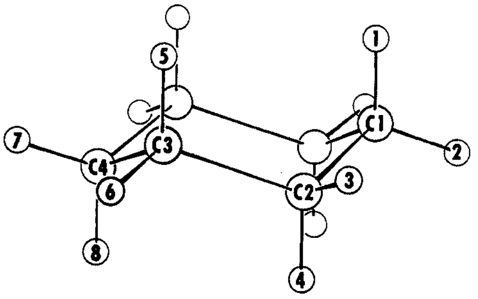


Figure 5. Molecular model of cyclohexane showing the notation used in Table III.

Table III
Experimental and Theoretical Proton nmr of Cyclohexane-$d_{10,11}$

	Spacing, Hz	
Lines	Experimental[a]	Theoretical[b]
(1,2)	1798.9 ± 5	(+1798.9)
(1,C1)	871.8 ± 2	+998.4[c]
(1,5)	326.3 ± 2	−392.9
(1,3)	200.0 ± 2	−169.2
(1,7)	99.7 ± 2	−107.4
(1,6)	98.1 ± 2	−107.0
(1,4)	78.4 ± 2	−88.1
(1,C3)	33.9 ± 1	−42.1
(1,C2)		−28.1
(1,C4)	20.0 ± 1	−21.2
(1,8)	16.0 ± 1	−8.8

[a] Experimental spacings at 102° in 4,4′-di-*n*-hexyloxyazoxybenzene. [b] Theoretical spacings are computed for rapidly interconverting chair forms with tetrahedral bond angles at the carbon and $r_{CH}/r_{CC} = 0.714$. The motional constant is scaled to make the (1,2) line coincident with experiment. [c] Equals the sum of D_{CH} of 875.4 and J_{CH} of 123 Hz (J. H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36,** 2644 (1962)). The other indirect couplings have been neglected.

accordingly. On this model, one expects a single strong peak from the molecules containing one proton and a symmetrical pair of lines for each molecular species containing two protons. There are seven such species, which we shall denote by (1,2), (1,3), ... (1,8), the numbers referring to the positions of the protons according to the numbering in Figure 5. The center trace in Figure 4 shows the strong single line due to molecules containing one proton. The bottom trace, which gives the spectrum at higher sensitivity, shows the symmetrical pairs of lines due to species with proton pairs. In traces with an expanded frequency scale, not reproduced here, additional lines near the center, as well as lines due to molecules containing one ^{13}C nucleus, can be identified. The first two columns of Table III give the observed frequency spacing for each line pair and their assignment. In the third column of this table are theoretical spacings, calculated on the assumption of tetrahedral bond angles at the carbon and a ratio of C–H to C–C distances of 0.714. The agreement between experimental and calculated line positions is sufficiently good to indicate that this simple model is not far from the actual structure. A detailed quantitative interpretation is at present in progress.

Conclusion

Up to now molecular structure determination from nematic-solvent nmr has been restricted to very simple molecules. We believe, however, that the technique of deuterium substitution may extend its usefulness significantly. One can even envision that quite complicated compounds of special interest could be studied by preparing a number of deuterated species, each with a proton at a different specific site. In this way a large amount of structural information could be obtained, though the labor involved would be far from trivial. Fourier transform nmr spectroscopy, which is rapidly evolving at this time, can be expected to provide the improvement in sensitivity which would be required for such a project.

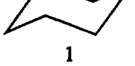
Structural Chemistry in Solution. The *R* Value

JOSEPH B. LAMBERT

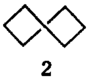
Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201

Received August 7, 1970

Six-membered rings that lack endocyclic double bonds are not restricted in conformation to the classic tetrahedral[1] chair (**1**) and twist-boat (**2**) forms. By

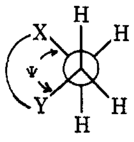


1



2

appropriate choice of substituent or heteroatom, internal dihedral (torsional) angles (Ψ), defined in structure

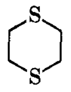


3

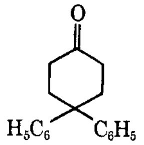
3, may range from 70° down to 45° within the basic chair form and even lower in boat and intermediate forms. For cyclohexane, Ψ is about 56° all around the ring;[2] for the puckered 1,4-dithiane **4**, the S–C–C–S tor-

---

(1) H. Sachse, *Ber.*, **23,** 1363 (1890).



4

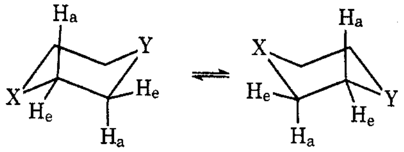


5

sional angle is 69°;[3] and for the flattened cyclohexanone **5**, the average CO–C–C–C(C_6H_5)$_2$ angle is 51°.[4] Such a large range of ring shapes is brought about by the wide variability of bond angles and bond lengths that can occur in six-membered rings.

Knowledge of ring conformation is necessary for the elucidation of stereoelectronically dependent organic and inorganic reaction mechanisms, for the design of stereochemically controlled syntheses, and for a full understanding of many chemical processes, such as substrate–enzyme interactions, that occur in biological systems. Heretofore, conformational information was derived almost exclusively from X-ray (in the solid), microwave (vapor phase), and electron diffraction (vapor phase) data. Mechanistic, synthetic, and biochemical studies, however, are most frequently carried out in solution, for which no general structural tool has previously been available. The methods described in this Account have been developed to serve as a convenient and widely applicable procedure for obtaining structural information on certain classes of molecules in solution.

