

butenes (2.5–3.7 c.p.s.) through cyclopentenes (5.4–7.0 c.p.s.) to cyclohexenes (9–11 c.p.s.) and then appears to level out, cycloheptenes (9–12.5 c.p.s.) and cyclooctenes (11–13 c.p.s.). Extrapolation of the value of the vinyl proton coupling constants for four-, five- and six-membered carbon rings to three-membered rings suggests that cyclopropenes should show very low, almost zero, vinyl proton coupling constants. This expectation has been confirmed recently for 3,3-dimethylcyclopropene by Laszlo and Schleyer.¹²

It has been pointed out recently that coupling constants are affected by the nature of substituents in the immediate vicinity.¹³ The close agreement in vinyl coupling constant in compounds of the same ring size with varying substituents rules out electronegativity effects as the origin of the observed effect.

The observation that the magnitude of the vinyl proton coupling constant is dependent on ring size should find important use in the determination of structure, although the origin of the effect is far from clear. The changing geometry and strain in the smaller rings, particularly as they are reflected in altered orbital hybridization of the trigonal carbon atoms, must contribute to the ring size effect.

Acknowledgment.—The author wishes to thank Professor E. Wenkert, Professor C. H. DePuy and Dr. R. W. King for nuclear magnetic resonance spectra and stimulating discussion. This investigation was supported in part by a research grant from the Alfred P. Sloan Foundation.

(12) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 2017 (1963).

(13) K. L. Williamson, *ibid.*, **85**, 516 (1963).

(14) Alfred P. Sloan Foundation Fellow.

DEPARTMENT OF CHEMISTRY
IOWA STATE UNIVERSITY OF
SCIENCE AND TECHNOLOGY
AMES, IOWA

O. L. CHAPMAN¹⁴

RECEIVED APRIL 10, 1963

N.m.r. Coupling Constants and Conformations of Cycloolefins

Sir:

Correlation of n.m.r. coupling constants (J) with dihedral angles (ϕ) is a major step in conformational and configurational analysis. The familiar Karplus equations¹ are applicable to saturated hydrocarbons, and progress has been made on a similar correlation for olefins.^{2–5} However, certain J 's have been shown to vary with the electronegativities of substituents near one of the coupled protons⁶ and one wonders if other factors are also important. We have solved the olefinic proton splitting pattern of unsubstituted cycloolefins and offer fresh evidence; evidence which not only clearly reveals another factor—variation of J_{56} (I) with ring size—but also discloses new data for possible correlations of J_{15} and J_{16} with dihedral angles.

With the aid of an IBM 7090 computer⁷ we interpreted the olefinic proton splitting pattern, as shown in Fig. 1 for *cis*-cyclooctene. Rings with 7, 8 and 10 carbons show nearly the same pattern. Those from cyclopentene and cyclohexene are compressed and not so revealing; *e.g.*, their calculated spectra did not agree

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

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

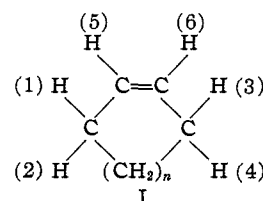
(3) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243 (1962).

(4) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).

(5) A. A. Bothner-By and C. Naar-Colin, *ibid.*, **83**, 231 (1961).

(6) (a) K. L. Williamson, *ibid.*, **85**, 516 (1963); (b) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962); (c) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 303 (1956).

(7) See ref. 2 and 5 for descriptions of the program.



perfectly with the experimental spectra and it seems clear that some lines are shifted by nearby lines.⁸ The spectra of cyclopentene-1-*d* and cyclohexene-1-*d* should unambiguously reveal J_{15} and J_{16} for these. Giving the computer some $\pm J_{13}$'s and $\pm J_{14}$'s slightly smaller than corresponding J_{16} 's⁹ resulted in 53-line

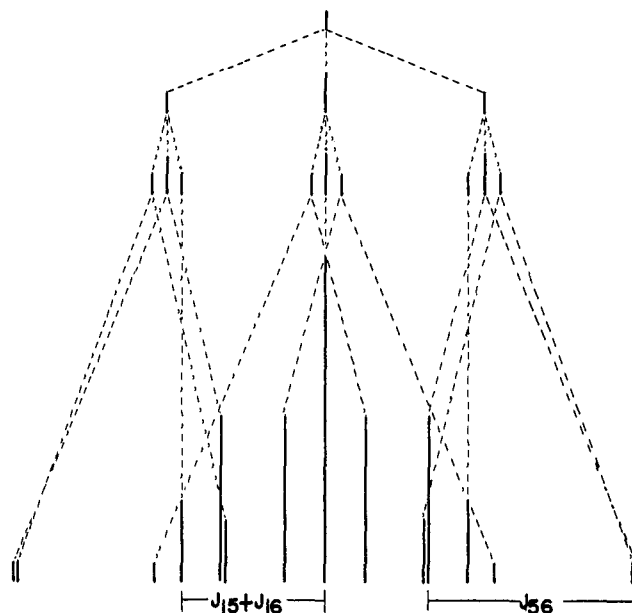


Fig. 1.—Olefinic proton splitting pattern of *cis*-cyclooctene.

spectra. This result causes mainly line broadening of the basic pattern and seems to preclude finding these allylic-allylic proton coupling constants without deuterium substitution.

