THE RELATION BETWEEN THE INFRARED SPECTRA AND STRUCTURE OF CARBOHYDRATES AND RELATED COMPOUNDS

Thesis by

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Abstract

Historically the investigation reported in this thesis was initiated as a study of the relation between the infrared spectra and structure of cellulose. It was soon found, however, that the large backlog of information about the infrared spectra of related compounds which would naturally be required in the study of such a complex substance was almost entirely missing. Consequently the material presented in this thesis consists principally of a study of the infrared spectra of simpler related compounds. The region of the spectrum which we have discussed is that from 7.6 to about 13μ.

The compounds which we have studied are either pyranoid carbohydrates or possess one or more of the following structural features in common with them: (1) many hydroxyl groups, (2) an oxygen-containing six-membered ring, (3) many hydroxyl groups attached to a six-membered ring. The infrared spectra of these compounds have been discussed on the basis of the tentative assumption that each atom may be assigned a fixed fractional charge and that the infrared activity of vibrations may be estimated roughly by considering their forms.

The glykitols (polyhydric acyclic alcohols), tetrahydropyran and p-dioxane, and some cyclitols (polyhydric cyclic alcohols) are discussed in Part II. By application

of the assumptions mentioned above fairly complete vibrational assignments are made for the spectral region 7 to 12.5μ for ethylene glycol, tetrahydropyran and p-dioxane. Ethylene glycol is shown to have a staggered C_2 structure rather than the flat C_{2h} trans structure, and new spectroscopic arguments, based on the above assumptions, are advanced against the flat D_{2h} and the C_{2v} boat structures for p-dioxane and the corresponding structures for tetrahydropyran.

The principal absorption bands of the cyclitols between 8 and 13μ are accounted for in terms of skeletal stretching vibrations only, and it is inferred that this holds true for the sugars also. Scyllitol, the all-trans cyclohexanehexol, is shown to have its hydroxyls in equatorial rather than polar positions.

In Part III the sugars are discussed, and it is shown that their structures are probably based on a somewhat strained chair-type pyranose ring. A correlation has been observed between the intensity distribution in the infrared spectra of the monosaccharides and the number of polar hydroxyls, assuming the hydroxymethyl group to be in an equatorial position. This correlation is quite good for the glucose oligosaccharides, but is not very useful for mixed oligosaccharides.

The infrared absorption spectra of animal cellulose, cellophane, starch, and some cellulose derivatives are presented in Part IV.

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Part I. Introduction

The original purpose of the investigation reported in this thesis was to study the relation between the infrared spectra and structure of cellulose and its derivatives. Although these substances do not have exceptionally complex spectra, their structures are exceedingly complex and are not well understood so that in order to establish any sort of relation between the two it is desirable to have available the spectra, interpreted where possible, of a large number of simpler compounds which have structural features in common with cellulose. Very few such spectra are at present available in the open literature. The features which we regard to be pertinent are (1) the presence of many hydroxyl groups, (2) the oxygen-containing ring and (3) the presence of many hydroxyl groups attached to a ring. All these structural features are found to give rise to strong absorption in the region 8 to 10μ, which in hydrocarbons is usually relatively transparent, but in the carbohydrates is characteristically opaque.

The pyranose sugars show all these features and exist in a variety of forms, but their structures are not well understood and the infrared spectra of many of them are appreciably more complex than that of cellulose. We have consequently extended our investigation to simpler compounds: namely the glykitols*, tetrahydropyran, p-dioxane and the cyclitols**. The structures of the glykitols are even more uncertain than those of the sugars, but we have felt it to be important that the spectra of several of these compounds be available for comparison in order to determine whether there are any fundamental differences between the infrared spectra of the cyclic and acyclic polyols. The cyclitols are of particular interest because of their close structural relationship to the sugars and because the relatively great symmetry of scyllitol offers some promise for the specific assignment of bands.

The carbohydrates in general cannot at present be conveniently handled by normal coordinate treatments because of the size and lack of symmetry of their molecules. Furthermore the shapes of band envelopes cannot be used in making assignments since they cannot be examined in the gaseous state. We have therefore investigated the possibility of using intensities as an aid in making assignments, and have made fairly complete vibrational assignments for ethylene glycol, tetrahydropyran and p-dioxane largely on the basis of the consideration of intensities in terms of the motions of formal charges. We feel that this approach shows considerable promise in the treatment of the spectra

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*Polyhydric, acyclic alcohols. The carbohydrate nomenclature of Pigman and Goepp (1) will be used throughout this thesis.

**Polyhydric, cyclic alcohols.

of compounds which cannot readily be treated by the usual methods and indeed would be a desirable supplement to normal coordinate treatments of simpler molecules.

While our work has not yet led to the specific assignment of bands in the cellulose spectrum, we have been able to make qualitative assignments for the strongly absorbing spectral region from 8 to 10μ and have accumulated a large quantity of supplementary data about related compounds which should be very helpful in subsequent work on the infrared spectra of cellulose and its derivatives.