The *R* Value. For a six-membered ring that is alternating rapidly between two equivalent forms (**6**),



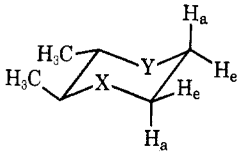
6

two vicinal coupling constants, J_{trans} and J_{cis}, may be readily extracted from the AA′BB′ or AA′XX′ spectrum of a CH_2CH_2 fragment (eq 1). The individual

$$J_{\text{trans}} = {}^1/_2(J_{\text{aa}} + J_{\text{ee}}) \qquad (1a)$$

$$J_{\text{cis}} = {}^1/_2(J_{\text{ae}} + J_{\text{ea}}) = J_{\text{ae}} \qquad (1b)$$

couplings are averaged by the chair–chair interconversion. For a ring that is frozen into a single conformation, such as **7**, these same averaged coupling



7

constants may be obtained by combining the individual parameters (J_{aa}, J_{ee}, J_{ae}, J_{ea}) derived from the ABCD or ABXY spectrum according to the procedure of eq 1. Although considerable qualitative structural information has been obtained from the individual couplings by the Karplus method,[5a,b] such results are severely limited by the strong dependence of the couplings on the electronegativities of the adjacent groups, X and Y in **6** and **7**. Thus for molecules with identical local dihedral arrangements about XCH_2CH_2Y fragments, the individual coupling constants will show great variability. Additive combinations such as J_{trans} and J_{cis} must show similar variations, since the dependence of J on the electronegativity of adjacent groups is a multiplicative one.[5b–d] The variability of J_{trans} and J_{cis} for CH_2–CH_2 fragments with similar dihedral relationships but differing substituent electronegativities is illustrated by entries 7–15 in Table I and 6–9 in Table II. The individual couplings or their additive combinations are therefore unreliable sources of quantitative structural information.

There is particular advantage in considering the averaged coupling constants, J_{trans} and J_{cis}, instead of the individual ones. Because this type of averaging (eq 1) introduces an equal weighting for the axial and the equatorial protons, the couplings should possess a nearly identical multiplicative[5b–d] dependence on the substituent electronegativities. The general form of this dependence has been found by several authors[5b–d] to be given by eq 2, in which J^0 is a coupling

$$J = J^0(1 - M\sum\Delta E) \qquad (2)$$

parameter with no electronegativity dependence, M is a constant for geometrically related couplings, and $\Sigma\Delta E$ is the sum of the differences between the electronegativity of hydrogen and those for the substituents X and Y. For the particular cases of J_{trans} and J_{cis}, the identity of the multiplicative factor has been observed experimentally, and M found to be 0.09.[6] Simple division of these two couplings (eq 3) therefore produces a

$$R = \frac{J_{\text{trans}}}{J_{\text{cis}}} = \frac{J_{\text{aa}} + J_{\text{ee}}}{J_{\text{ae}} + J_{\text{ea}}} \qquad (3a)$$

$$R = \frac{J^0{}_{\text{trans}}(1 - 0.9\sum\Delta E)}{J^0{}_{\text{cis}}(1 - 0.09\sum\Delta E)} = \frac{J^0{}_{\text{trans}}}{J^0{}_{\text{cis}}} \qquad (3b)$$

ratio, R, that is dependent only on conformation.[6] No ratio of individual couplings can effect such a removal of the dependence on substituent electronegativity. For a given dihedral arrangement, the R value will remain constant from system to system, even though J_{trans} and J_{cis} are variable. For cyclohexane, R is calculated to be 2.16 from the individual couplings reported by Garbisch.[7] Entries 7–15 in Table I and 6–9 in Table II show that molecules with the undistorted cyclohexane shape have R values in the range

---

[2] H. R. Buys and H. J. Geise, *Tetrahedron Lett.*, 2991 (1970); M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).

[3] R. E. Marsh, *Acta Cryst.*, **8**, 91 (1955); H. T. Kalff and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **85**, 198 (1966).

[4] J. B. Lambert, R. E. Carhart, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **91**, 3567 (1969).

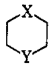
[5] (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); (c) R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963); (d) K. L. Williamson, *J. Amer. Chem. Soc.*, **85**, 516 (1963).

[6] J. B. Lambert, *ibid.*, **89**, 1836 (1967).

[7] E. W. Garbisch, Jr., and M. G. Griffith, *ibid.*, **90**, 6543 (1968).

