bromic acid (*p*H 0.7) gives the diaquo complexes having different absorption spectra (Fig. 6). However, if the hydroxoaquo salts are dissolved in water and allowed to stand at room temperature for one hour before acidifying, the resulting diaquo complexes have the same absorption spectrum (Fig. 6). It should likewise be noted that this spectrum lies between those of *cis* and *trans* [Co $en_2(H_2O)_2$]Br_3 suggesting that it is an equilibrium mixture of these stereoisomers. These observations of the ease with which *cis* and *trans* [Co en_2H_2OOH]Br_2 rearrange in neutral or slightly alkaline solution as compared to the stability of *cis* and *trans* [Co $en_2(H_2O)$]Br_3 in strongly acid solutions is in accord with findings of Brüll.[24]

It might be expected that analogous compounds of the same configuration would have similar absorption spectra. That this is the case is seen in Figs. 2, 3 and 5. In every instance the propylenediamine complex of known configuration has an absorption spectrum which closely resembles that of the corresponding ethylenediamine salt of the same configuration.

Acknowledgment.—The author takes this opportunity to thank Professor John C. Bailar, Jr., for supplying some of the compounds that were studied and Professor Ralph G. Pearson for valuable suggestions in the interpretation of some of the absorption spectra.

Summary

The absorption spectra of several ions of the type [Ma_4b_2], [Ma_4bc], [$M(AA)_2b_2$] and [$M(AA)_2bc$] have been determined.

It has been shown that absorption spectra data can be applied to establish the configuration of geometric isomers whenever the position of the absorption maxima of the second and third bands are significantly shifted. It is likewise possible to determine the structure of a complex by comparing its spectrum to the spectra of analogous *cis* and *trans* salts.

The *cis* isomers of [$Co(NH_3)_4(NO_2)_2$]$^+$, [Co $en_2(NO_2)_2$]$^+$ and [Co en_2Cl_2]$^+$ have an absorption band at approximately 240 mμ. There is no absorption band at this short wave length for the stereoisomers of either [Co en_2ClSCN]$^+$ or [Co $en_2(SCN)_2$]$^+$.

cis and *trans*-[Co en_2H_2OOH]Br_2 rearrange rapidly in neutral or slightly alkaline solutions to yield an equilibrium mixture of the two isomers.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 3, 1950

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[24] Brüll, *Compt. rend.*, **209**, 630 (1939).

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The Vibrational Spectra of Tetrahydropyran and *p*-Dioxane[1]

BY STANLEY C. BURKET AND RICHARD M. BADGER

In the course of an investigation of the infrared spectra of the carbohydrates it was found that no really thoroughgoing attempts have been made to interpret the spectra of simpler compounds which have structural features in common with them, in particular with the pyranose sugars. The features which we have regarded to be particularly pertinent are (1) the oxygen-containing ring and (2) the presence of many hydroxyl groups attached to a ring. Both of these structural features are found to give rise to strong absorption in the region 8–10μ, which in hydrocarbons is usually relatively transparent, but in the carbohydrates is characteristically opaque.

Our major purpose in the present paper will be to identify the bands which arise from the stretching vibrations of the tetrahydropyran ring. While it is not expected that these bands will occur unshifted in sugar spectra, their identification may be expected to be of assistance in the discussion of sugar spectra. In the carbohydrates the hydrogens which are attached to carbons are predominantly tertiary and bands involving them may be expected to fall at somewhat higher frequencies than C–C or C–O stretchings (*e.g.*, see Rasmussen[1a]), but in tetrahydropyran and *p*-dioxane some of the hydrogen frequencies do lie in this spectral region so that we include a brief treatment of the methylene vibrations.

Our general procedure has been to start from the results of a normal coördinate analysis of cyclohexane by Lu, Beckett and Pitzer (to be published) as reported in an article by Beckett, Pitzer and Spitzer[2] and to extend these results to tetrahydropyran and *p*-dioxane. We have attempted to choose symmetry coördinates for cyclohexane which are probably a reasonable approximation of the normal coördinates and the ring vibrations have been regarded as a first approximation to those in tetrahydropyran and *p*-dioxane, while the approximate form of the hydrogen vibrations has been estimated by considering the effect of removing two or four hydrogens from cyclohexane. Rough relative intensities and activities were then estimated and the most reasonable possible assignments consist-

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[1] This paper is based on work supported by the Bureau of Ordnance, United States Navy, and done under contract with the Office of Naval Research, Contract N6-ori-102, Task Order VI.

[1a] R. S. Rasmussen, *J. Chem. Phys.*, **16**, 712 (1948).

[2] C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

ent with this simplified picture were made. By this procedure we have been able to account for the more intense Raman and infrared bands of tetrahydropyran and *p*-dioxane in such a way as to assign reasonable frequencies to the ring stretching vibrations.

Tentative assignments have previously been made for some of the Raman lines of tetrahydropyran and *p*-dioxane by Kahovec and Kohlrausch,[3] and Ramsay[4] has made simple valence force calculations of the ring frequencies of *p*-dioxane. The infrared spectrum of *p*-dioxane has previously been published by McKinney, Leberknight and Warner[5] and by Ramsay,[4] both of whom examined the vapor as well as the liquid.

The cyclohexane ring is shown in Fig. 1 with the atoms numbered and with the coördinates indicated which will be used in our discussion. The oxygen in tetrahydropyran is taken to be in the 1 position, and the oxygens in *p*-dioxane in the 1 and 4 positions. We assume the chair-form ring throughout for all three compounds. The evidence for the structure of cyclohexane has been summarized by Ramsay and Sutherland,[6] and that for *p*-dioxane by Ramsay.[4]

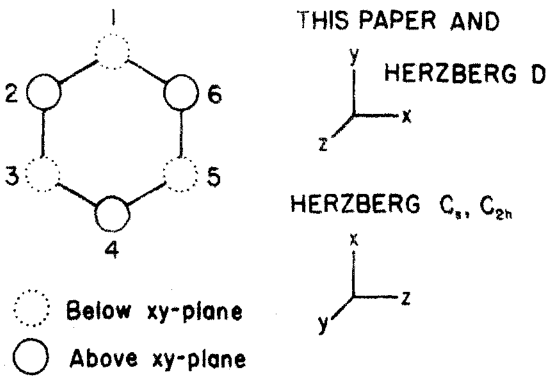

Fig. 1.—Coördinates and numbering of ring atoms as adopted in this paper for cyclohexane, tetrahydropyran and *p*-dioxane. The coördinates used by Herzberg[6] for six-membered rings of the indicated symmetry are also shown.

