboxylic acid-d_2 (7.2 g., 0.05 mole) was dissolved in anhydrous benzene (150 ml.) and pyridine (6 ml., 0.075 mole). Lead tetraacetate (23.3 g., 0.0525 mole) was then added and the mixture was stirred and heated slowly while dry nitrogen was passed consecutively through the reaction mixture, a 25% solution of potassium hydroxide, a drying tower, and a trap held at −75°. Heating was interrupted when a vigorous reaction occurred and resumed when the reaction subsided. Finally, the solution was refluxed for 2 hr. The product was collected in the trap and transferred into an n.m.r. tube. The n.m.r. spectrum revealed an essentially complete deuteration of the vinylic position and traces of benzene as the only impurity.

Nuclear Magnetic Resonance Spectroscopy. The Effect of Solvent on Magnetic Nonequivalence Arising from Molecular Asymmetry[1a]

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The chemical shift between the geminal methylene protons of 1-phenylethyl benzyl ether has been measured in a variety of solvents. An approximate correlation observed between solvent dielectric constant and the degree of the magnetic nonequivalence of the methylene protons, $\nu_A - \nu_B$, is discussed in light of similar results for structurally related compounds. It is suggested that the variation in $\nu_A - \nu_B$ with solvent may reflect changes in the conformation of the benzylic phenyl ring with respect to the methylene group.

Introduction

In a previous paper,[2] correlations have been developed between the degree of the magnetic nonequivalence of the protons of a methylene group close to an asymmetric center[3] and the structure of the molecule close to the methylene group, using 1-phenylethyl benzyl ether and related compounds as model compounds. The available evidence led to the conclusion that although a number of different structural features probably contributed to some extent to the chemical shift differences in these compounds, the most important single factor in determining the magnitude of the chemical shift between the geminal methylene protons was the conformation of the methylene group with respect to the directly bonded phenyl ring.[2]

The present paper presents data pertinent to an understanding of the marked solvent dependence observed for the methylene proton chemical shift difference in these ethers, and provides further support for the hypothesis that the major contribution to $\nu_A - \nu_B$ originates in the magnetic anistropy of the phenyl ring.

Results

The chemical shift difference between the geminal methylene protons of 1-phenylethyl benzyl ether is quite solvent sensitive (Table I). In benzene, cyclohexane, carbon tetrachloride, and similar solvents, the chemical shift is approximately 10–11 c.p.s.; in dimethyl sulfoxide, acetone, and nitromethane it drops to approximately 2 c.p.s. The magnitude of the

(1) (a) Supported in part by the Office of Naval Research and the undergraduate research participation program of the National Science Foundation; (b) N.A.T.O. Fellow, 1963.
(2) G. M. Whitesides, D. Holtz, and J. D. Roberts, J. Am. Chem. Soc., 86, 2628 (1964).
(3) The term "asymmetric center" used in this paper refers to the single carbon atom in each of the compounds examined which bears four different substituents. A similar magnetic nonequivalence of stereochemically distinct geminal methylene protons has of course also been observed in both axially dissymmetric compounds [cf. W. L. Meyer and R. B. Meyer, ibid., 85, 2170 (1963)], and in a variety of bridged biphenyls[4] which formally do not contain an asymmetric center.
(4) A similar suggestion has been advanced by Mislow and co-workers to account for the solvent dependence of the n.m.r. spectra of certain bridged biphenyls: K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. Wahl, Jr., ibid., 86, 1710 (1964). For another recent

examination of magnetic nonequivalence in benzylic methylene groups, see J. C. Randall, J. J. McLeskey, III, P. Smith, and M. E. Hobbs, ibid., 86, 3229 (1964).