Table I

R Values from Molecules with the Structure



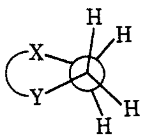
Entry	X	Y	J_{trans}, Hz	J_{cis}, Hz	*R*	Ψ (nmr), deg	Ψ (X-ray), deg	Source
1	S	S	8.2	2.1	3.9	66	69	*a, b*
2	O	S	7.9	2.7	2.9	62		*c*
3	Te	CD_2	8.62	3.12	2.76	61		*d*
4	Se	CD_2	8.46	3.09	2.74	61		*d*
5	S	CD_2	8.51	3.26	2.61	61		*d*
6	S	$C(CH_3)_2$	8.58	3.29	2.61	61		*e*
7	O	O	6.11	2.78	2.20	58	57	*f, g*
8	NH	O	6.66	3.04	2.19	58		*h*
9	NCH_3	O	6.65	3.05	2.18	58		*h*
10	CD_2	CD_2	8.07	3.73	2.16	58	56	*g, i*
11	NH	NH	6.54	3.04	2.15	58	56	*f, g*
12	NH	CD_2	7.88	3.77	2.09	57		*d, j, k*
13	NCH_3	CD_2	7.52	3.65	2.06	57		*k*
14	$C(CH_3)_2$	$C(CH_3)_2$	8.27	4.03	2.05	57		*f*
15	O	CD_2	7.41	3.87	1.91	56		*d*
16	O	NNO	6.65[l]	3.4	1.96	56		*m*
			6.5[l]	3.8	1.7	54		*m*
17	NCH_3	NNO	6.95[l]	3.6	1.9	56		*m*
			7.0[l]	4.0	1.75	55		*m*
18	$C{=}CH_2$	CD_2	8.05	4.31	1.87	56		*n*
19	C=O	CD_2	8.61	5.01	1.72	54	52	*f, g*
20	C=O	$C(C_6H_5)_2$	8.4	5.1	1.6	53	51	*o, p*
21	NNO	NNO	7.45	4.94	1.51	52		*q*
22	$C{=}CH_2$	$C{=}CH_2$	7.52	5.31	1.42	51		*f*
23	C=O	C=O	8.05	6.23	1.29	50		*f*
24	C=NOH	C=NOH	7.3	6.5	1.12	47	47	*r, s*

[a] C. Altona and E. Havinga, *Tetrahedron*, **22,** 2275 (1966); when X ≡ Y, the parameters are obtained from the ^{13}C satellite spectra. [b] Reference 3. [c] N. deWolf, P. W. Henniger, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **86,** 1227 (1967). [d] Reference 10. [e] D. S. Bailey and J. B. Lambert, unpublished results. [f] Reference 6. [g] References 2 and 11. [h] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69,** 579 (1965). [i] Reference 7. [j] J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Amer. Chem. Soc.*, **89,** 3761 (1967). [k] J. B. Lambert, unpublished results. [l] Syn and anti CH_2CH_2 groups. [m] R. K. Harris and R. A. Spragg, *J. Mol. Spectrosc.*, **23,** 158 (1967). [n] J. T. Gerig and R. A. Rimerman, *J. Amer. Chem. Soc.*, **92,** 1219 (1970). [o] J. B. Lambert, R. E. Carhart, P. W. R. Corfield, and J. H. Enemark, *Chem. Commun.*, 999 (1968). [p] Reference 4. [q] J. B. Lambert, J. L. Gosnell, Jr., D. S. Bailey, and B. M. Henkin, *J. Org. Chem.*, **34,** 4147 (1969). [r] H. Saitô and K. Nukada, *J. Mol. Spectrosc.*, **18,** 355 (1965). [s] P. Groth, *Acta Chem. Scand.*, **22,** 128 (1968).

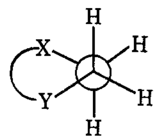
1.9–2.2. Deviations from this small range are indicative of distortions from the normal shape of the ring.

The double manipulation is required to produce *R*: averaging to obtain J_{trans} and J_{cis}, so that the dependence on electronegativity is identical, and division to remove the multiplicative factor $[(1 - M\Sigma\Delta E)]$. The method may be applied to any six-membered ring containing a CH_2CH_2 fragment with an analyzable nmr spectrum.

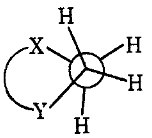
Types of Distortions. Three classes of XCH_2CH_2Y conformations may be distinguished: (1) the flattened form (**8**), in which the methylene groups are more nearly eclipsed; (2) the undistorted, or cyclohexane arrangement (**9**);[8] and (3) the puckered conformation (**10**). It should be noted that the internal X–C–C–Y torsional angle Ψ (**3**) decreases on flattening and increases on puckering. Molecules **4** and **5** serve as examples that contain the puckering and flattening distortions, respectively.



8



9



10

Each type of distortion has a characteristic *R* value. To see how *R* varies with changes in geometry, one must examine the trends in the component coupling constants. The dependence of a vicinal proton–proton coupling on the H–C–C–H dihedral angle, φ, is given by the Karplus relationship[5a] (eq 4) in which *A* is generally treated as an empirically determined parameter.

$$^3J_{H-H} = A \cos^2 \varphi \qquad (4)$$

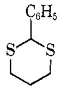
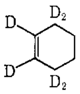
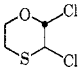
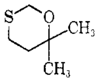
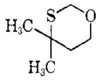
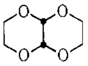
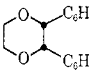
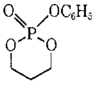
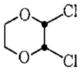
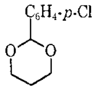
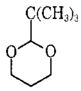
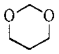
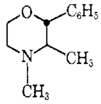
In the undistorted chairs, φ_{aa} is close to 180°, so J_{aa} is at a maximum; φ_{ee} and φ_{ae} are close to 60°, so the values of J_{ee} and J_{ae} fall to the left of the minimum at $\varphi = 90°$ (Figure 1).