We will be concerned in our discussion only with the spectral region from about 6 to 14μ so that carbon–hydrogen stretchings and ring bendings will not be included.

Experimental Details

The spectra of liquid cyclohexane, tetrahydropyran and *p*-dioxane shown in Fig. 2 were obtained with a Beckman IR-2 infrared spectrophotometer[7] fitted with rocksalt optics. The wave length scale was not specially calibrated for this investigation, but the uncorrected values which we find for the positions of the bands of cyclohexane and *p*-dioxane are in general within two or three wave numbers of those appearing in the literature.

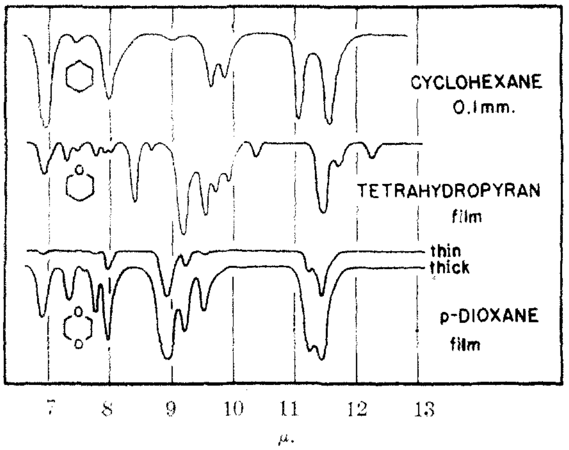

Fig. 2.—Infrared absorption spectra of liquid cyclohexane, tetrahydropyran and *p*-dioxane. The ordinate is transmission.

A list of the frequencies in cm.$^{-1}$ of the infrared bands of tetrahydropyran and *p*-dioxane as shown in Fig. 2 follows, with relative intensities shown in parentheses: tetrahydropyran 818 (3), 856 (4), 875 (8), 969 (3), 1012 (6), 1033 (6), 1050 (8), 1097 (10), 1160 (2), 1202 (7), 1256 (3), 1272 (3), 1296 (3), 1348 (2), 1381 (4), 1451 (5); *p*-dioxane 875 (10), 890 (7), 1020 (0s), 1052 (5), 1086 (6), 1122 (10), 1256 (7), 1290 (5), 1321 (1), 1366 (4), 1453 (6). The strongest band in each spectrum is assigned an intensity of 10. Ramsay[4] assigned somewhat lower intensities to the 875 and 1122 cm.$^{-1}$ *p*-dioxane bands, probably because his samples were thicker than ours.

The cyclohexane was manufactured by Shell Chemical Corporation. It was examined in a 0.1 mm. liquid absorption cell. The excellent agreement with previously published spectra[8,9] shows that its purity is satisfactory.

The tetrahydropyran was du Pont Elchem-596. Its boiling point of 88°, as quoted by du Pont, compares favorably with that of 87.5–88.5° reported by Allen and Hibbert[10] for the pure product which they prepared for electric moment measurements. The spectrum shown in Fig. 2 was obtained by examining a drop of tetrahydropyran pressed between two silver chloride plates; a curve which was obtained by use of the 0.1 mm. liquid absorption cell showed excessive absorption.

The *p*-dioxane was distilled over sodium but was not fractionated. The agreement between our spectra and those previously published[4,5] is excellent. The "thick" film was obtained in the same way as the tetrahydropyran sample and the thin film was obtained by use of rocksalt plates. The silver chloride plates were not suitable for the thin sample because their surfaces were not sufficiently flat and retained too much liquid; the variation in thickness of the thicker sample is not important since we are not concerned with absorption coefficients.

We regard the greatly increasing intensity of absorption in the order cyclohexane, tetrahydropyran and *p*-dioxane as very significant.

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(3) L. Kahovec and K. W. F. Kohlrausch, *Z. physik. Chem.*, **B35**, 29 (1937).

(4) D. A. Ramsay, *Proc. Roy. Soc.* (*London*), **A190**, 562 (1947).

(5) D. S. McKinney, C. E. Leberknight and J. C. Warner, THIS JOURNAL, **59**, 481 (1937).

(6) D. A. Ramsay and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (*London*), **A190**, 245 (1947).

(7) Manufactured by National Technical Laboratories, South Pasadena, California.

(8) G. B. Carpenter and R. S. Halford, *J. Chem. Phys.*, **15**, 99 (1947).

(9) American Petroleum Institute Research Project 44, Infrared Spectrograms, Nos. 17 and 368.

(10) J. S. Allen and H. Hibbert, THIS JOURNAL, **56**, 1398 (1934).

