ing very similar. The deposition could be explained by assuming adsorption of insoluble hydroxo forms of zinc onto the platinum foil.

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The Hydrogen Bond. II. The Intramolecular Bond in Cyclic 1,2-Diols

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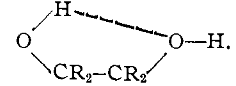
The value of $\Delta\nu$, which is a measure of the length of the hydrogen bond, has been determined for a number of *cis* and *trans* cyclic 1,2-diols. The relationship between ring size and $\Delta\nu$ for both the *cis* and *trans* series is shown. In rings smaller than cyclodecane OH groups are closer together in the *cis* than in the *trans* diols. In rings larger than cyclodecane the OH groups of the *trans* isomer are closer together than those of the *cis*. Some conclusions are drawn concerning the constellation of cyclic compounds, and evidence is adduced which supports H. C. Brown's I-strain theory of the chemical reactivity of cyclic compounds.

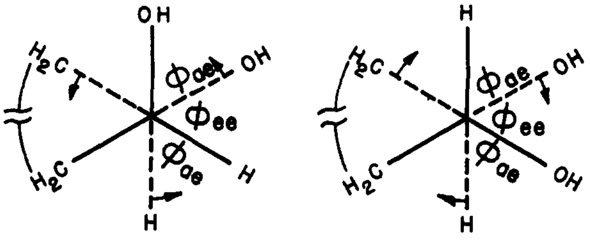
In part I of this series,[1] it was shown that many dihydroxy compounds in dilute solution in carbon tetrachloride have two OH bands in the three-micron region. The higher frequency band is due to the free OH group and the lower frequency band is due to the bonded OH, indicating that these compounds exist in the form



$$\overset{\diagup H \cdots\cdots \diagdown}{O \qquad\qquad O{-}H.}\atop{\diagdown CR_2{-}CR_2 \diagup}$$

The separation between the two bands, $\Delta\nu$, was found to increase as the length of the hydrogen bond decreases, thus in a series of closely related compounds where polarity differences are small, the observed values of $\Delta\nu$ can be used as a measure of the distance between the OH groups. In the work to be described here, this technique has been applied to a study of cyclic diols in which the H–O distance is determined by the constellation of the ring.[2]

The orientation of the exocyclic bonds around an endocyclic C–C bond is conveniently described by the angle ϕ which is defined as the angle formed by two exocyclic bonds as the observer looks down the axis of the C–C bond. This is illustrated for the cyclic 1,2-diols in Fig. 1 where the solid lines represent the bonds of carbon atom number 1 and the dashed lines represent the bonds of carbon number 2. The C–C bond is perpendicular to the plane of the paper. The angle that is formed by an axial and an equatorial bond[3] will be called ϕ_{ae}, and the angle formed by two equatorial bonds will be called ϕ_{ee}.



cis. *trans.*

Fig. 1.

The positions of the OH bands of the *cis* and *trans* isomers of cyclic 1,2-diols containing 5, 6, 7, 8, 9, 10, 12 and 16 carbon atoms were carefully determined. The values of $\Delta\nu$ are shown in Table I.

In using these data to draw conclusions concerning the constellation of the molecules studied, it is necessary to assume that (a) differences in $\Delta\nu$ between members of the series are due to differences in H–O distance, and (b) the bond angles and distances in the portion of each molecule containing the grouping –CHOH–CHOH– are the same. This means that the differences in H–O distance are due to differences in ϕ_{ae} for the *cis* diols and in ϕ_{ee} for the *trans* diols.

TABLE I

BAND SEPARATION OF CYCLIC 1,2-DIOLS

Compound, -1,2-diol	$\Delta\nu$ in cm.$^{-1}$	ϕ_{ae}, deg.	ϕ_{ee}, deg.
cis-Cyclopentane	61[a]	0	
trans-Cyclopentane	0[a]		<120
cis-Cyclohexane	38	50	
trans-Cyclohexane	33		60
cis-Cycloheptane	44	42	
trans-Cycloheptane	37		51
cis-Cyclooöctane	51	33	
trans-Cyclooöctane	43		44
cis-Cyclononane	49	36	
trans-Cyclononane	45		41
cis-Cyclodecane	44	42	
trans-Cyclodecane	45		41
cis-Cyclododecane	38	50	
trans-Cyclododecane	51		33
cis-Cyclohexadecane	..[b]	..	
trans-Cyclohexadecane	50		34

[a] Values taken from previous paper.[1] [b] Each band here was a doublet making it impossible to obtain an unambiguous value for $\Delta\nu$.