Distortions in the chair produce alterations in the dihedral angles, and hence in the couplings from which *R* is derived. In the flattened conformation **8**, φ_{aa} and φ_{ae} have decreased, and φ_{ee} has increased. These changes cause decreases in J_{aa} and J_{ee} but an increase in J_{ae} (Figure 1). As a result, the denominator of *R*

---

[8] Cyclohexane is actually[2] slightly flattened toward **8**, but structure **9** is a convenient standard.

Table II
Representative R Values

Entry	Structure	J_{trans}, Hz	J_{cis}, Hz	R	Ψ (nmr), deg	Ψ (X-ray), deg	Source
1		8.4	2.6	3.2	63	62	*a*, *b*
2		8.94	2.95	3.03	63	63	*c*, *d*
3		7.2	2.85	2.53	60	60.5	*a*, *b*
4		8.85	3.55	2.49	60		*e*
5		8.05	3.25	2.48	60		*e*
6		6.34	2.95	2.15	58		*f*
7		6.39	3.05	2.10	57.5		*f*
8		7.2	3.6	2.0	57	59	*a*, *b*
9		6.35	3.21	1.98	57	58	*g*, *h*
10		6.8	3.75	1.81	55	55	*a*, *b*
11		6.85	3.8	1.80	55		*i*
12		6.7	3.8	1.8	55		*i*
13		5.9	3.6	1.6	53		*j*

[a] H. R. Buys, submitted for publication. [b] See footnote *a* for the source of the X-ray diffraction data. [c] E. W. Garbisch, results quoted in ref 11. [d] Microwave results: L. H. Scharpen, J. E. Wollrab, and D. P. Ames, *J. Chem. Phys.*, **49**, 2368 (1968). [e] N. deWolf and H. R. Buys, *Tetrahedron Lett.*, 551 (1970). [f] C. Altona and E. Havinga, *Tetrahedron*, **22**, 2275 (1966). [g] D. Jung, *Ber.*, **99**, 566 (1966). [h] C. Altona and C. Romers, *Acta Crystallogr.*, **16**, 1225 (1963). [i] H. R. Buys and E. L. Eliel, *Tetrahedron Lett.*, 2779 (1970). [j] G. Klose and A. Zschunke, *Z. Chem.*, **10**, 146 (1970).

(eq 3a) becomes larger, and the numerator becomes smaller. The net result is thus a decrease in R. Entries 16–24 in Table I and 10–13 in Table II illustrate molecules that contain flattened segments, as demonstrated by the R value. Such a distortion is present in the flattened chair (**11**) and to a greater extent in twist-boat conformations (**2**). Bis(*exo*-methylene)cyclohexane is an example of a particularly flattened chair (Table I, entry 22, R = 1.42),[9] and 1,4-cyclohexanedione, of a twist boat (entry 23, R = 1.29).

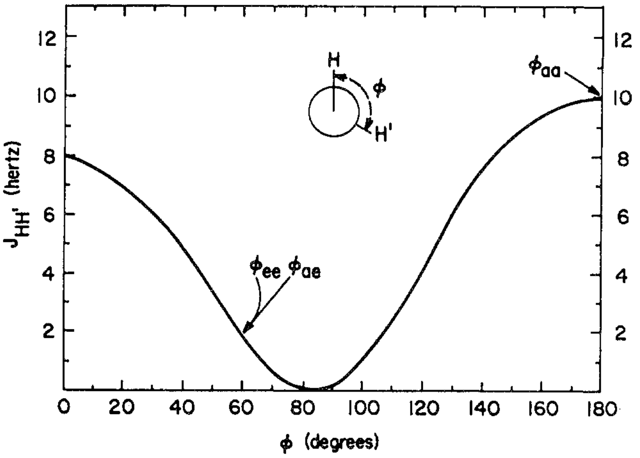
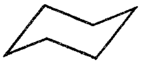


Figure 1. The H–C–C–H vicinal coupling constant as a function of the dihedral angle.

11



12

The puckering distortion produces the opposite results. There are decreases in φ_{aa} and φ_{ee}, and an increase in φ_{ae}, causing decreases in J_{aa} and J_{ae}, but an increase in J_{ee}. The denominator of R therefore becomes smaller, but, because of the compensating effects of J_{aa} and J_{ee}, the numerator is not appreciably changed (actually, the increase in J_{ee} probably dominates). The net result is an increase in the R value, as illustrated by entries 1–6 in Table I and 1–5 in Table II, which contain puckered segments. The puckered chair (**12**) is generally associated with a decreased bond angle within the ring. Thus, puckering is most frequently found in group VI heterocycles,[10] which contain, for example, small C–S–C angles. Puckering is also found in the C_4–C_5 segment of cyclohexene (Table II, entry 2, R = 3.03). Conversely, flattened chairs generally contain one enlarged bond angle, usually caused by the presence of an sp^2 atom. Although bond angle effects frequently dominate, there may be other causes of distortions, such as nonbonded interactions or possibly bond length effects.

In summary, for any CH_2CH_2 fragment in a six-membered ring with an analyzable nmr spectrum, the R value gives a direct, qualitative picture of the dihedral relationships. Assignments of molecular fragments into flattened, undistorted, and puckered classes may be made.