Investigations which are primarily concerned with the accumulation of data and empirical relationships rather than with theoretical interpretations are currently being carried out on sugars and their derivatives by Dr. Lester Kuhn (2) at the Ballistics Research Laboratories, Aberdeen Proving Ground, Maryland and on polysaccharides and their derivatives by Dr. John Rowen and co-workers at the National Bureau of Standards, Washington, D. C..

The spectral region beyond about 6μ is the most structure sensitive part of the spectrum so that our work has been principally concentrated in this region. Since mineral oil mulls were used for examining crystalline solids, we have largely ignored the spectral region from 6.5 to 7.5μ, in which mineral oil has strong absorption bands (see Fig. 1).

Part II. Simpler Related Compounds

A. Glykitols

1. Experimental part

a. The spectrophotometer

Spectra were taken by use of a Beckman IR-2 recording infrared spectrophotometer* fitted with rock salt optics. The instrument is fitted with a string drive which yields an approximately linear wave length scale, and provision is made for continuously opening the slit by driving the slit knob directly from the coarse adjustment wave length knob, using a string belt. The ratio between the diameters of the two knobs is such that by this simple means spectra from about 1.8 to 14μ can be recorded without otherwise adjusting the slit. The reproducibility of spectra obtained by this arrangement is quite satisfactory.

The string drive consists essentially of a motor-driven cone pulley on which the string is wound up, and a system of pulleys and a weight to keep the string taut; it is connected to the prism through a pulley which has been substituted for the fine adjustment wave length knob. The cone pulley has a diameter of 3/4-inch at one end and three inches at the other, and has the effect of driving the wave length knob faster at the longer wave lengths. The speed

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*Manufactured by National Technical Laboratories, South Pasadena, California.

of the recorder chart is of course constant, so that the overall effect is to compress the scale of the long wave length region relative to that of the short wave length region and to give the roughly linear wave length scale shown in Fig. 1.

Provision has been made for flushing the spectrophotometer out with high purity dry nitrogen (Linde Air Products) in order to reduce the absorption of water vapor and carbon dioxide. The monochromator section is flushed continuously at a rate of about eight liters per hour, which is sufficient to maintain a minute positive pressure inside the monochromator. The 27-centimeter cell in the source section and the liquid cell compartment are flushed out immediately before each run. The effectiveness of this treatment can be seen from the weakness of the usual water and carbon dioxide bands in the curve in Fig. 1.

The rock salt window on the 27-centimeter cell has been removed, for two reasons: (1) to permit us to flush the cell out with dry nitrogen, and (2) to prevent condensation on the window of distillate from the glower. Before this window was removed a prominent "ghost" absorption band had been observed in the background tracings at about 7.3μ, as well as a very weak "ghost" at about 3.4μ.

The tank nitrogen which we use is sufficiently dry that a drying train consisting of nine twelve inch by one inch tubes of desiccant in series, three each of potassium hydroxide, magnesium perchlorate and phosphorus pentoxide, does not affect its effectiveness in reducing the water absorption in our background curves. A noticeable effect is obtained, however, if the nitrogen is passed through a train of three tubes packed with silica gel and immersed in liquid air.

b. Methods and results

The spectra of liquid ethylene glycol and glycerol before and after exchange with D_2O are shown in Fig. 2 for the spectral region 6.5 to 14μ, and the spectra of crystalline erythritol, D-arabitol, ribitol (adonitol), D-mannitol, D-glucitol (sorbitol) and galactitol (dulcitol) are shown in Fig. 3 for the spectral region 7.6 to 14μ.

The frequencies in cm.$^{-1}$ of the infrared bands of the above substances as shown in Figs. 2 and 3 are given below with approximate relative intensities in parentheses (the strongest band in each spectrum is assigned an intensity of 10):

Ethylene glycol 864 (5), 886 (6), 1045 (10), 1089 (10), 1206 (1), 1256 (0), 1335 (2), 1421 (4), 1451 (4).

Ethylene glycol (deuterated) 796 (1), 861 (5), 880 (6), 983 (6), 1035 (8), 1089 (10), 1212 (?), 1335 (0), 1368 (3), 1391 (2), 1414 (2), 1454 (4).

Glycerol 853 (3), 870 (3), 926 (4), 999 (5), 1049 (10), 1116 (8), 1223 (3), 1348 (4), 1429 (5), 1460 (5).

Glycerol (deuterated)* 849 (4), 925 (6), 1008 (8), 1053 (10), 1121 (7), 1236 (2), 1337 (2), 1372 (3), 1395 (3), 1416 (3), 1460 (5).

Erythritol 698 (2), 724 (3), 867 (3s), 886 (6), 919 (1) 967 (7), 1056 (9), 1083 (10), 1218 (3), 1256 (5), 1272 (2s), 1306 (1).

D-Arabitol 736 (3), 782 (2), 853 (4), 866 (4), 876 (2s), 887 (0s), 905 (4), 942 (5), 994 (4), 1025 (10), 1052 (10), 1067 (0s), 1085 (10), 1101 (0s), 1124 (0s), 1140 (2), 1211 (2), 1233 (0), 1257 (1), 1314 (3).