Using the methods of trigonometry, the relationship between ϕ and the H–O distance was calculated and is shown graphically in Fig. 2. It was as-

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(1) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(2) The term constellation is used to denote the geometric forms of cyclic compounds which arise by rotation around the C–C bonds, thus the chair and the boat forms of cyclohexane are possible constellations of this molecule: V. Prelog, *J. Chem. Soc.*, 423 (1950).

(3) It has been recommended that the two types of exocyclic bonds of cyclohexane, which have been previously called ε and K by some, and polar and equatorial by others, now be called axial and equatorial. This new nomenclature will be used here; D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Science*, **119**, 49 (1954).

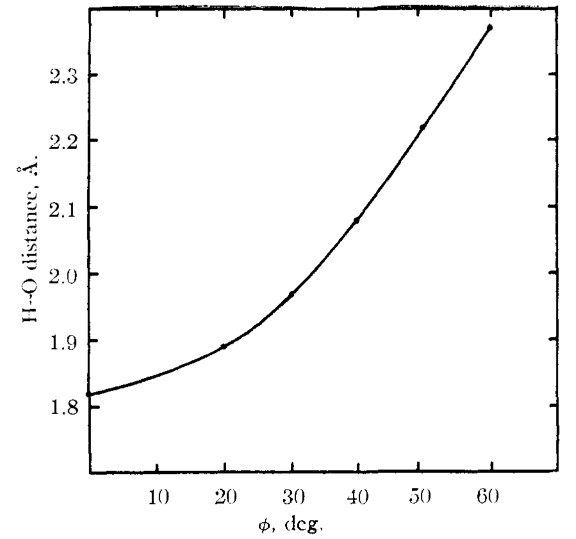


Fig. 2.—H–O distance *versus* ϕ. The following values were used in calculating the H–O distance: C–C, 1.54; C–O, 1.42; O–H, 0.96; O–C–C angle, 109° 28′; C–O–H angle, 108°.

sumed in these calculations that the orientation of the OH group around the C–O bond is such that the H–O distance is a minimum. The observed values of $\Delta\nu$ were converted to H–O distances by the relationship given in the previous paper,[1] and the H–O distances were expressed in terms of the angle ϕ. These values are shown in Table I. Because of the assumptions on which the relationship between $\Delta\nu$ and H–O distance are based,[1] no claim is made for the absolute accuracy of the values of ϕ, nevertheless it is felt that they represent in a semiquantitative manner the variation of ϕ with ring size.

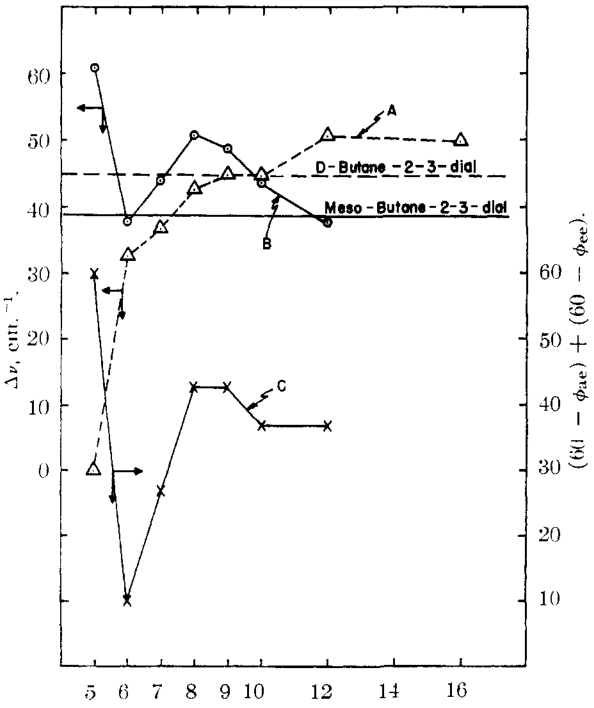
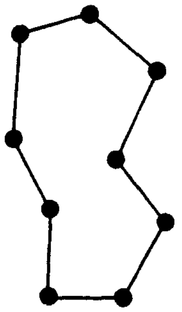
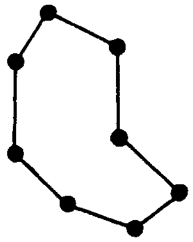


Fig. 3.—Curve A, *trans* diols; curve B, *cis* diols; curve C, $(60° - \varphi_{ae}) + (60° - \varphi_{ee})$.

