Tetrahedron Letters No.47, pp. 4755–4758, 1967. Pergamon Press Ltd. Printed in Great Britain.

QUALITATIVE STRUCTURAL CHEMISTRY IN SOLUTION. THE COMPLETE R-VALUE ANALYSIS OF SIX-MEMBERED RINGS

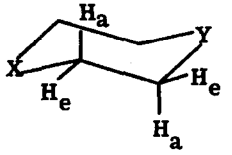
Joseph B. Lambert and Robert G. Keske[1]

Department of Chemistry
Northwestern University
Evanston, Illinois 60201

(Received in USA 14 August 1967)

Electron diffraction, microwave spectroscopy, and X-ray crystallography have traditionally been the methods of choice for conformation-structure determination in the gas and the solid phases. Unfortunately lacking has been an adequate method for obtaining structural information in the isotropic liquid phase. Recently, we introduced a qualitative method for the assessment of certain aspects of the conformations of six-membered rings.[2] The original study was limited to molecules of the type I, in which the ratio (R) between the average J_{trans}

I



$$J_{trans} = {}^1/_2(J_{aa} + J_{ee})$$
$$J_{cis} = {}^1/_2(J_{ae} + J_{ea})$$

and the average J_{cis} was found to be diagnostic for the conformation of the ring and independent of the electronegativities of X and Y. The conclusions of the study are summarized in Table I.

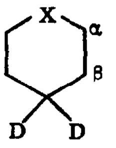
TABLE I.

The Single R-Value Criteria

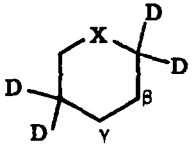
$R=J_{trans}/J_{cis}$	Conformation	φ_{ee}[a]
1.9-2.2	Cyclohexane-like chair	$\sim 60°$[b]
>2.5	Puckered chair	$<60°$
<1.8	Flattened chair or flexible form	$>60°$

[a] The dihedral angle between the vicinal equatorial protons. [b] If cyclohexane had the diamond structure, this number would be exactly 60°; the actual value is probably somewhat larger.

Since the R value can only determine the dihedral relationships about the two C_α-C_β bonds, the conformation of the entire molecule cannot always be determined.[2] If, however, one considers the pentamethylene rings [II, $(CH_2)_5X$], spectral analysis of the appropriately deuterated species will yield two independent R values, one between the atoms of C_α and C_β



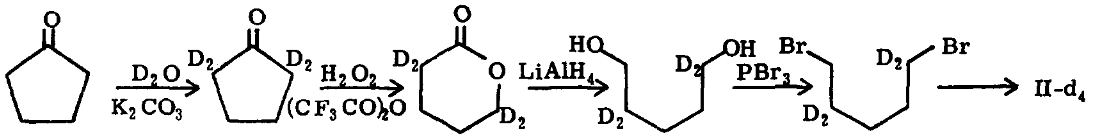
II-4,4-d_2



II-2,2,5,5-d_4

($R_{\alpha\beta}$, from II-d_2) and another between those of C_β and C_γ ($R_{\beta\gamma}$, from II-d_4). We have found that this pair of numbers may be conjoined to yield a nearly complete conformational description of the ring. In this preliminary account of our work, we describe the double R-value analysis of thiane[3] (II, X = S) and 1,1-dibromotellurane[2,4] (II, X = $TeBr_2$).

The synthesis of the 1,5-dibromopentane precursor of II-d_2 has been described previously.[2] Baeyer-Villiger oxidation of cyclopentanone-2,2,5,5-d_4, followed by lithium aluminum hydride reduction of the resulting lactone, yields 1,5-pentanediol-1,1,4,4-d_4, which may be

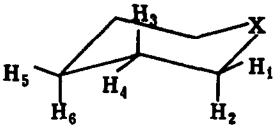


converted to the dibromide progenitor of II-d_4. Spectra of thiane-d_2 and -d_4 and of 1,1-dibromotellurane-d_2 and -d_4 were recorded at room temperature in dilute methylene chloride solution on a Varian A-60 spectrometer with simultaneous irradiation at the frequency of the deuterium resonance. Analysis of the AA'BB' patterns was accomplished by the method of Swalen and Reilly[5] on the CDC-3400 computer with the Calcomp plotting accessory.