Quantification of the R-Value Method. Although the extent of deviation of R from the region close to 2.0 gives an indication of the degree of distortion,[6] the method remained essentially qualitative until Buys in 1969 presented a quantitative extension, which we will

---

(9) The boat forms are excluded for this molecule by the vibrational spectra (J. B. Lambert and D. S. Bailey, unpublished results reported at the XXI Mid-America Symposium on Spectroscopy, Chicago, Ill., June 3, 1970); also see A. Aihara, C. Kitazawa, and F. Iwasaki, *Bull. Chem. Soc. Jap.*, **41**, 1034 (1968).

(10) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.*, **89**, 5921 (1967).

now describe.[11] It is assumed that the XCH_2CH_2Y fragment possesses pseudotrigonal projection symmetry, as illustrated by structures **8**–**10**. The relationships of eq 5 therefore hold between the X–C–C–Y

$$\begin{aligned}\varphi_{aa} &= 120 + \Psi \\ \varphi_{ee} &= 120 - \Psi \\ \varphi_{ae} &= \varphi_{ea} = \Psi\end{aligned} \tag{5}$$

torsional angle Ψ and the various H–C–C–H dihedral angles. Substitution into eq 3a and 4 yields eq 6, in

$$R = \frac{A\cos^2(120 + \Psi) + A\cos^2(120 - \Psi)}{2A\cos^2\Psi} = \frac{3 - 2\cos^2\Psi}{4\cos^2\Psi} \tag{6}$$

which the Karplus factor *A* is no longer present. Solving for cos Ψ gives an expression (eq 7) for Ψ in

$$\cos\Psi = \left(\frac{3}{2 + 4R}\right)^{1/2} \tag{7}$$

terms of the measurable *R*. By this means, a quantitative determination of the dihedral arrangements within the XCH_2CH_2Y fragment may be made. Tables I and II include many such determinations. These quantities refer to structures in solution. Several of these molecules have also been subjected to analysis by X-ray diffraction techniques. The results from the available crystal structure determinations are included in the tables. It may be seen that the X-ray and *R*-value torsional angles Ψ rarely differ by more than 1–2° over the range from 47 to 69°. Such differences are close to the standard deviations for Ψ as measured by diffraction methods.

Buys has pointed out[11] that the rate of change of Ψ with respect to *R* is given by eq 8. Above 60°, Ψ is

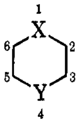
$$\frac{\partial\Psi}{\partial R} = \frac{120\cos^3\Psi}{\pi\sin\Psi}\ (\Psi \text{ in degrees}) \tag{8}$$

less sensitive to changes in *R*. Thus, relatively inaccurate values of *R* can still give good values of Ψ. Near 64°, for example, a change of 0.3 in *R* is required for a variation of 1° in Ψ. The function described in eq 7 changes more rapidly near Ψ = 45°. As a result, in this region a 1° change in Ψ is caused by a change of only 0.05 in *R*. More careful spectral analyses are therefore required for smaller values of *R*. A graph of *R* *vs.* Ψ has been presented in ref 11. Table III should serve as a convenient source of corresponding values of Ψ and *R* for the range *R* = 1.0–4.0.

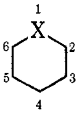
Multiple *R*-Value Determinations. A single *R* value describes the geometry about the one CH_2CH_2 fragment under consideration. Frequently the same segment is repeated by symmetry elsewhere in the molecule. Thus, the entire dihedral geometry of the sixfold symmetric cyclohexane is determined by a single *R* value. Much of the shape of molecules of the type **6** is determined by the one available *R* value because of the plane of symmetry through X and Y. Frequently, a molecule contains several distinct CH_2CH_2 groupings. Under favorable analytical circumstances, an *R* value and hence Ψ may be measured for each segment. In this manner, the shape of the molecule may be mapped from atom to atom around the ring.[12] A detailed picture of the entire conformation can thus emerge.

Table III
Tabular Presentation of Ψ as a Function of *R*

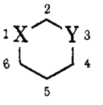
R	Ψ, deg	*R*	Ψ, deg	*R*	Ψ, deg
1.0	45	1.8	55	2.6	60.5
1.1	47	1.9	56	2.7	61
1.2	48.5	2.0	57	2.8	61.5
1.3	50	2.1	57.5	2.9	62
1.4	51	2.2	58	3.1	63
1.5	52	2.3	59	3.4	64
1.6	53	2.4	59.5	3.7	65
1.7	54	2.5	60	4.0	66



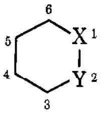
6



13



14



15

The method has been particularly successful with molecules of type **13**. By deuteration[12] or by double irradiation, two *R* values, R_{23} and R_{34}, may be obtained, and the plane of symmetry between positions 1 and 4 assures that the geometry from atoms 2 through 6 is thereby determined. Three such systems have been analyzed fully (Table IV). Thiane (entry 1) has a smoothly puckered shape all the way around the ring. Tellurane 1,1-dibromide (entry 3), on the other hand, is considerably flattened in the 2,3 and 5,6 regions, since the tellurium atom is at the center of a trigonal bipyramid with a considerably enlarged C–Te–C angle. The 3,4,5 portion of the ring is severely puckered in order to compensate for the flattening in the opposite portion of the molecule.

Various sets of *R* values may be obtained for molecules with other types of symmetry—two *R* values from **14**, three from **15**, etc. Two molecules of the type **14** are included in Table IV. Both entries show that the segment near sulfur is slightly puckered, but the segment near oxygen is relatively undistorted. The only limit to the multiple *R*-value method is the nmr spectrum itself. If the protons are not chemically shifted enough to permit analysis, the method cannot be applied.