The relationship between $\Delta\nu$ and ring size is shown graphically in Fig. 3. In the *trans* series of compounds, $\Delta\nu$ increases with increasing ring size and reaches a limiting value at cyclododecane. This limiting value is slightly greater than the $\Delta\nu$ of D-butane-2,3-diol which is the open chain analog of the cyclic *trans* diols. In the *cis* series of compounds the curve is quite irregular. It goes through a minimum at C_6, through a maximum at C_8, and appears to reach a limiting value at C_{12} which is the same as $\Delta\nu$ of the open chain analog, *meso*-butane-2,3-diol. In rings containing less than 10 carbon atoms the *cis* substituents are closer together than the *trans*. In rings containing more than 10 carbon atoms, the *trans* substituents are closer than the *cis*.

For the H–O distance to be decreased in the *cis* series of compounds from what it is in cyclohexane the rotation around the C–C bond is such as to make the ring more planar as shown in Fig. 1, leading ultimately to the constellation in which $\phi_{ae} = 0$ and four contiguous carbon atoms are coplanar as in cyclopentane. The extent to which such a constellation can be achieved appears to be greater for the 8- and 9-membered rings than for the other sized rings. It is possible to picture constellations for cycloöctane and for cyclononane in which $\phi_{ae} = 0$ and in which the normal angles for the C–C bonds prevail as shown below. The fact that the observed values of $\Delta\nu$ for these diols correspond to angles of 33 and 36° indicate that these constellations are not the correct representation of these molecules. These constellations require a close approach of carbon atoms 1 and 5 in cycloöctane and of 1 and 6 in cyclononane, when numbered as shown above. The OH bands of the *cis* and *trans* isomers of cyclooctane-1,5-diol and of cyclonononane-1,6-diol have been examined. In each case only one OH band was observed, indicating that there is no intramolecular hydrogen bond in these diols.





To reduce the H–O distance of the *trans* diols by rotation around the C–C bond, the ring must be made more puckered as shown by the arrows in Fig. 1. As might be expected, the tendency to achieve a more puckered constellation increases with increasing size of the ring until the limiting value is reached at C_{12}. At first glance it might appear anomalous that the H–O distance in the larger rings is smaller for the *trans* diols than for the *cis* compounds. This is only because one is more familiar with the chemistry of small ring compounds in which *cis* substituents are closer than *trans*. The smaller H–O distance in the *trans* diols of the larger rings can be explained in the following manner. The hydrogen bond, being an attractive force between the two OH groups, tends to decrease ϕ_{ae} in the case of the *cis* diols and to decrease ϕ_{ee} in the case of the *trans* diols. A decrease in ϕ_{ae} brings the methylene groups closer together, whereas a decrease in ϕ_{ee} brings the methylene groups closer to hydrogen atoms. Because the methylene group is larger than a hydrogen atom the repulsion between two methylene groups is larger than the repulsion between a methylene and a hydrogen, hence for a given expenditure of energy ϕ_{ee} can be made smaller than ϕ_{ae}. In rings smaller than cyclodecane the requirement that the normal carbon bond angle be maintained opposes the repulsion of the methylene groups and is the decisive factor in determining the relative values of ϕ_{ee} and ϕ_{ae}.

The stability of a particular constellation is determined largely by two factors. The first is the requirement that the normal bond angles be maintained, and the second is that there be a minimum overlap of the van der Waals radii of the non-bonded atoms. The strain produced by these two factors has been called I-strain.[4] In general, the latter requirement is best met when all the ϕ's are 60°. In cyclohexane both requirements are met perfectly, but in many other rings the former requirement causes one or more of the ϕ's to deviate from 60°. In the case of the cyclic 1,2-diols a decrease in ϕ will be accompanied by an increase in stability due to the strengthening of the hydrogen bond, hence the OH groups of the *cis* diols will be attached to the C–C group which has the smallest ϕ_{ae}, and the OH groups of the *trans* diols will be attached to the C–C which has the smallest ϕ_{ee}. Thus we know the orientation around the two C–C bonds of each ring. For example, from the data in Table I we can conclude that the constellation of the cyclooctane ring is such that the smallest ϕ_{ae} is no less than approximately 33° and the smallest ϕ_{ee} is no less than approximately 44°. A complete description of the constellation of a ring would require the knowledge of ϕ_{ae} or ϕ_{ee} associated with each C–C bond.

