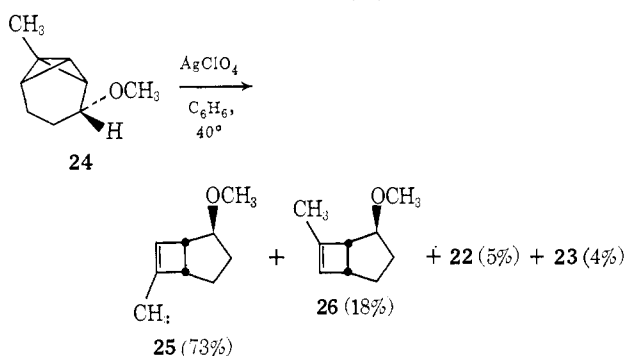
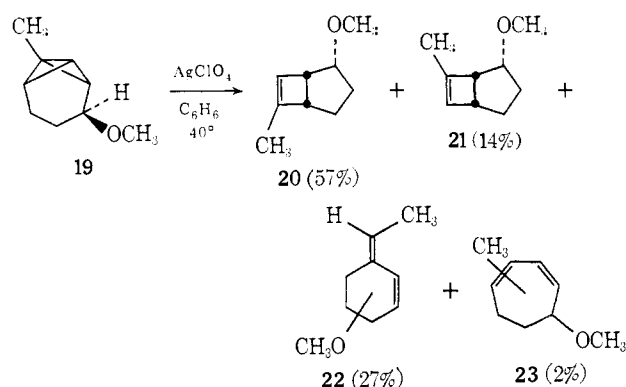
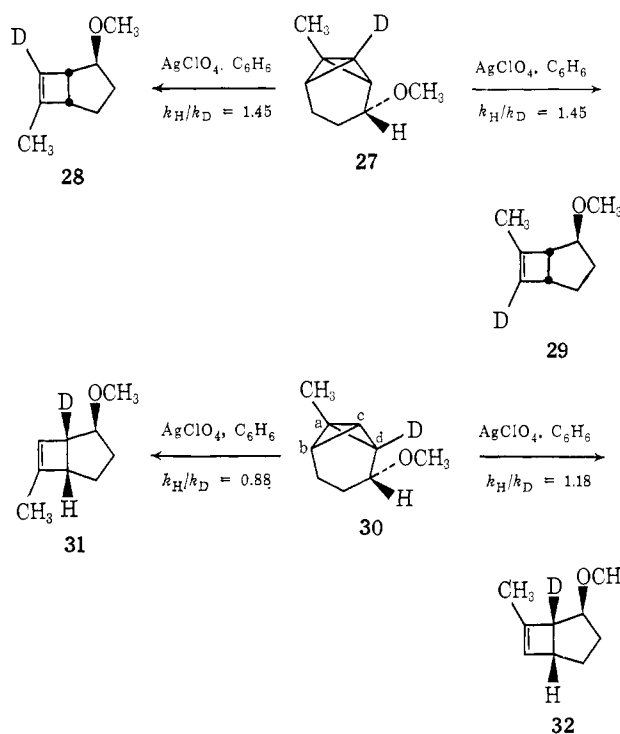


Scheme II



were again significantly influenced, but in *opposite* directions.



The stereospecificity exhibited by **9**, **16**, **19**, and **24** demonstrates that the 1,3-hydride shift of H₇ to C₁ in the rate-determining step³ (or at another time during reaction) is not operative, since this pathway would uniquely provide bicycloheptenes of configuration opposite to that observed. Formal cleavage of the a-b or a-d bonds (*cf.* **30**) at the onset of rearrangement likewise cannot account for the combined experimental evidence. Under the terms of this mechanistic option, not only would improper C₂ stereochemistry again be

realized, but argento carbonium ion intervention would have to be bypassed despite the presence of an electron-donating bridgehead substituent which favors generation of such a species.²⁻⁴ A mechanism⁵ involving edge attack at bonds b-c or c-d followed by 1,2-carbon shift accounts for the above stereospecificity and production of **6**; however, because the combined kinetic, multiple substituent,^{3b} and isotope effect data are not readily accommodated by this pathway, concurrent weakening of side bond b-c or c-d and the central bond must be considered as a viable alternative. A full discussion of this point is deferred to our full paper on this subject.

In either case, rupture of the b-c linkage is kinetically preferred to a small degree in the present systems (6-methyl-/7-methylbicycloheptenes = 1.5-4.0) owing to steric congestion engendered by the C₃ group which perturbs what otherwise would be isoenergetic reaction modes. The propensity of the tricycloheptanes to rearrange more rapidly to bicycloheptenes when substituted in stereoproximal fashion is explainable in terms of steric accessibility to that surface of the molecule containing C₇. Since the C₃-R group in stereoproximal systems presumably commands equatorial orientation and consequently forces the C₄ methylene flap to the opposite side of the structure, approach by the exceedingly bulky Ag⁺ is facilitated. Similar considerations in stereodistal systems force the C₄ methylene group to adopt a relative orientation which shields this general area of attack.