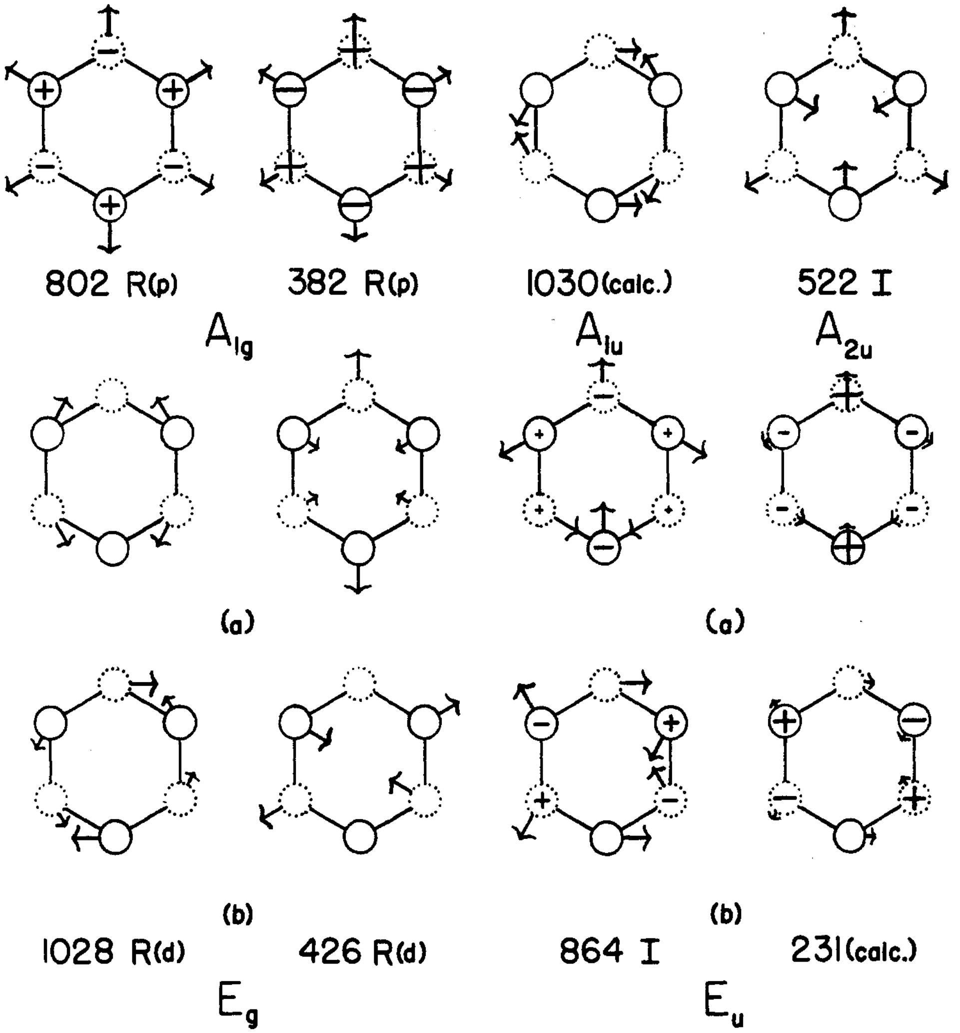

Fig. 3.—Approximate normal vibrations of a puckered X_6 ring of symmetry D_{3d} and assignments in cm.$^{-1}$ for cyclohexane as reported by Beckett, Pitzer and Spitzer.[2] Arrows indicate motion in the *xy*-plane, plus and minus signs motion parallel to the *z*-axis. All symbols are drawn to the same scale in a given vibration or degenerate pair of vibrations. The *z*-components of the motions of the atoms in the E_g vibrations are too small to indicate in the figure; if the magnitude of the longest arrows in the E_g vibrations (*i. e.*, 1 and 4 of E_g(b) stretching and E_g(a) bending) is taken to be unity the *z*-components are as follows for atoms 1 to 6, respectively: E_g(a) stretching, +0.175, +0.0875, −0.0875, −0.175, −0.0875, +0.0875; E_g(b) stretching, 0, +0.152, +0.152, 0, −0.152, −0.152; E_g(a) and E_g(b) bending, the same magnitudes as for the corresponding stretchings, but opposite signs. The *z*-components of the motions of the atoms in the A_{1u} and A_{2u} vibrations are identically zero.

Plausible Forms for the Normal Vibrations of Cyclohexane

Ring Vibrations.—In the present discussion cyclohexane will be treated as though it were an X_6 ring of symmetry D_{3d} (chair-form), and any possible coupling with hydrogen vibrations will be ignored.

Symmetry coördinates of a flat X_6 ring have been given by Herzberg[11] and have been adopted by Ramsay and Sutherland[7] for the ring vibrations of cyclohexane. We have adapted these to the puckered X_6 ring as shown in Fig. 3, and, with the exception of the E_g vibrations, have accepted them as plausible forms, although only the A_{1u} and A_{2u} vibrations are uniquely determined by symmetry. The radial-tangential set of E_g vibrations shown in Fig. 3 are obtained by simply taking the vector sum and difference of those shown by Herzberg and by Ramsay and Sutherland; we have selected these forms for reasons discussed below under the assignment of ring frequencies. The assignments which are reported by Beckett, Pitzer and Spitzer[2] for cyclohexane are shown in Figs. 3 and 4.

Cyclohexane, tetrahydropyran and *p*-dioxane have only one element of symmetry in common,

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(11) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 93.