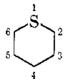
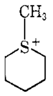
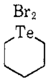
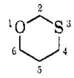
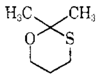
Scope of the *R*-Value Method. The *R* value may be meaningfully determined only under certain circumstances. It is used to enumerate the structural categories that are acceptable, and the particular limitations associated with each.

---

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

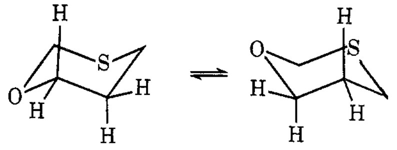
[12] J. B. Lambert and R. G. Keske, *Tetrahedron Lett.*, 4755 (1967).

Table IV
Multiple R-Value Determinations

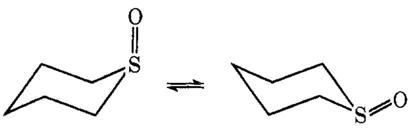
Entry	Molecule	Segment	J_{trans}, Hz	J_{cis}, Hz	R	Ψ, deg	Source
1		2, 3	8.51	3.26	2.61	61	*a*
		3, 4	8.47	3.28	2.58	60	
2		2, 3	8.63	3.24	2.66	61	*b*
		3, 4	8.30	3.59	2.31	59	
3		2, 3	7.8	5.2	1.5	52	*a*
		3, 4	9.21	2.56	3.60	65	
4		4, 5	8.6	2.9	2.97	62	*c*
		5, 6	7.45	3.25	2.29	59	
5		4, 5	8.4	3.4	2.5	60	*c*
		5, 6	7.45	3.85	1.94	56	

[a] Reference 12. [b] J. B. Lambert and R. G. Keske, unpublished results. [c] N. deWolf and H. R. Buys, *Tetrahedron Lett.*, 551 (1970).

(*A*) *A CH_2CH_2 Group in a Molecule with Two Rapidly Equilibrating, Equivalent Conformers.* The averaged spectrum gives J_{trans} and J_{cis} directly. The R


(9)

value characterizes the geometry of the frozen conformation. A molecule with two rapidly equilibrating, but nonequivalent, conformers does not give an unambiguous R value. Analysis of the CH_2CH_2 spectrum would give an R that is the average for the two conformational extremes. Thus, at room temperature thiane 1-oxide gives a spectrum that is an average from two conformers (eq 10). A derived R_{23} value

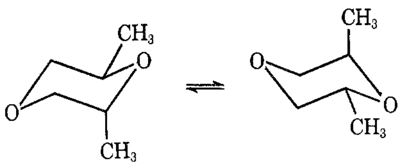

(10)

would characterize the mean geometry of both molecules.

(*B*) *A CH_2CH_2 Group in a Completely Rigid Molecule.* Spectral analysis yields three or four different couplings (J_{aa} and J_{ee}; J_{ae} and J_{ea}, which sometimes are identical by symmetry). These couplings are converted to the R value (eq 3a). If an equilibrium such as the one in eq 10 may be slowed down on the nmr time scale by lowering the temperature, the R values for each conformer may be obtained from the individual spectra. Similarly, if an equilibrium between equivalent forms (eq 9) may be "frozen out," the R value from the ABCD or ABXY spectrum at slow exchange will be identical with that from the AA'BB' or AA'XX' averaged spectrum. Some conformations, such as twist boats, do not "freeze out" even at the lowest available temperatures. The measured R value therefore corresponds to the average over all the individual forms.

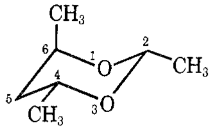
There are two other classes to which the method may be applied somewhat less rigorously.

(*C*) *A CH_2CHR Group in a Molecule with Two Rapidly Equilibrating, Equivalent Conformers.* In such cases, the average J_{trans} and J_{cis} again come directly


(11)

from the spectral analysis. The obtained R value is the average for the two sides of the molecule. In the instantaneous structure each side has its own geometry, so the derived Ψ must be interpreted as a mean. Table V contains four such examples (entries 1–4).

(*D*) *A $CHRCH_2CHR'$ Group in a Completely Rigid Molecule with R and R' Trans to Each Other.* Molecules of which **16** is an example can yield J_{aa}, J_{ee}, J_{ae},


16

and J_{ea}, from which an R value may be calculated. The corresponding torsional angle is actually an average of Ψ_{45} and Ψ_{56}. Anteunis and coworkers have presented several analyses of such molecules (Table V, entry 5).[13] Flexible molecules of this sort are also acceptable.

Further possible classes of molecules to which the R-value method may be applied will be discussed in the last section, and others may yet be found.

Limitations. The R-value method remains valid so long as electronegativity enters multiplicatively and equivalently into the averaged coupling constants. This condition has been found to hold for all cases in the usual range of electronegativities.[5b–d,6] There is some chance that it may not hold for extremely electropositive elements,[14] since the relationship between coupling constant and electronegativity may assume a different form over the wider range. Experiments to test this possibility are underway in our laboratories.