The direction and magnitude of the isotope effects in the reaction **27** → **28** + **29** and 1-7-d → 2-7-d³ remain difficult to fully comprehend. The C₇-H(D) bond in the reactant, characterized by a high level of s character (sp^{1.68}), must experience a substantial influx of p character. Analogy with solvolytic reactions is clearly not valid here, since this change should lead to an inverse isotope effect. Apart from contributions arising from major alterations in C₇-H(D) hybridization, the sizable positive fractionation factors also arise partly from extensive movement of this bond in the rate-determining transition state and possibly to some degree from bonding of Ag⁺ to this carbon atom.

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Conformations of Five-Membered Rings. Limitations on the R-Value Method

Sir:

In the conformational analysis of six-membered rings, the R-value method has served as an important source of structural data for molecules in solution.¹ Analysis of the vicinal coupling constants in a -CH₂-CH₂- fragment within a ring gives a ratio ($R = J_{\text{trans}}/$

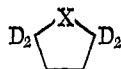
(1) J. B. Lambert, *Accounts Chem. Res.*, **4**, 87 (1971).

J_{cis}), independent of electronegativity effects, from which the internal torsional angle Ψ can be derived (eq 1).² By this method, torsional angles have been deter-

$$\cos \Psi = [3/(2 + 4R)]^{1/2} \quad (1)$$

mined in a wide variety of structural systems, yielding values ranging from 45° ($R = 1.00$) in a bicyclic hexahydropyrimidine³ to 74° ($R = 8.7$) in benzocycloheptene.⁴ In comparisons between R -value-determined and X-ray-determined values of Ψ ,¹ differences are usually less than 2° , and in only one case has a difference of 3° been registered. Applications of the R -value method to five-membered rings are beginning to appear in the literature,⁵ but the applicability of the method to this area has not yet been demonstrated. In order to provide a basis for such studies, we have now examined minimally substituted five-membered rings and wish to report the conformational information gleaned from the R -value analysis. We find that the resulting torsional angles Ψ are overestimated by a considerable amount, in contrast to the situation for six-membered rings. Although limitations are thus placed on the quantitative applicability of the R value to five-membered rings, qualitative application to an homologous series remains valid. For this study, we report the vicinal coupling constants between the β protons in the following fundamental five-membered rings: cyclopentane (1), tetrahydrofuran (2), pyrrolidine (3), tetrahydrothiophene (4), cyclopentanone (5), and cyclopentanol (6). Average torsional angles have been obtained by a classical Karplus analysis. The torsional arrangement of the β - β' section of these rings has thus been determined for the first time in solution.

We prepared the deuterated derivatives of the above-named compounds (1-5) and measured the vicinal



1, X = CD₂
2, X = O
3, X = NH

4, X = S
5, X = C=O
6, X = CDOH

coupling constants from the carbon-13 satellites with simultaneous irradiation at the deuterium resonance frequency. Compound 6 gave an analyzable AA'BB' spectrum. The coupling constants and other pertinent parameters are presented in Table I. In contrast to six-membered rings, these molecules may exist in several conformations, *i.e.*, envelopes and half-chairs in which the heteroatom or substituted carbon is located at various positions. The torsional angle Ψ must be considered to be an average over all such conformations unless there is good reason to believe that the molecule exists in only a single form. The average value of Ψ in cyclopentane has been found both by experiment and by machine calculation to be 27 - 28° .⁶

(2) H. R. Buys, *Recl. Trav. Chim. Pays-Bas*, **88**, 1003 (1969).

(3) S. F. Nelsen, P. J. Hintz, and R. T. Landis, II, *J. Amer. Chem. Soc.*, **94**, 7105 (1972).

(4) M. St-Jacques and C. Vaziri, *Org. Magn. Resonance*, **4**, 77 (1972).

(5) J. B. Lambert and F. R. Koeng, *ibid.*, **3**, 389 (1971); L. A. Sternson, D. A. Coviello, and R. S. Egan, *J. Amer. Chem. Soc.*, **93**, 6529 (1971); K. Bergeson, *Acta Chem. Scand.*, **26**, 2156 (1972).

(6) W. J. Adams, L. S. Bartell, and H. J. Geise, *J. Amer. Chem. Soc.*, **92**, 5013 (1970); J. B. Hendrickson, *ibid.*, **83**, 4537 (1961); **85**, 4059 (1963).