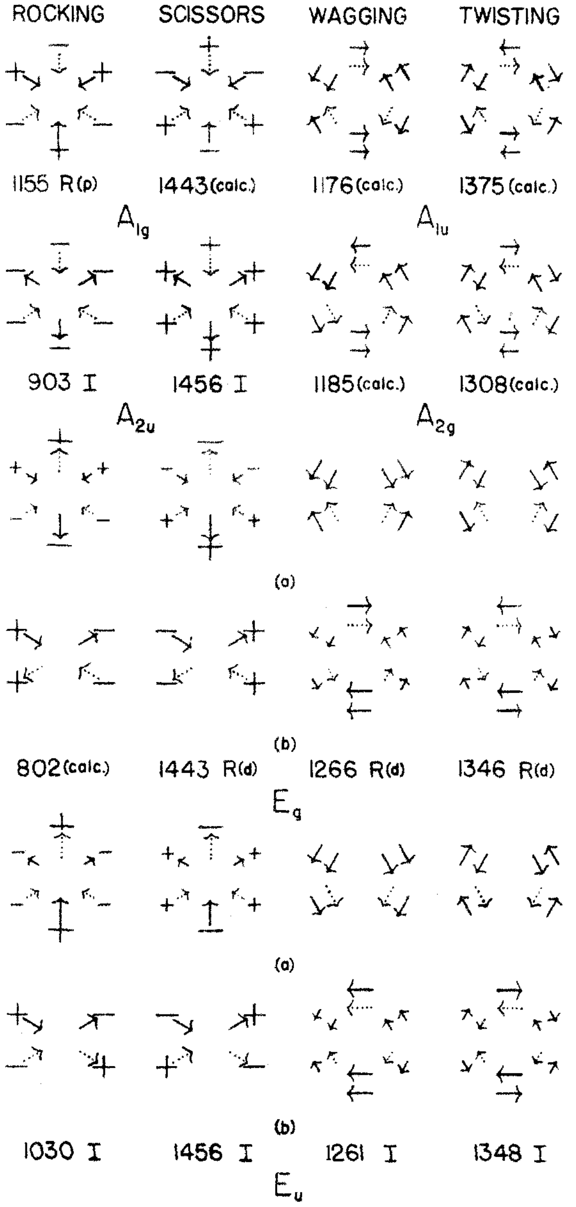

Fig. 4.—Methylene bending vibrations of cyclohexane as determined by the assumptions given in the text, and assignments in cm.$^{-1}$ as reported by Beckett, Pitzer and Spitzer.[2] Peripheral symbols represent the motions of equatorial hydrogens, interior those of polar hydrogens. Dotted interior arrows represent polar hydrogens below the plane of the paper, solid interior arrows those above the plane of the paper. All symbols are drawn to the same scale in a given vibration or degenerate pair of vibrations.

namely, a plane of symmetry. Since all tetrahydropyran and *p*-dioxane vibrations must be symmetric or antisymmetric with respect to this plane, it is necessary to follow Ramsay and Sutherland[6] in choosing for discussion those pairs of degenerate vibrations which meet this condition, so that they may be comparable. The important features of the degenerate vibrations are, for our purposes, not their exact forms, but (1) that the two ring frequencies of each degenerate symmetry class are probably quite different so that we may speak of a stretching and a bending vibration in each class, and (2) that each of the two pairs of degenerate ring stretching vibrations consists of one which involves principally stretching of the 1-2, 1-6, 4-3, and 4-5 bonds and one which involves principally stretching of the 2-3 and 5-6 bonds. The latter type of vibration will be expected to show little change when oxygen is substituted in the 1 and 4 positions, whereas the former will be expected to show relatively great effects.

The forms selected for the A_{1g}, E_g and E_u vibrations are of course completely arbitrary, but the actual forms will, in the absence of coupling with C–H vibrations, be linear combinations of those shown. The forms of the two A_{1g} vibrations as shown in Fig. 3 represent pure stretching and bending, respectively. The forms of the E_g vibrations were selected for reasons described later and the forms of the E_u vibrations were fixed by arbitrarily requiring that during the E_u(a) stretching vibration the 1,2,6- and 3,4,5-planes remain fixed.

Hydrogen Bending Vibrations.—It is customary in discussing the bending vibrations of methylene hydrogens to speak of bending, rocking, wagging, and twisting vibrations.[12] Any such discussion implies the assumptions (1) that there are only negligible interactions between carbon–hydrogen bendings and carbon–carbon stretchings, (2) that there are only negligible interactions between motions of a hydrogen parallel and perpendicular to the plane defined by the three adjacent carbons and (3) that the motions of the methylene hydrogens are either symmetrical or antisymmetrical with respect to that plane.

The above assumptions and the symmetry of the molecule are sufficient to determine the forms of the carbon–hydrogen bending vibrations. The motions of the hydrogens alone, as so determined, are shown in Fig. 4. In many of the vibrations, of course, the ring is required to move also, in order to satisfy the requirements of zero angular and linear momentum; the reader can readily supply such motions.

The Normal Vibrations of Tetrahydropyran and *p*-Dioxane

Plausible Forms.—A set of vibrations which satisfies the orthogonality requirements of *p*-dioxane or tetrahydropyran can be drawn which is so closely similar to that shown in Fig. 3 that it would be difficult to show the differences in a figure. We shall assume that the differences are actually small, and that Fig. 3 can be used as a basis for discussion since the exact forms of the vibrations of tetrahydropyran and *p*-dioxane are not important in the present consideration.

The hydrogen bending vibrations of *p*-dioxane

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(12) See R. S. Rasmussen[1] for definitions. Recently the more descriptive term "scissors" has come into use for "bending" and will be adopted in the present paper.

can be approximated by removing the proper hydrogens from the vibrations shown for cyclohexane in Fig. 4. The resulting vibrations are identified throughout our discussion by the designations of the cyclohexane vibrations, with the symmetry class of the vibrations in *p*-dioxane included in parentheses. The same notation is used for the ring vibrations. The removal of two methylene groups introduces some ambiguity into the notation since one member of each degenerate pair of vibrations may be said to have merged with a non-degenerate vibration as follows: E_g(a) rocking or scissors with A_{1g} rocking or scissors, E_g(a) rocking or scissors with A_{2u} rocking or scissors, E_g(b) wagging or twisting with A_{2g} wagging or twisting, and E_u(b) wagging or twisting with A_{1u} wagging or twisting. We shall arbitrarily adopt the non-degenerate designation.

The removal of one methylene group in going from cyclohexane to tetrahydropyran must necessarily result in a decrease of four in the number of methylene bending vibrations, one of each type and two of each tetrahydropyran symmetry class. This means either that four cyclohexane vibrations have no counterpart among the tetrahydropyran vibrations, or that at least four of the tetrahydropyran vibrations are each related to more than one cyclohexane vibration. This uncertainty in the forms of the methylene vibrations will be discussed below under intensities.

Frequencies.—The introduction of the stronger C–O bonds in place of C–C bonds may be expected to result in general increases in the ring stretching frequencies. The non-degenerate ring stretching vibrations involve all the ring bonds equally so that the change in frequency should not be large in going from cyclohexane to tetrahydropyran to *p*-dioxane. On the other hand, the degenerate vibrations do not involve all the ring bonds to the same extent, as pointed out earlier. One of each pair of degenerate stretching vibrations involves chiefly C–C bonds, in both tetrahydropyran and *p*-dioxane, and should show little change in frequency, whereas the other member of each pair becomes a pure C–O vibration in *p*-dioxane and should show a relatively large shift to higher frequencies.

An exhaustive discussion of possible shifts in the hydrogen frequencies would be exceedingly complex, but consideration of the spatial relationships of the hydrogens indicates that the frequencies are likely to be quite different in tetrahydropyran and *p*-dioxane even in the absence of other effects.