An attempt will now be made to correlate the data in Fig. 3 with chemical reactivity. The relationship between chemical reactivity and ring size for two different types of reactions is shown in Fig. 4. Curve A, taken from the work of V. Prelog,[2] shows the effect of ring size on the equilibrium constant for the dissociation of cyclic cyanhydrins,

$$(\mathrm{CH_2})_n\mathrm{C(OH)CN} = (\mathrm{CH_2})_n\mathrm{C{=}O} + \mathrm{HCN}.$$

Curve B, taken from the work of Brown and Borkowski,[4] shows the effect of ring size on the rate constant for the unimolecular solvolysis of methyl cycloalkyl chlorides. The similarity between the curves in Fig. 4 and the curve for the *cis* compounds in Fig. 3 is so striking that it strongly suggests a common basis of explanation, namely, the variation of ϕ. The observed effect of ring size on chemical reactivity has been explained by H. C. Brown[4] on the basis of I-strain. Those reactions will go more readily which are accompanied by a decrease in I-strain. The conversion of cyclohexanone to its cyanhydrin is accompanied by a decrease in I-strain, whereas the same reaction with cyclopentanone is accompanied by an increase in I-strain, hence the former equilibrium constant for the dissociation of the cyanhydrin should be the smaller as shown in Fig. 4. Similarly, in the S_N1 reaction in which the rate-determining step is the formation of a carbonium ion, there will be a much larger increase in I-strain of the cyclohexyl compound than of the cyclopentyl compound, hence the former should react more slowly.

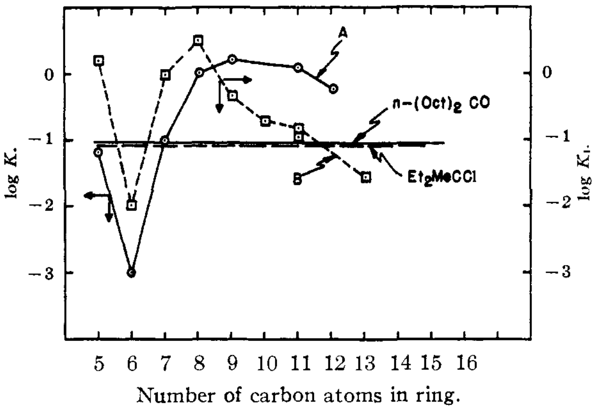


Fig. 4.—Curve A, equilibrium constant for the reaction $(\mathrm{CH_2})_n\mathrm{C(OH)CN} \rightleftarrows (\mathrm{CH_2})_n\mathrm{C{=}O} + \mathrm{HCN}$. Curve B, first-order rate constant for the solvolysis of $(\mathrm{CH_2})_n\mathrm{CMeCl}$.

Let us now consider how I-strain, insofar as it is produced by the overlap of van der Waals radii of non-bonded atoms on adjacent carbon atoms, is related to the values of ϕ_{ae} and ϕ_{ee} given in Table I. As stated earlier, I-strain is a minimum when $\phi = 60°$, so that the deviation of the observed ϕ_{ae} and ϕ_{ee} from 60° will be a measure of I-strain. In Fig. 3, curve C, the term $(60 - \phi_{ae}) + (60 - \phi_{ee})$ is plotted against ring size. The similarity between this curve and the curves in Fig. 4 supports Brown's I-strain theory and substantiates the belief that the overlap of the van der Waals radii of non-bonded atoms makes a major contribution to the I-strain. The I-strain will be the summation of the effects produced by the orientation around each of the C–C bonds whereas the data in Table I relate to only two C–C bonds of each ring. Since the smallest ϕ_{ae} and ϕ_{ee} will make the largest contribution to the I-strain, it is to be expected that the term used in Fig. 3 curve C will be an approximate measure of I-strain.