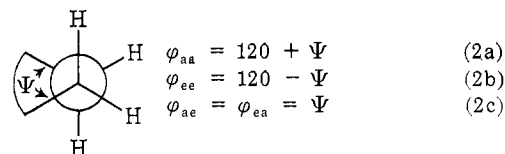
Table I. Coupling Constants and Derived Parameters in Five-Membered Rings

X	No.	J_{trans} , Hz	J_{cis} , Hz	R	Ψ , ^a deg	Ψ , ^b deg
S	4	7.25	5.45	1.33	50	42
C=O	5	6.75	6.75	1.00	45	34.5
CD ₂	1	6.30	7.90	0.80	40	(27)
NH	3	6.30	8.30	0.76	39	24
CDOH	6	6.02	8.25	0.73	38.5	25
O	2	6.25	8.65	0.72	38	21

^a Calculated from the R value (eq 1). ^b Calculated from the Karplus equation (eq 5b), with $A = 9.95$.

The deviation (13°) of this number from the R -value-derived figure of 40° therefore is far larger than in any previous case (3°) in the six-membered and higher series.¹ The failure to reproduce the known torsional angle in cyclopentane renders the R -value-determined figures in Table I and ref 5 suspect.

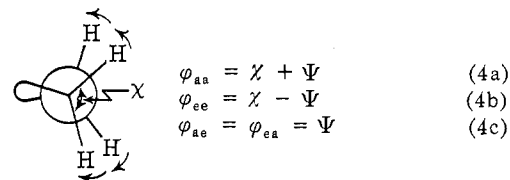
We believe that the overestimation of torsional angles is due at least in part to the breakdown in threefold symmetry that is assumed in the derivation of eq 1.⁷ In six-membered rings the projection angle χ of a CH₂ group is very close to 120° . To convert the R value to Ψ , the HCCH dihedral angles are expressed in terms of Ψ (eq 2),² and the Karplus expression is substituted for



each coupling constant (eq 3). Use of trigonometric

$$R = \frac{J_{trans}}{J_{cis}} = \frac{1/2(A \cos^2(120 + \Psi) + A \cos^2(120 - \Psi))}{A \cos^2 \Psi} \quad (3)$$

identities and cancellation of A reduces eq 3 to eq 1. In five-membered rings, the projection angles are no longer 120° , because the H-C-H angle is distorted through ring strain. As χ increases beyond 120° , φ_{aa} and φ_{ee} become larger, whereas φ_{ae} and φ_{ea} are not changed (eq 4). The applicable expressions for J_{trans}



and J_{cis} (eq 5), when substituted into an expression

$$J_{trans} = 1/2(A \cos^2(\chi + \Psi) + A \cos^2(\chi - \Psi)) \quad (5a)$$

$$J_{cis} = A \cos^2 \Psi \quad (5b)$$

analogous to eq 3, do not reduce to eq 1. For $\chi > 120^\circ$, J_{trans} becomes larger for constant Ψ and J_{cis} is not changed (eq 5), so that R is artificially increased. As a result, application of eq 1 gives a value of Ψ that is larger than the actual angle. Although other factors may also be important in overestimating the torsional angle, this effect is probably dominant. Straightfor-

(7) The possibility of such a limitation of the R -value method was discussed in ref 1.

ward application of eq 1 thus cannot be made to five-membered rings.

It is noted that J_{cis} is not affected by changes in the H-C-H projection angle χ (eq 5b). The torsional angle Ψ can therefore be calculated from this equation, with A evaluated to be 9.95 from J_{cis} (7.90 Hz) and Ψ (27°) in cyclopentane. The values of Ψ obtained by this classical Karplus approach for the remainder of the series (2-6) are recorded in the last column of Table I. Only the value for cyclopentanone (34.5°) can be compared with experimental data⁸ (37.4° , electron diffraction). The agreement (3°) is quite good for a quantitative Karplus-type analysis. The figures in the last column of Table I offer the best current torsional angles for five-membered rings in solution. Just as in six-membered rings,¹ the shorter C-O and C-N bonds flatten the ring slightly and the longer C-S bonds and smaller C-S-C angle pucker the ring considerably.

In six-membered rings, calculation of Ψ from eq 1 and from eq 5b should give identical results, since distortions from threefold symmetry are very small. For molecules of the type **7** ($X = CH_2, S, +SCH_3, Se,$



$SeBr_2, TeBr_2$),⁹ the two methods indeed give essentially the same values of Ψ , in contrast to the situation in five-membered rings (Table I, last two columns). For molecules without angle strain, the methods can therefore be considered to be equivalent. Application of the Karplus approach requires the evaluation of A and demonstration that it is constant throughout a series. The R -value method is therefore to be preferred for six-membered rings, since the A factor cancels out (eq 3). For five-membered rings of the type 1-6, the present work shows that the standard Karplus approach is the more reliable (Table I). For systems such as **8**, however, the A factor is strongly dependent on the electronegativity of X and neither method is quantitatively accurate. Within an homologous series of five-membered rings, qualitative trends in the R values, as originally propounded,¹⁰ can still give a valid indication of the relative shapes of the molecules.