In *p*-dioxane both the 2,6 and 3,5 pairs of polar hydrogens are very close together, probably in van der Waals contact. If Hassel and Viervoll's model[13] is used appreciable distortion of the tetrahedral angles must be assumed in order to avoid overlapping of the van der Waals radii of the polar hydrogens, and in the model proposed by Shand[14] the polar hydrogens are almost, but not quite, in van der Waals contact (assuming that the van der Waals radius of hydrogen is 1.2 Å.[15]). In tetrahydropyran, however, only the 2,6 pair of polar hydrogens is closer together than in cyclohexane and the 3,5 pair of polar hydrogens is farther apart. A simple Tinker Toy or Hirschfelder model will help the reader to visualize the above. In our considerations we have assumed that C–C $\geqslant$ 1.51 Å., C–O $\leqslant$ 1.44 Å., $\angle$ C–O–C < 113° and that all carbon valence angles are tetrahedral.

Rough Estimated Intensities of Tetrahydropyran Bands

All tetrahydropyran vibrations are permitted by symmetry to be active in both the Raman and infrared spectrum. The intensities of the bands will vary widely, however, and we shall indicate below the rather unsophisticated arguments which we have used to predict rough relative intensities. As previously mentioned, the ring vibrations are identified by the designation of the cyclohexane vibration from which they may be regarded as derived; the symmetry class of the vibration in tetrahydropyran is added in parentheses.

Intensities of Raman Lines.—Without knowing the numerical values of the components, α_{ij}, of the polarizability tensor, or of their derivatives with respect to the normal coördinates, α'_{ij},[16] we can nevertheless indicate by use of well-known principles which derivatives will have non-zero values for a given vibration. In the absence of further information one might expect that in general those vibrations which are derived from Raman-active cyclohexane vibrations will give rise to the strongest Raman shifts.

Two Raman shifts of reasonable intensity, prohibited in cyclohexane, may be expected to arise from ring stretching vibrations of tetrahydropyran. One arises from the splitting of the E_g frequency, discussed above, and the other from the fact that the polarizability is not the same in opposite phases of the E_u(a)(A′) vibration. The remaining ring stretching vibrations would be inactive at the intensity level under discussion since the diagonal derivatives are zero, and the orientation of the polarizability ellipsoid is changed only very little so that the off-diagonal derivatives are exceedingly small.

In spite of the uncertainty in the forms of the methylene vibrations of tetrahydropyran mentioned above it seems probable that certain of the cyclohexane vibrations, at least, will have reasonably close counterparts among the tetrahydropyran vibrations, in particular the eight E vibrations which involve only four methylene groups.

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(13) O. Hassel and H. Viervoll, *Acta Chem. Scand.*, 1, 149 (1947). C–C = 1.54 Å., C–O = 1.42 Å., $\angle$C–C–O = 106°, $\angle$C–O–C = 108°.

(14) W. Shand, Jr., Thesis, California Institute of Technology, 1946. C–C = 1.51 ± 0.04 Å., C–O = 1.44 ± 0.03 Å., <C–C–O = 109.5 ± 5°, $\angle$C–O–C = 112.5°, average ring angle = 110.5 ± 2°, 0.94 $\leqslant$ C–O–/C–C $\leqslant$ 0.98.

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1942, p. 189.

(16) The derivative we are discussing, α'_{ij}, is the coefficient of the linear term of the expansion of α_{ij} as a function of the normal coördinate ξ about the equilibrium configuration, *e*, or, briefly, $\alpha'_{ij} = (\partial\alpha_{ij}/\partial\xi)_e$ (Herzberg,[6] p. 244).

and the four A_2 vibrations, which require all the methylene groups to be vibrating in the same sense. Among these the four E_g vibrations will be expected to be active with fair intensity, with the possible exception of the $E_g(b)(A'')$ rocking vibration, which does not appear in the cyclohexane spectrum. There is some question also as to whether the degenerate scissors vibration will split, since its frequency appears to depend mostly on the bending force constant of the individual methylene group, and very little on interactions outside the group.

Of the hydrogen bending vibrations in general we may say that we expect no strong bands which are forbidden for cyclohexane. If a Raman-active cyclohexane vibration is combined with a Raman-inactive cyclohexane vibration to give the form of a tetrahydropyran vibration the resulting band should be weaker than if it were related to the Raman-active cyclohexane vibration alone.

Intensities of Infrared Bands.—The intensity of the infrared band corresponding to a given vibration depends on the magnitude of the changes in the electric moment of the molecule during the vibration. In many cases, particularly when resonance between structures of nearly equal energy but different charge distribution is not important, we may discuss the magnitude of these changes in terms of the motions of formal charges. Such a discussion cannot account for the infrared activity of carbon–carbon stretchings, or methylene twistings, but is probably a satisfactory approximation for the other types of vibrations.

The infrared spectrum of tetrahydropyran shows an appreciably greater difference from cyclohexane than does the Raman spectrum presumably because the introduction of an oxygen atom in place of a CH_2 group has a larger effect on the charge distribution than on the polarizability. Not only does the highly electronegative oxygen atom introduce a formal negative charge in the 1 position but the opposing positive charge is probably to a large extent passed on to the hydrogens so that the intensity of both ring and hydrogen bands should be increased over cyclohexane. This is in line with the experimental fact noted earlier that the intensity of absorption increases markedly in the order cyclohexane, tetrahydropyran, *p*-dioxane.

The negative charge on the oxygen is probably sufficiently large, and enough of the opposing positive charge is probably passed on to the other end of the ring, so that all vibrations which involve motion of the oxygen will have appreciable intensity in the infrared. Thus the very strong $A_{1g}(A')$ ring-stretching Raman line should be accompanied by an infrared band of medium intensity, as should the other ring-stretching Raman lines.

The $A_{2u}(A'')$ stretching vibration, which is inactive in cyclohexane, should be one of the strong bands in the infrared spectrum of tetrahydropyran because the change in moment due to the motion of the oxygen atom is of the same sign as the change due to the motion of the rest of the ring. Both E_u stretching frequencies should be very strong also, for the same reason.