The rate of oxidation of glycols by lead tetraacetate according to the equation

$$\mathrm{RCHOH{-}CHOHR} + \mathrm{Pb(OAc)_4} = 2\mathrm{RCHO} + 2\mathrm{AcOH} + \mathrm{Pb(OAc)_2}$$

was believed at one time to depend upon the distance between the OH groups. This belief was based upon the observations that the rate of oxidation of the *cis* 1,2-diols of cyclopentane and cyclo-

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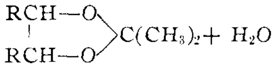
[4] H. C. Brown and M. Borkowski, THIS JOURNAL, **74**, 1894 (1952).

hexane is greater than that of the *trans* isomers.[5] The rates of oxidation of certain cyclic glycols were taken from the literature[6] and are shown in Table II. In four of the six pairs of isomers for which data are available, the isomer in which the OH groups are closer together also reacts more quickly with $Pb(OAc)_4$. A comparison of the data with the data in Table I shows that there is no simple correlation between the reaction rates and $\Delta\nu$, which indicates that the distance between the OH groups is not the major factor that determines the reaction rate.

The ability of 1,2-diols to react with acetone to form cyclic ketals according to the equation

$RCHOH—CHOHR + (CH_3)_2CO =$



appears to be related to the distance between the OH groups. Only qualitative data could be found in the literature. These data are given in the last column of Table II, where + indicates that reaction takes place and − indicates that no reaction takes place. Comparison of these data with Table I shows that compounds with a $\Delta\nu$ greater than 36 react with acetone and compounds with a $\Delta\nu$ less than 34 do not react.

TABLE II

REACTIVITY OF CYCLIC DIOLS

Compound, -1,2-diol	With $Pb(OAc)_4$[a]	With acetone
cis-Cyclopentane	40,000	+
trans-Cyclopentane	12.8	−
cis-Cyclohexane	5	+
trans-Cyclohexane	0.2	−
cis-Cycloheptane		+
trans-Cycloheptane		+
cis-Cyclooöctane		+
trans-Cyclooöctane		+
cis-Cyclononane	2.87	+
trans-Cyclononane	20.7	+
cis-Cyclodecane	2.6	+
trans-Cyclodecane	100	
cis-Cyclododecane	1.27	
trans-Cyclododecane	73.6	
cis-Cyclohexadecane	7.84	
trans-Cyclohexadecane	91.2	

[a] The figures in this column are the second-order rate constants for reaction in glacial acetic acid, k^{20} (mole^{-1} l. min.$^{-1}$).

Experimental.—The purity of the diols was determined by their melting points. In each case the melting point checked with that in the literature. Solutions of 0.005 molarity or less for the less soluble compounds in reagent grade CCl_4, which had been dried and distilled over P_2O_5, were used. The absorption curves were obtained with a Perkin-Elmer double-beam spectrometer, which was equipped with a LiF prism, and which was purged with dry nitrogen while in use. The slit width was 25 microns and the cell length was 2 cm. A 2-cm. cell containing pure CCl_4 was used in the reference beam. The band widths at minimum transmission varied from less than 1 to 5 cm.$^{-1}$. The center of the band at the transmission minimum was chosen as the position of the band. The value of the % transmission at the transmission minimum varied from 15 to 40%. In each case there was no large difference between the intensities of the free OH and the bonded OH bands.

The frequencies of all the compounds studied are given in Table III.

TABLE III

OH BANDS OF CYCLIC DIOLS IN CM.$^{-1}$

Compound, -1,2-diol	Free OH	Bonded OH
cis-Cyclohexane	3626	3588
trans-Cyclohexane	3633	3600
cis-Cycloheptane	3632	3588
trans-Cycloheptane	3626	3589
cis-Cyclooöctane	3635	3584
trans-Cyclooöctane	3631	3588
cis-Cyclononane	3631	3582
trans-Cyclononane	3632	3587
cis-Cyclodecane	3629	3585
trans-Cyclodecane	3633	3588
cis-Cyclododecane	3629	3591
trans-Cyclododecane	3635	3584
cis-Cyclohexadecane	3632, 3626	3591, 3587
trans-Cyclohexadecane	3635	3585
cis-Cyclononane	3627	
trans-Cyclononane	3627	
cis-Cyclooöctane-1,5-diol	3627	
trans-Cyclooöctane-1,5-diol	3627	

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ABERDEEN PROVING GROUND, MD.

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[5] R. Criegee, E. Bucher and W. Walther, *Ber.*, **73**, 571 (1940).

[6] (a) V. Prelog, K. Schenker and W. Kung, *Helv. Chim. Acta*, **36**, 471 (1953); (b) V. Prelog, K. Schenker and H. Gunthard, *ibid.*, **35**, 1598 (1952); (c) the data on the cyclododecanediols and the cyclohexadecanediols were kindly supplied in advance of publication by Professor Prelog.