TABLE I

COUPLING CONSTANTS AND DIHEDRAL ANGLES OF SOME CYCLOOLEFINS

	J_{56}^a (c.p.s.)	J_{15}^a (c.p.s.)	J_{16}^a (c.p.s.)	ϕ_{15}^b deg.	ϕ_{25}^b deg.
Cyclopropene	...	1.8 ^c	...	66	66
Cyclobutene	(4.0) ^d	(1.5) ^e	(-1.5) ^e	68	68
Cyclopentene	5.1	2.1	-1.4	63	63
Cyclohexene	8.8	3.1	-1.4	43 ^f	77 ^f
Cycloheptene	10.8	5.7	-1.0	11	109
<i>cis</i> -Cyclooctene	10.3	7.8	-0.8	15	135
<i>cis</i> -Cyclononene	10.7 ^g	8.2 ^g	-.7 ^g	37 ^h	157 ^h
<i>cis</i> -Cyclodecene ⁱ	10.8	7.8	-.8	15	135
<i>trans</i> -Cyclodecene ⁱ	15.1	6.8	-.8	1	121

^a Probable errors are ± 0.1 to ± 0.2 c.p.s. See text for discussion of errors in cyclohexene and cyclopentene. ^b Calculated by ignoring probable influence of ring size on J_{15} ; see text. ^c Reference 13, p. 1228. ^d "High Resolution NMR Spectra Catalog" Varian Associates, Palo Alto, California, 1962, spectrum 22 of 1,1-dioxathietene; we appreciate Dr. A. A. Bothner-By bringing this to our attention. ^e Estimated from an empirical extrapolation of our data; see also *d*. ^f Assuming $\phi_{12} = 120^\circ$; it may be larger. ^g Dr. A. A. Bothner-By, private communication, has informed us that Mr. Kreiter at Munich has analyzed this splitting pattern and obtains these values. ^h Other probable angles are 27 and 147°. ⁱ Chemical shifts are for *cis*, 322, and *trans*, 326 c.p.s., from TMS at 60 Mc.; for other shifts, see ref. 13.

(8) See F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961), for examples and discussion of this effect.

(9) R. R. Fraser, *ibid.*, **38**, 549 (1960).

While ϕ_{56} is constant at 0° , J_{56} increases from approximately 4.0 to an average of 10.6 c.p.s. (Table I). If this were due entirely to ring strain then J_{56} for cycloheptene would be smaller by about 1 c.p.s.¹⁰ Total ring strain, however, does not reflect the geometry between H-5 and H-6; in succeeding smaller rings the H-5-H-6 distance probably increases as the two protons are bent away from each other and the coupling is smaller.¹¹

Modifying the Karplus equations to

$$J \begin{cases} = 10.6 \cos^2 \phi & (0^\circ \leq J_{15} \leq 90^\circ) \\ = 11.4 \cos^2 \phi & (90^\circ \leq J_{15} \leq 180^\circ) \end{cases}$$

we calculated ϕ_{15} 's (identical with ϕ_{16} 's) as shown in Table I. Comparison with models and X-ray data on similar compounds¹² indicates good agreement with present conformational ideas¹⁰ for 7, 8, 9 and 10 carbon rings. Since J_{56} is almost constant for these larger rings, it seems reasonable to assume that their J_{15} 's (and J_{16} 's) are not influenced greatly by ring size. Although the calculated angles for the smaller rings also seem reasonable, caution is signaled by variations in J_{56} with ring size. For example, if ϕ_{15} in cyclohexene is assumed to be 60° ,¹³ then J_{15} is 12.4 when ϕ_{15} is 0° . However, when ϕ_{15} is 60° in acyclic systems,² J_{15} is 3.7, and this gives J_{15} as 14.8 when ϕ_{15} is 0° . The extent of variation of J_{15} with ring size is obscured by variations in dihedral angles; however, J_{15} seems to change less than J_{56} .

Cyclobutene has been reported to show no splitting of its olefinic protons.^{13,14} Extrapolation of our data suggests $J_{15} = -J_{16} \cong 1.5$ c.p.s. Comparison with other J_{15} 's and angles, however, indicates a larger value; here also, deuterium substitution should furnish the answer.

Acknowledgments.—Professor Paul E. Fanta supplied us with *cis*- and *trans*-cyclohexene and Dr. A. A. Bothner-By furnished us with the FREQUENT IV computer program, which we converted for use on the IBM 7090. Cooperation of the computer centers of both the Illinois Institute of Technology and the IIT Research Institute aided materially. George Behnke ran most of the n.m.r. spectra. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We acknowledge a grant for research from the Monsanto Chemical Company which supported this research in part.