Thus the tetrahydropyran ring may be expected to contribute three infrared bands of moderate to strong intensity, each of which appears also in the Raman spectrum, and three strong infrared bands one of which appears weakly in the Raman spectrum, a total of five new infrared bands as compared with cyclohexane.

Of the hydrogen frequencies we would expect the $A_{2u}(A')$ and $E_u(b)(A'')$ rocking and scissors and the $E_u(a)(A')$ wagging vibrations to give the strongest bands. The activity of the other hydrogen bending bands will depend on the relative amplitudes of the motions of the methylene groups and on the extent to which various cyclohexane vibrations may be regarded to have interacted in giving the forms of the tetrahydropyran vibrations. If the $E_u(b)(A'')$ wagging vibration interacts only a very little with other A'' wagging vibrations it may be expected to give rise to a fairly strong band; if, on the other hand, it has "interacted" extensively its potential intensity will be distributed among two or more bands. If any twisting vibrations are active it would probably be those which are most closely related to the E_u vibrations, which are active in the cyclohexane spectrum. It seems likely that the infrared activity of the twisting vibrations arises from a departure from our assumption three under our discussion of the forms of hydrogen vibrations of cyclohexane.

Rough Estimated Intensities of *p*-Dioxane Bands

There are no absolute selection rules in the liquid state, but the vapor selection rules are nevertheless useful for discussing the more intense lines. Neither cyclohexane nor *p*-dioxane shows significant differences between the vapor and liquid infrared spectra at the intensity level which will be discussed here. Since we have assumed the chair structure for *p*-dioxane we expect therefore that no vibration will be active in both the Raman and infrared spectra.

Three ring stretching and eight hydrogen bending vibrations are permitted by symmetry to be active in the Raman spectrum. The $A_{1g}(A_g)$ ring breathing vibration will be expected to yield the strongest shift. We might expect also that the $E_g(b)(B_g)$ ring stretching shift will be somewhat stronger than the corresponding tetrahydropyran shift because its intensity depends to some extent on the quantity $\alpha_{xx} - \alpha_{yy}$, which should be twice as large for *p*-dioxane as for tetrahydropyran. The $E_g(b)(B_g)$ rocking and scissors and the $A_{2g}(B_g)$ wagging vibrations are expected to give weaker shifts than the A_g vibrations because the motion of the ring tends to offset that of the hydrogens in these vibrations.

In the infrared spectrum, also, three ring stretching and eight methylene bending vibrations are permitted by symmetry to be active. The introduction of a second oxygen will be expected to accentuate the effects mentioned above for tetrahydropyran except, of course, for the dissymmetry of the latter. Each of the three ring stretching vibrations will be expected to appear with good intensity, with the two E_u frequencies the strongest if the effect which is responsible for the activity of these vibrations in cyclohexane is in the right direction. If the activity of the cyclohexane vibrations arises from the attraction of the positively charged nuclei for the electrons of the C–C bonds of adjoining carbons, for example, the effect would be in the right direction.

Each of the eight methylene bending vibrations except the two twistings is expected to appear with fair intensity. The $E_u(b)(A_u)$ rocking and scissors vibrations might give somewhat weaker bands than the others because the change in moment is brought about by the motion of only four hydrogens as compared with eight for the other vibrations (not including twistings, of course).

Assignment of Bands

The assignments which we have made on the basis of the highly simplified picture described above are summarized in Fig. 5. The reasons for these assignments are given briefly below. The specific assignment of methylene frequencies is not unique in view of the uncertainty of the forms of the vibrations, but since the assignment of ring frequencies seems reasonable our major purpose has been achieved.

In Fig. 5 we have arbitrarily related each methylene bending band of tetrahydropyran to only one cyclohexane vibration, not so much to identify the tetrahydropyran bands as the *p*-dioxane bands.

Ring Bands.—The first step in assigning ring frequencies was to combine the above intensity considerations with Ramsay's approximate calculations[4] to make tentative assignments for *p*-dioxane. The assignments for both *p*-dioxane and tetrahydropyran were then made in such a way as to be as nearly as possible consistent with each other, with Lu, Beckett and Pitzer's assignments for cyclohexane,[2] and with our simplified picture described above.

The results of Ramsay's calculations for the ring stretching frequencies of *p*-dioxane are as follows, in cm.$^{-1}$: $A_{1g}(A_g)$ 834, $E_g(a)(A_g)$ 1111, $E_g(b)(B_g)$ 1126, $A_{1u}(A_u)$ 1141, $E_u(b)(A_u)$ 927 and $E_u(a)(B_u)$ 982. The positions of bands and Raman shifts which have been found experimentally in this spectral region can be seen in Fig. 5. We will not consider the 852 and 1020 cm.$^{-1}$ bands because of their low intensity, and the 1052 cm.$^{-1}$ band is not a ring stretching band as shown by its parallel character.[4] Thus there are only four bands in the ring stretching region remaining to be assigned in each of the Raman and infrared spectra.

Of the four infrared bands one of the two higher frequency bands is the $A_{1u}(A_u)$ stretching frequency so that the splitting of the E_u ring stretching bands is either about 200 cm.$^{-1}$ or only 15 cm.$^{-1}$. The latter seems excessively low in view of the difference in character of the two vibrations so that the higher value is probably correct. One would expect the splitting of the E_g shifts to be at least of the same order of magnitude. If the 1014 and 1111 cm.$^{-1}$ shifts are assigned to the two E_g ring stretching frequencies the splitting would be 97 cm.$^{-1}$, which seems consistent.

The assignment of the 1014 cm.$^{-1}$ shift to the $E_g(a)(A_g)$ vibration is supported by its intensity. In the cyclohexane spectrum the E_g stretching shift is second only to the A_{1g} ring breathing shift in intensity and is the only other intense Raman shift below 1250 cm.$^{-1}$. We have assigned the 1111 cm.$^{-1}$ shift to the $E_g(b)(B_g)$ vibration because of the general tendency of Ramsay's calculated frequencies to be high.[17] The 834 cm.$^{-1}$ shift is no doubt the A_{1g} breathing vibration, in agreement with the assignments of Ramsay[4] and of Kahovec and Kohlrausch.[3]

The intensity of the 875 and 1122 cm.$^{-1}$ infrared bands is so great compared with the 1453 cm.$^{-1}$ scissors band that they can probably be eliminated as methylene bands.[18] The 875 cm.$^{-1}$ band is then the $E_u(b)(A_u)$ ring stretching band. Assignment of the 1122 cm.$^{-1}$ frequency is not as straightforward, but we favor the $E_u(a)(B_u)$ over the $A_{1u}(A_u)$ stretching vibration because it appears to fit better with our assignments for the tetrahydropyran spectrum, which is discussed below. The $A_{1u}(A_u)$ stretching vibration would then be assigned the 1086 cm.$^{-1}$ frequency. Our assignments are within about 2 to 10% of Ramsay's calculated frequencies, which is satisfactory.