In Table II we have listed the spectral parameters determined at room temperature, for which ring inversion should be NMR-fast. The values of $R_{\alpha\beta}$ and $R_{\beta\gamma}$ for thiane are almost equal. Their magnitudes (~2.6) indicate that φ_{ee} has diminished somewhat all around the ring. This puckering distortion is the same as that described for dithiane;[2] previous data for thiane[6] could not yield a clear conformational picture. For 1,1-dibromotellurane, $R_{\alpha\beta}$ is rather small

TABLE II.

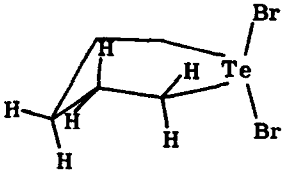
The Complete Analysis of Thiane and 1,1-Dibromotellurane



	Thiane (X = S)	1,1-Dibromotellurane (X = TeBr$_2$)
$\Delta\nu(\alpha,\beta)$	48.55 ± 0.1 hertz	88.11 ± 0.1 hertz
$\Delta\nu(\beta,\gamma)$	12.93	20.10
$\Delta J_{gem}(\alpha,\beta)$	0.0	3.5[a]
$\Delta J_{gem}(\beta,\gamma)$	0.0	0.0
$J_{13} = J_{24}$	3.26	5.2[a]
$J_{14} = J_{23}$	8.51	7.8[a]
$J_{35} = J_{46}$	3.28	2.56
$J_{36} = J_{45}$	8.47	9.21
$R_{\alpha\beta}$	2.61	1.5
$R_{\beta\gamma}$	2.58	3.60

[a]The accuracy for these quantities is probably ±0.2 hertz.

(1.5) and $R_{\beta\gamma}$ is quite large (3.6). The molecule has apparently assumed a conformation in which part of the ring is flattened and part is considerably puckered.



These two examples serve to demonstrate the utility of the double R-value method. Criteria for differentiation among the various conformational possibilities for the pentamethylene rings may now be stated through enumeration of the expected R-value pairs. It should be recalled that, in general, any R value less than about 1.8 indicates a widening of φ_{ee} and (for the chair) a flattening of the ring, whereas a value greater than about 2.5 indicates a closing of φ_{ee} and a puckering of the ring. Four conformational classes may be delineated. (1) If both $R_{\alpha\beta}$ and $R_{\beta\gamma}$ are 1.9-2.2, the ring is rather close to the "perfect chair" of cyclohexane. (2) If both quantities are considerably larger than 2.2, the ring is substantially puckered. (3) If $R_{\alpha\beta}$ is small, but $R_{\beta\gamma}$ large (or *vice versa*), part of the ring is flattened, and part puckered. (4) If both R values are small, the molecule is either "doubly flattened" or in the flexible family.[7] Even though individual twist forms can have R values greater than 2.0, the averaging of dihedral angles through pseudorotation will always bring both $R_{\alpha\beta}$ and $R_{\beta\gamma}$ to less than 2.0.[8] It was stated in the original work[2] that an R value less than 1.8 for I could not distinguish between the flattened chair and the flexible manifold. For molecules II, however, such a differentiation becomes possible by the above-outlined consideration of $R_{\beta\gamma}$.

Although these general rules can be utilized as diagnostics for conformational distortions, borderline cases will undoubtedly be encountered. The principal shortcoming of the R-value empiricism is that only the qualitative nature, and not a quantitative assessment of the distortions is available.[9]

Acknowledgments. This work was supported by the National Science Foundation (Grant GP-6611) and by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-A4, 5). The authors are indebted to Dr. M. I. Levenberg of Abbott Laboratories for numerous 100-MHz spectra and to Dr. E. W. Garbisch, Jr., of the University of Minnesota for the generous use of his deuterium irradiation equipment.

REFERENCES

1. National Science Foundation Undergraduate Fellow, 1965-1967. Present address: Iowa State University, Ames, Iowa.
2. J. B. Lambert, *J. Am. Chem. Soc.*, **89**, 1836 (1967).
3. J. B. Lambert and R. G. Keske, *J. Org. Chem.*, **31**, 3429 (1966).
4. G. T. Morgan and H. Burgess, *J. Chem. Soc.*, 324 (1928).
5. J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).
6. J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Am. Chem. Soc.*, **89** (in press).
7. The doubly flat form may invariably be unstable with respect to the twist forms.
8. To be convinced, one must examine models of the entire continuum, or fleet, or boat forms, then assign an R value to each of the six twist forms, and effect an averaging appropriate to the substitution on X.
9. A method of conformational assessment has been described that is more quantitative, but less general than ours; see C. Altona, H. R. Buys, H. J. Hageman, and E. Havinga, *Tetrahedron*, **23**, 2265 (1967).