(8) H. J. Geise and F. C. Mijlhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 577 (1971).

(9) Data from J. B. Lambert, D. H. Johnson, R. G. Keske, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 8172 (1972); E. W. Garbisch, Jr., and M. G. Griffith, *ibid.*, **90**, 6543 (1968). The Karplus $A = 13.28$ was determined from $\Psi = 58^\circ$ in cyclohexane.

(10) J. B. Lambert, *ibid.*, **89**, 1836 (1967).

(11) (a) This work was supported by the National Science Foundation (Grants GP-34259X and GP-35868X) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4); (b) NSF Trainee, 1969-1970; NDEA Fellow, 1970-1973; (c) NSF Trainee, 1969-1970.

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Ab Initio Valence Bond Calculation of Benzene

Sir:

The qualitative concepts of resonance, in particular the relative importance of specific valence bond func-

tions, have been based almost entirely on empirical and semiempirical calculations. The first of these for aromatic hydrocarbons was the valence bond calculation on benzene done by Pauling and Wheland¹ which showed, in part, that the Kekule structure (I) of benzene is approximately four times more important than the Dewar structure (II). These workers assumed that polar structures are unimportant. More recently Craig² examined the question of the importance of polar structures in benzene, again using semiempirical arguments. He found the ortho singly polar structures to contribute no more than 0.5% to the ground state.

Recently, an *ab initio* valence bond program capable of including many valence bond functions has been developed in this laboratory. The theory behind this program, which utilizes the symmetric group and Young Tableaux to handle the spin degeneracy problem, has been published elsewhere.³⁻⁶ We have used this program to perform a "full π " VB calculation of benzene.

The fixed GTO basis of Whitten⁷ was used and the calculation was done at the experimental geometry. All $1s$ and σ bonded electrons were included explicitly in the calculation by keeping the first 18 SCF molecular orbitals paired. The "full π " VB calculation includes 175 individual valence bond functions which in unnormalized form may be written

$$\theta_i = \alpha \Phi_i(1, \dots, 6) \Xi(7, \dots, 42)$$

where α is the antisymmetrizer, and

$$\Xi(7, \dots, 42) = 1a_{1g}(7)1a_{1g}(8)(\alpha_7\beta_8 - \alpha_8\beta_7) \dots$$

$$3e_{2g_a}(39)3e_{2g_a}(40)(\alpha_{39}\beta_{40} - \alpha_{40}\beta_{39}) \times \\ 3e_{2g_b}(41)3e_{2g_b}(42)(\alpha_{41}\beta_{42} - \alpha_{42}\beta_{41})$$

represents the 18 σ molecular orbitals which are kept doubly occupied throughout the calculation.⁸

Each of the Φ_i refers to a specific valence bond function. Chart I gives a schematic representation for the

Chart I

H_{ii}, au	-230.2971	-230.2838	-229.8101	-229.7185
Occupation no.	0.0622	0.0194	0.0234	0.0381
H_{ii}, au	-230.0452	-229.7039	-230.3244	-230.1732
Occupation no.	0.098	0.0078	0.4753	0.2756

covalent and singly polar functions in terms of a representative Rumer diagram. As an example, structure I, one of the two Kekule structures, is represented by

$$\Phi_k(1, \dots, 6) = p_1(1)p_2(2)p_3(3)p_4(4)p_5(5)p_6(6) \times \\ (\alpha_1\beta_2 - \alpha_2\beta_1)(\alpha_3\beta_4 - \alpha_4\beta_3)(\alpha_5\beta_6 - \alpha_6\beta_5)$$

(1) L. Pauling and G. W. Wheland, *J. Chem. Phys.*, **1**, 362 (1933).

(2) D. P. Craig, *Proc. Roy. Soc., Ser. A*, **200**, 401 (1950).

(3) G. A. Gallup, *Int. J. Quantum Chem.*, **6**, 899 (1972).

(4) G. A. Gallup and J. M. Norbeck, *Chem. Phys. Lett.*, in press.

(5) G. A. Gallup and J. M. Norbeck, *Chem. Phys. Lett.*, in press.

(6) J. M. Norbeck and G. A. Gallup, *Int. J. Quantum Chem.*, in press.

(7) J. Whitten, *J. Chem. Phys.*, **44**, 359 (1965).

(8) The 18 occupied σ orbitals are listed with their respective orbital energies in ref 9.