If the above ring assignments for *p*-dioxane are accepted, the ring assignments for tetrahydropyran as shown in Fig. 5 follow with little additional discussion. The three vibrations which may presumably be derived from Raman-active cyclohexane and *p*-dioxane vibrations are assigned the strongest bands in the ring stretching region of the Raman spectrum (813, 1007 and 1041 cm.$^{-1}$) and the two vibrations which may presumably be derived from infrared-active cyclohexane vibrations are assigned the two strongest bands in the infrared spectrum (875 and 1097 cm.$^{-1}$). In accordance with our expectations each of the Raman bands is accompanied by an infrared band, and the strongest infrared band is accompanied by a weak Raman band.

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(17) The ring stretching frequencies calculated by Ramsay and Sutherland[6] for the cyclohexane ring by the same method which Ramsay used for dioxane are 4 to 6% higher than those given by Beckett, Pitzer and Spitzer.[2] The latter were presumably obtained on the basis of a somewhat more sophisticated treatment since hydrogen frequencies are also included.

(18) The scissors band is generally the most intense band in the infrared spectra of hydrocarbons except for the carbon–hydrogen stretching band. See, for example, the Infrared Absorption Spectrograms published by the American Petroleum Institute's Research Project 44.

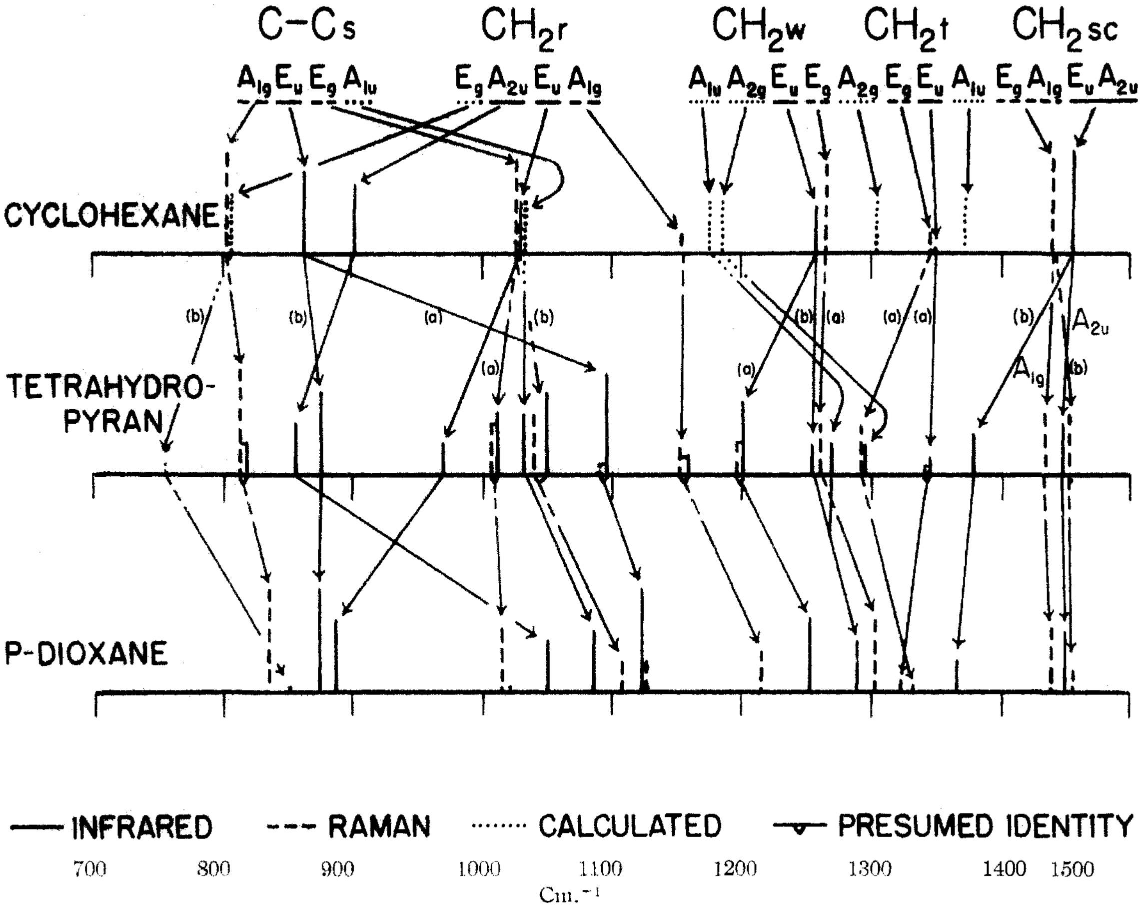

Fig. 5.—Assignments of infrared and Raman bands of tetrahydropyran and *p*-dioxane in the spectral region 700-1500 cm.$^{-1}$. The assignments reported by Beckett, Pitzer and Spitzer for cyclohexane are shown at the top. The letters s, r, w, t and sc indicate stretching, rocking, wagging, twisting and scissors, respectively. Raman lines from Kahovec and Kohlrausch.[3] The letters (a) and (b) near some of the arrows identify the member of the degenerate pair which the arrows represent; where space permits the identifying letter is placed to the left of its arrow.