The vicinal coupling depends not only on the H–C–C–H dihedral angle and on substituent electronegativity but also on the H–C–C bond angles (θ) and the C–C bond length (b).[5b] Since these factors are contained in the A term of the Karplus expression (eq 4), which is removed in the calculation of R, their influence may be minimal. Nonetheless, almost all cases studied have

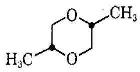
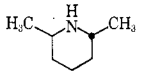
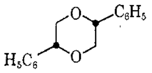
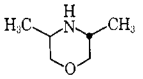
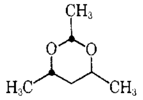
---

(13) J. Gelan, G. Swaelens, and M. Anteunis, *Bull. Soc. Chim. Belg.*, **79**, 321 (1970).

(14) T. Schaefer and H. M. Hutton, *Can. J. Chem.*, **45**, 3153 (1967).

Table V

R Values from CH_2CHR Fragments

Entry	Molecule	J_{trans}, Hz	J_{cis}, Hz	R^a	Ψ,^{a} deg	Source
1		5.7	2.6	2.2	58	*b*
2		6.6	3.2	2.1	57.5	*b*
3		5.7	3.09	1.84	56	*b*
4		5.80	3.36	1.73	55	*b*
5		6.16	3.66	1.68	54	*c*

[a] The average over the two sides of the ring. [b] Taken from ref 11. [c] Reference 13.

had relatively similar values for θ and b. So long as applications are made only to six-membered rings, these factors should remain constant. Investigations of torsional angles in nonplanar four-membered rings, for example, might require further scrutiny of the effects of changes in θ and b.

The above limitations apply to the theoretical foundations for the R value. The only practical limit to measurement of an R value is the availability of the coupling constants. The spectra involved are usually AA′BB′, AA′XX′, ABCD, or ABXY, which for the most part may be readily analyzed. It should be emphasized that only J_{trans} and J_{cis} are needed from the spectra. The geminal couplings need not be determined, and frequently their sum is impossible to determine. Knowledge of their difference, however, is usually a necessary part of the analysis. Normally, computer techniques are used for spectral analysis, but for most cases the analyses may be done by hand. Analysis can prove impossible if the spectrum is too closely coupled or if it is deceptively simple. Inaccuracies in the analysis will inevitably lead to unreliable R values.

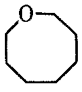
Further limitations may exist in the quantitative extension of the method[11] to give torsional angles. The assumption that the molecules have pseudotrigonal projection symmetry, expressed by eq 5, is basic to the derivation of eq 7. Some molecules may not have such symmetry, but small deviations would not be important. Even with larger deviations, the validity of the R value as a qualitative conformational probe is not altered. The main result of the lifting of trigonal symmetry is that J_{ae} and J_{ea} are no longer equal; however, the averaging in J_{cis} circumvents this problem on the qualitative level.

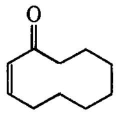
A second possible limiting assumption in the derivation of eq 7 is the neglect of all but the first term in the Karplus equation. Buys pointed[11] out that more complicated expressions such as eq 12 yield unmanageable

$$^3J_{HH} = A\cos^2\varphi - B\cos\varphi + C \qquad (12)$$

expressions for R. Since A/B is about 20 and A/C even larger,[11] the one-term expression is probably quite good. Neglect of the B and C terms gives values of Ψ that are slightly too high,[11] although the differences are still within the error of most determinations of Ψ from diffraction data.

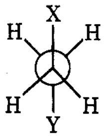
Future Applications. The R value has been found to be valid for almost all types of six-membered rings. It will continue to find its widest applicability in this field. Its utility remains to be proved for rings of other sizes. Experiments have already begun both in our own group and elsewhere[11] on five-membered rings. At present there appears to be no theoretical reason to preclude applications to all common and medium rings. Because of the reservations expressed in the previous section, it is not yet known whether four-membered rings may be included. In theory, the multiple R-value method could provide dihedral angle information for several segments in medium rings such as **17** or **18**,


17

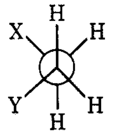

18

although the spectral analysis would be the limiting factor.

Acyclic compounds of the type XCH_2CH_2Y exist in two rotational conformations (**19**, **20**). Rotamer **20**



19



20

has the same set of couplings as do cyclic molecules, so the averaged couplings J_{trans} and J_{cis} may be computed. Interactions between X and Y could cause distortions similar to flattening (**8**) and puckering (**10**) in cyclic molecules. It may be possible therefore to probe distortions in acyclic molecules by the R-value method. Unfortunately, couplings for the individual rotamers are not readily available. A method introduced by Abraham and coworkers[15] permits calculation and identification of the appropriate couplings by a solvent effect. With these couplings, a distortion analysis may be possible.

Conclusions

The R-value method yields a detailed and quantitative picture of the dihedral arrangements within an XCH_2CH_2Y fragment in all types of six-membered rings, independent of the electronegativities of X and Y. The structural data refer to conformations in solution and hence fill a long-standing lacuna in structural chemistry.

(15) R. J. Abraham, K. G. R. Pachler, and P. L. Wessels, *Z. Phys. Chem.* (*Frankfurt am Main*), **58**, 257 (1968).

This work has been supported by the National Science Foundation (Grant GP-9257), the Advanced Research Projects Agency of the Department of Defense through the Northwestern University Materials Research Center, the Petroleum Research Fund administered by the American Chemical Society (Grant 2970-A4,5), and the Alfred P. Sloan Foundation. I am indebted to Dr. Robert G. Keske for valuable discussions during the formulation of the theory. I am also grateful to Dr. H. R. Buys for forwarding much information prior to publication.