(10) J. Sicher, "Progress in Stereochemistry," P. B. D. De La Mare and W. Klyne, Ed., Butterworth, Inc., Washington, D. C., 1962, pp. 210-213, and references therein.

(11) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, pp. 193-197.

(12) Dr. P. E. Fanta, private communication.

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

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Intern. Series Monographs on Org. Chem., Vol. V, Pergamon Press, London, 1959, p. 86.

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO 16, ILLINOIS

GERARD V. SMITH
HARVEY KRILOFF

RECEIVED MARCH 8, 1963

Ring Size Effect on *cis*-Olefinic Coupling Constants of Cycloalkenes. Use of ¹³C Patterns¹

Sir:

It has been postulated that the coupling constant, J , between adjacent hydrogens on trigonal carbon atoms depends only on the dihedral angle, *i.e.*, 0° for *cis*-olefins

(1) A preliminary account of this work was presented at the Fourth Omnibus Conference on the Experimental Aspects of Nuclear-magnetic-resonance Spectroscopy (OCEANS), Mellon Institute, Pittsburgh, Pa., March 2, 1963 by P. Laszlo, L. C. Allen, P. von R. Schleyer and R. M. Erdahl.

and 180° for *trans*-olefins.² From the Karplus equation, $J \cong 10$ c.p.s. would then be predicted for *cis*-olefinic protons; such values were indeed observed for ethylene³ and for alkyl-substituted ethylenes.⁴ We have found that this is not general behavior. Ring size affects markedly the magnitude of the coupling constants in *cis*-cycloalkenes.

J 's between the isochronous protons of 3,3-dimethylcyclopropene, norbornene, norbornadiene, cyclopentene and cyclohexene—cyclic hydrocarbons possessing varying degrees of strain—were determined by examination of ¹³C patterns in natural abundance. This technique simplifies complicated interactions.⁵ A practical drawback to this method is the difficulty of observing ¹³C patterns in anything but pure liquid samples or very concentrated solutions. Much easier observation, even for relatively dilute samples, is possible through time integration achieved with a Varian A-60 n.m.r. spectrometer adapted with a Mnemotron CAT digital computer.¹

¹³C patterns were observed as the multiplets predicted by first-order theory, but the only coupling constants which can be deduced rigorously are J_{23} (notation used throughout this paper is that of Fig. 1). The difference in chemical shift between the olefinic and the allylic protons is great (>3 p.p.m.); the clean doublet splitting of H2 with the other olefinic proton H3 then is equal to J_{23} . The other spectral features due to interactions of H2 with H1 and with H4 are also those expected from first-order theory, but these may be "deceptively simple"⁶ since in these symmetrical molecules all the allylic protons, H1 and H4, have the same chemical shift. We do not believe this is the case since it was possible to observe in bicycloheptadiene $J_{24} = 0.95$ c.p.s. In the other cases J_{24} probably is just as small or smaller, resulting in line broadening. J_{14} should be negligible. The observed splittings are labeled A, A', A'' and the deduced coupling constants J (Table I). These are related by the equation: $A + A' + A'' = \Sigma J$, the sum of all the coupling constants present.

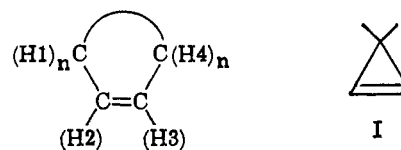


Fig. 1.—Numbering convention.

The results show that there is a marked decrease in the magnitude of J_{23} and also in the sum of all the coupling constants, ΣJ , with a decrease in ring size, from six to five-membered. There is only a poor correlation with double bond strain^{6a} since norbornene and norbornadiene are considerably more strained than cyclopentene. This shows that geometry about the double bond is the chief influence on J 's. The ring size trend appears to be general for small and common rings: *cis*-olefinic J 's from 11.8 c.p.s. for cyclooctatetraene⁷ and 11.7 c.p.s. for ethylene,⁷ through 9.6 c.p.s. for cyclohexene and 5.4 c.p.s. for cyclopentene

(2) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

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

(4) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962); A. A. Bothner-By, C. Naar-Colin and H. Günther, *J. Am. Chem. Soc.*, **84**, 2748 (1962).

(5) A. D. Cohen, N. Sheppard and J. J. Turner, *Proc. Chem. Soc.*, 118 1958; N. Sheppard and J. J. Turner, *Proc. Royal Soc. (London)*, **A252**, 506 (1959); G. S. Reddy and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 583 (1962).

(6) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 216 (1961).

(6a) Estimated, *e.g.*, by C=C stretching frequencies; see P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958); K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

(7) F. A. L. Anet, *ibid.*, **84**, 671 (1962).