Independent of whether the *p*-dioxane assignments are accepted or not, the 1012 and 1050 cm.$^{-1}$ bands are quite positively identified by the presence of the associated 1007 and 1041 cm.$^{-1}$ Raman shifts so that only the 1033 and 1097 cm.$^{-1}$ infrared bands are left to be assigned to the $A_{1u}(A_u)$ and $E_u(a)(B_u)$ ring stretching vibrations. The appearance of a weak Raman shift at 1090 cm.$^{-1}$ supports our assignment of the 1097 cm.$^{-1}$ infrared frequency to the latter vibration.

The Raman 1041 cm.$^{-1}$ and infrared 1050 cm.$^{-1}$ bands are more intense than expected on the basis of our earlier discussion. The 1041 cm.$^{-1}$ Raman shift is characterized as "broad" by Kohlrausch so that it is probably complex and some of its intensity may perhaps come from the first overtone of the $A_{2u}(A')$ ring bending vibration, from some combination frequency, or from a methylene vibration which we have assigned to a different frequency (*e.g.*, the $A_{1g}(A')$ methylene rocking vibration). The high infrared intensity as compared with that of the $E_g(a)(A')$ vibration indicates that the actual "E_g" vibrations approach the tangential form shown in Fig. 3 because in the $E_g(b)(A'')$ stretching vibration of the tangential form the positively charged 2 and 6 methylene groups move in the opposite direction to that of the oxygen and so would be expected to give an appreciably stronger band than the $E_g(a)(A')$ stretching vibration. A pair of infrared bands corresponding to the forms shown by Ramsay[4] would be expected to have nearly equal intensities. It is not clear why the $E_g(b)(A'')$ vibration should give a stronger infrared band than the $A_{1u}(A'')$ vibration, but this seems to us preferable to having the $E_u(a)(A')$ vibration give the weaker band. The infrared intensity of the $E_u(b)(A'')$ vibration indicates that the changes in moment arising from the effect which is responsible for the infrared activity of this vibration in the cyclohexane spectrum and from the motion of the oxygen are additive, and we therefore expect that the infrared intensity of the $E_u(a)(A')$ vibration will be appreciably greater than that of either of the E_g vibration

In our analysis the frequency of the E_u(a) ring stretching vibration is affected far more by the introduction of the first oxygen than by the introduction of a second. This may be accounted for by an interaction with the E_u(a)(B_u) methylene wagging vibration of *p*-dioxane.

Methylene Bands.—Our primary concern is not to assign the methylene bands specifically, but rather to show that our assignment of ring bands is not inconsistent with the requirements of the methylene bands. As shown in Fig. 5 we have accounted in a reasonable manner for the number and relative intensities of the infrared bands and Raman shifts in this spectral region.

The unassigned 1125 cm.$^{-1}$ Raman shift of *p*-dioxane might be a combination of the E_u(b)(A_u) ring bending and methylene rocking vibrations.

The parallel nature of the 1050 cm.$^{-1}$ infrared band of *p*-dioxane requires that it arise from either a B_u rocking or B_u scissors vibration. The frequency decides unambiguously in favor of the A_{2u}(B_u) rocking vibration. The high frequency of this band in *p*-dioxane may probably be attributed to the fact that the polar hydrogens are either in van der Waals contact or very nearly so, as discussed above. The remaining unassigned band of *p*-dioxane in this spectral region, at 889 cm.$^{-1}$, is then the E_u(b)(A_u) methylene rocking vibration; in this latter vibration it will be noted that the polar hydrogens move in the same direction and their close proximity may be expected to have little effect on the frequency.

From the wagging vibrations we may expect at least one Raman band and one moderately strong infrared band. The fact that there is only one strong infrared band in the 1150–1300 cm.$^{-1}$ region in the tetrahydropyran spectrum, at 1202 cm.$^{-1}$, indicates that the A″ wagging vibrations have been appreciably modified as compared with those of cyclohexane. Our assignment of the 1202 and 1097 cm.$^{-1}$ bands to vibrations of the same symmetry raises the question of the possibility of the former "borrowing" some intensity from the latter.

Structure of Tetrahydropyran and of *p*-Dioxane

A question which is not related to our major purpose, but is of general interest, is whether the approach outlined in the present paper can contribute any new arguments for or against the chair structure for *p*-dioxane or for tetrahydropyran. The estimation of relative intensities by the rough methods of the present paper can hardly compare in rigor with the usual spectroscopic arguments and arguments based on our approach cannot be regarded as proof, but should serve as supporting evidence.

To the extent that our predictions are valid, the planar structure for both tetrahydropyran and *p*-dioxane can be immediately eliminated, because if this structure were correct the only rocking vibration which could give a strong infrared band would be the one related to the A_{2u} vibration of cyclohexane, and the infrared spectra of these compounds cannot be explained reasonably unless at least two rocking vibrations give moderately strong infrared bands.

The C_{2v} boat structure for *p*-dioxane can be eliminated on several counts, such as dipole moment and number of bands, but as to the latter the mere fact that the number of bands is smaller than the number permitted by symmetry is a weak argument at best. Our considerations show that specifically the C_{2v} structure would require a strong infrared band in the same position as the strong A_1 ring breathing Raman band whereas actually there is no strong infrared band within 50 cm.$^{-1}$ of this position. The argument against the corresponding C_s boat structure for tetrahydropyran is weaker. However, with that structure, since the z-component of the change in moment arising from the motion of the oxygen atom in the A′ ring breathing vibration has the same sign as that arising from the motion of the four nearest, and probably most highly charged, methylene groups, we would expect that the infrared intensity of this vibration would more nearly approach that of the other ring stretching bands than it actually does.

We feel that the consideration of probable intensities will enter more and more in the future into discussions of the structures of polyatomic molecules.

Summary

1. The infrared spectrum of liquid tetrahydropyran between 7.5 and 14μ has been presented and compared with those for liquid cyclohexane and *p*-dioxane.

2. Frequencies have been assigned to the ring stretching vibrations of tetrahydropyran and *p*-dioxane and the assignments have been shown to be consistent with a reasonable assignment of methylene bending frequencies. The procedure for making the assignments, which is described in some detail, depends much more than is customary on the consideration of intensities.

3. New spectroscopic arguments, based on the consideration of intensities, are presented against the flat D_{2h} and the C_{2v} boat structures for *p*-dioxane and the corresponding structures for tetrahydropyran.

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