The Chemistry of Trichlorosilane–Tertiary Amine Combinations

ROBERT A. BENKESER†

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received September 21, 1970

Trichlorosilane ($SiHCl_3$; bp 33°) is a relatively inexpensive, commercially available chemical. First reported[1] in 1857, its method of preparation has since been considerably refined.[2] Since one of its principal uses is in the preparation of transistor-grade silicon, it can be purchased in high purity.

In 1947 it was reported[3] that trichlorosilane adds to the olefinic linkage of 1-octene, forming *n*-octyltrichlorosilane under the influence of peroxide or ultraviolet light. This was an extremely important discovery since it constituted an entirely new method of forming a silicon–carbon bond.[4] In the intervening years the addition of the $\geqslant$SiH linkage to olefinic and acetylenic bonds has received considerable attention, and, aside from the so-called "direct process,"[5] today constitutes perhaps the most important method of synthesizing organosilicon compounds.

$$CH_3(CH_2)_5CH{=}CH_2 \xrightarrow{SiHCl_3} CH_3(CH_2)_7SiCl_3$$

Two of the many reasons why these $\geqslant$SiH addition reactions are so important is that they are highly stereoselective[6] and that they can be effected under a wide variety of conditions. For example, the additions can be brought about thermally,[7] by noble metals on a solid support (Pt on carbon),[8] or by soluble metal complexes. Much of the intriguing chemistry exhibited by the latter systems has been explored and developed in commercial laboratories.[9]

Prior to 1962, there were only three reports of $\geqslant$SiH additions to olefins catalyzed by tertiary amine. Acrylonitrile was reported[10] to add trichlorosilane under these conditions to yield the β-silyl isomer. 2-Vinylpyridine added trichlorosilane at 160° without the assistance of additional base, and allyl cyanide underwent a similar addition in the presence of pyridine, but in poor yield.[11] It was a report[12] in 1962 that tertiary amines and phosphines could effect the addition of trichlorosilane to olefins and acetylenes which attracted our attention and provided the stimulus for our foray into tertiary amine–trichlorosilane chemistry.

$$CH_2{=}CHCN \xrightarrow[R_3N]{HSiCl_3} Cl_3SiCH_2CH_2CN$$

Interaction between Tertiary Amines and Trichlorosilane. The literature contains numerous reports of amine complexes with silicon compounds[13] of the general formula $SiH_{4-n}X_n$. There can be little doubt that silanes can and do form complexes of varying compositions with amines like pyridine and trimethylamine.

While studying the addition of trichlorosilane to phenylacetylene in the presence of tertiary amines like tri-*n*-propyl- or tri-*n*-butylamine, we detected, by nmr spectroscopy, an interaction between the amine and silane which led us to postulate the existence of a tri-

---

† Recipient of the 1969 Frederic Stanley Kipping Award in Organosilicon Chemistry, sponsored by Dow Corning Corporation.

(1) H. Buff and F. Wöhler, *Justus Liebigs Ann. Chem.*, **104**, 94 (1857).

(2) C. A. Kraus and W. K. Nelson, *J. Amer. Chem. Soc.*, **56**, 195 (1934); H. S. Booth and W. D. Stillwell, *ibid.*, **56**, 1529 (1934); A. G. Taylor and B. V. Walden, *ibid.*, **66**, 842 (1944); F. C. Whitmore, E. W. Pietrusza, and L. H. Sommer, *ibid.*, **69**, 2108 (1947).

(3) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, *ibid.*, **69**, 188 (1947); see also H. C. Miller and R. S. Schreiber, U. S. Patent 2,379,821 (1945).

(4) See E. G. Rochow, "Introduction to the Chemistry of the Silicones," Wiley, New York, N. Y., 1946, pp 19–30, for a review of the synthetic methods then available.

(5) E. G. Rochow, *J. Amer. Chem. Soc.*, **67**, 963 (1945); U. S. Patent 2,380,995 (1945).

(6) R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *J. Amer. Chem. Soc.*, **83**, 4385 (1961).

(7) A. J. Barry, L. DePree, J. W. Gilkey, and D. E. Hook, *ibid.*, **69**, 2916 (1947).

(8) G. H. Wagner, U. S. Patent 2,637,738 (1953); J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Amer. Chem. Soc.*, **79**, 974 (1957).

(9) J. W. Ryan and J. L. Speier, *ibid.*, **86**, 895 (1964); A. J. Chalk and J. F. Harrod, *ibid.*, **87**, 16, 1133 (1965).

(10) S. Nozakura and S. Konotsune, *Bull. Chem. Soc. Jap.*, **29**, 322 (1956).

(11) S. Nozakura, *ibid.*, **29**, 784 (1956).

(12) R. A. Pike, *J. Org. Chem.*, **27**, 2186 (1962).

(13) U. Wannagat, R. Schwarz, H. Voss, and K. G. Knauff, *Z. Anorg. Allg. Chem.*, **277**, 73 (1954); A. B. Burg, *J. Amer. Chem. Soc.*, **76**, 2674 (1954); H. J. Campbell-Ferguson and E. A. V. Ebsworth, *J. Chem. Soc. A*, 1508 (1966), 705 (1967).