

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.

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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.

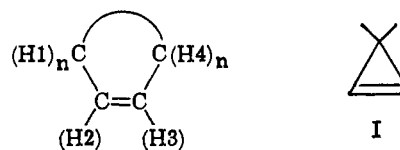


Fig. 1.—Numbering convention.

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

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TABLE I
COUPLING CONSTANTS OF CYCLOALKENES, C.P.S.

Compound	$J^{13}\text{C-H}$	$A (= J_{23})$	$A' (J_{\geq 12})$	$A'' (= J_{23})$
Cyclohexene, $n = 2$	(157)	9.60 ± 0.10	3.60 ± 0.10^a	...
Cyclopentene, $n = 2$	160 ± 1	5.40 ± 0.10^b	3.70 ± 0.10	...
Norbornene, $n = 1$	174 ± 1	5.80 ± 0.10^c	2.95 ± 0.10^c	...
Bicycloheptadiene, $n = 1$	168 ± 1	5.05 ± 0.10^d	2.70 ± 0.10^d	0.95 ± 0.10^d

^a In agreement with ref. 4 and with E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243 (1962), for J olefinic-allylic when $\phi \cong 60^\circ$. ^b $J_{23} = 5.58 \pm 0.02$ c.p.s. for the cyclopentenyl protons in indene; D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 2346 (1962). ^c We have measured the J 's in 5- and 5,6-substituted 2-norbornenes. The results, $J_{23} = 5.1$ to 6.0 c.p.s. and $J_{12} = 2.2$ - 3.3 c.p.s., show that coupling constants also depend significantly on the nature of substituents. ^d According to F. S. Mortimer, *J. Mol. Spectry.*, **3**, 528 (1959), $J_{12} = 2.9 \pm 0.1$, $J_{23} = 3.45 \pm 0.1$, $J_{13} = 0.95 \pm 0.1$. The separation of the two outer lines in the ^{13}C pattern, 8.60 ± 0.1 c.p.s., 1.3 c.p.s. in excess of the sum of Mortimer's J 's and the structure of this multiplet make our values more likely.

(Table I), to 2.5-3.5 c.p.s. for substituted cyclobutenes⁸ and ca. 0.5-1.5 c.p.s. for 3,3-dimethylcyclopropene (I)⁹ illustrate the trend.¹⁰

Pople, Schneider and Bernstein have observed that J_{ortho} in aromatic hydrocarbons increased from 1-4 c.p.s. in five-membered carbocyclic rings to 5-9 c.p.s. in six-membered rings and to 10-13 c.p.s. in seven-membered aromatic rings.¹¹ More recent work has substantiated this generalization.^{12,13} We show that olefinic J 's follow a similar trend and that, for a given ring size, they are superior in magnitude to J_{ortho} in aromatic hydrocarbons. A variation of J_{ortho} in six-membered aromatic hydrocarbons with bond order has recently been reported.¹⁴ Hence, vicinal coupling constants in unsaturated hydrocarbons are dependent both on ring size and on the aromatic character of the molecule. This phenomenon may be useful for detecting "aromaticity," supplementing the so-called ring current effect.¹³

To test this idea, we examined the ^{13}C patterns of the conjugated double bond in the five-membered fragment (positions 1 and 2) of acenaphthylene which yielded $J_{^{13}\text{C-H}} = 174 \pm 1$ and $J_{12} = 5.2 \pm 0.1$ c.p.s. This latter coupling constant, slightly smaller than those of indene ($J = 5.58$ c.p.s.) and cyclopentene ($J = 5.4$ c.p.s.), but considerably larger than those observed for typical five-membered aromatics, indicates that the C_1 - C_2 double bond in acenaphthylene has only a slight amount of aromatic character, a conclusion in agreement with the known properties of the molecule.¹⁵

Acknowledgments.—A sample of 3,3-dimethylcyclopropene (I) from Dr. G. L. Closs, transmitted by Dr. J. I. Musher, was kindly provided. We wish to thank the Alfred P. Sloan Foundation for partial support of this research. Dr. L. C. Allen and Mr. R. M. Erdahl

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(9) The ^{13}C pattern of compound I was observed as a single unresolved band of width at half height = 4.8 c.p.s. The vinyl protons of this molecule are known to be coupled to the six equivalent methyl hydrogens by 0.7 c.p.s. (G. L. Closs, *Proc. Chem. Soc.*, 152 (1962)), hence, the width at half height should be 4.2 c.p.s. due to this factor alone. It is clear that the magnitude of olefinic-olefinic coupling in I must be very small.

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developed the time integration method utilized here. We are indebted to the Mnemotron Corp. for the loan of the CAT computer.

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A New Class of Double-Bridged Coördination Polymers Based on Chromium(III)

Sir:

Earlier reports from this laboratory have concerned the preparation of coördination polymers of types which we write symbolically as $[\text{M}(\text{AB})\text{X}_2]_n$ ¹ and $[\text{MX}_2]_n$ ² where AB represents a uninegative bidentate ligand and X represents a uninegative bridging group. We now wish to report a third class, $[\text{M}(\text{a})(\text{b})\text{X}_2]_n$, where a represents a neutral unidentate ligand and b a uninegative ligand. The preparation of this new class differs in method from that in the earlier series and appears to lead to polymers with substantially higher molecular weight than we have found for the other two types. The non-bridging ligands a and b are inorganic, so that this material is an example of a coördination polymer which in addition to its inorganic backbone has inorganic blocking groups in the repeating unit.

The synthesis is a two-step process in which chromium(II) acetate is treated with a potassium phosphinate (KOPR_2O) to yield the corresponding chromium(II) phosphinate ($\text{R} = \text{C}_6\text{H}_5$, I). The latter is then oxidized with air in the presence of water to yield the composition $\text{Cr}(\text{H}_2\text{O})(\text{OH})(\text{OPR}_2\text{O})_2$ ($\text{R} = \text{C}_6\text{H}_5$, II) which has polymeric properties. II has been prepared by these reactions under a variety of conditions, but here we will only describe a set of conditions which gives a product exhibiting a high intrinsic viscosity in chloroform.

A suspension of 2.7 g. of freshly prepared $\text{Cr}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 125 ml. of deoxygenated water is refluxed under nitrogen with stirring for 1 hr. After the addition of a deoxygenated solution of $\text{KOP}(\text{C}_6\text{H}_5)_2\text{O}$ (prepared by the exact neutralization of 8.0 g. of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OH}$ with 1 M KOH) without exposure to air, the refluxing is continued for 2-3 hr. under nitrogen. The precipitated intermediate I is then separated by filtration at room temperature and washed several times with deoxygenated water, all operations being conducted under nitrogen. I is next dispersed in 500 ml. of water and oxidized to II by exposure to the atmosphere. After crude II has been removed by filtration, washed thoroughly with water, and dried at 100° , it is dissolved

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