Ribitol 749 (3), 857 (5), 890 (6), 915 (4), 950 (1), 1034 (10), 1077 (10), 1101 (5), 1119 (1s), 1211 (0), 1267 (1).

D-Mannitol 707 (3), 789 (2), 866 (3), 885 (5), 933 (4), 962 (1), 1024 (10), 1048 (3), 1087 (10), 1211 (1), 1235 (0s), 1250 (0s), 1263 (2), 1285 (3), 1304 (2).

D-Glucitol 726 (3), 774 (1), 872 (6), 887 (5), 937 (3), 999 (9), 1015 (8), 1052 (9), 1076 (4s), 1094 (10), 1114 (3s), 1136 (2), 1185 (1), 1208 (1), 1230 (1), 1253 (2).

Galactitol 716 (4), 862 (6), 905 (0s), 926 (8), 958 (0s), 999 (3), 1029 (10), 1047 (10), 1078 (10), 1088 (2s), 1100 (5), 1116 (8), 1205 (4), 1259 (1), 1287 (1).

Kuhn (2) has examined erythritol, D-mannitol, D-glucitol and galactitol, but his resolution is not as good as ours, and his erythritol and mannitol were examined in the form of evaporated films rather than as mulls. In general the agreement is fairly good except for the D-glucitol spectrum below 990 cm.$^{-1}$; Kuhn shows a band at about 857 cm.$^{-1}$ which we do not find, and the intensities

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*Positions and intensities not very accurate due to thickness of sample and diffuseness of bands.

of the 872 and 887 cm.$^{-1}$ bands are reversed. The agreement for D-mannitol is not very good, but in view of the difference in the nature of the samples this is not surprising.

Spectra of ethylene glycol and glycerol were obtained by examining a drop pressed between two silver chloride plates. Crystalline solids were examined in the form of a mull in mineral oil; about 25 mg. of crystals of the substance to be examined were placed in a mullite mortar together with a drop of mineral oil, and the mixture was ground to a thin paste. This paste was then smeared as evenly as possible on a silver chloride plate. In general each crystalline sample was examined in several thicknesses although only one curve for each is shown in the figures. A reproduction of a tracing obtained with mineral oil alone is shown in Fig. 1.

The "deuterated" ethylene glycol and glycerol were prepared by adding several drops of 99.4% D_2O to a drop of the alcohol and removing the D_2O by heating one and one-half hours at each of 100° and 80°C. (ethylene glycol) or one and one-half hours at 100° and three hours at 150°C. (glycerol). Earlier investigators (3) (4) have shown that the exchange reaches equilibrium very rapidly, probably in less than one minute, and that the ratio of the proportion of D to H in the glykitols to that in water is slightly larger than one.

2. Discussion

Our purpose in examining the glykitols is twofold: (1) to obtain data which will assist us in determining whether the ring makes any unique contribution to the spectra of cellulose and the pyranose sugars, and (2) to locate the spectral region in which OH bendings occur. We shall discuss the spectrum of ethylene glycol in relatively great detail because both the spectrum and structure of this compound are relatively simple so that we may expect to have a better chance of relating the two than we would with the other glykitols.

a. Ethylene glycol

The oxygen-carbon skeleton of ethylene glycol has the symmetry C_{2h}, C_{2v} or C_2 according to whether the oxygens are trans, cis or in between, respectively. The problem of the actual structure is somewhat complicated by the possibility of intra-molecular hydrogen bonding so that it is not comparable with the 1,2-dihalogen ethanes, for which Hassel (5) has concluded from electron diffraction data that the trans form is the equilibrium form, with oscillation about this position. Smyth and Walls (6) have shown that the dipole moment of ethylene glycol is close to that predicted on the assumption of free rotation around the C-C and C-O bonds, but such a model can hardly be taken seriously since the interactions can scarcely be less than in the 1,2-dihalogen ethanes. If the C-H and C-O bond moments are assumed to be 0.4 and 0.8 debye, respectively, (see Pauling (7), p. 68) the C_2 model in which the two O-C-C planes make an angle of 60° with each other gives a moment of 1.90 debyes without considering the hydroxyls; there are numerous possible positions of the hydroxyl hydrogens which would bring this moment within the range of the reported values, 2.0 (6) and 2.2 (8) debyes, since the contribution of a given OH can be anywhere from -0.26 to + 0.75 debye, depending on its orientation, if the OH moment is taken to be 1.5 debye and the C-O-H angle is taken to be 100°, for example. A larger C-O-H angle would permit a still larger range in the possible contribution of each hydroxyl group. The most probable structures are based on the trans form and on the C_2 model described above, since they correspond to the so-called staggered form of ethane. The C_2 model seems preferable because the measured dipole moment would require an excessively large amplitude of oscillation about the equilibrium position in order to be in agreement with the trans form.

In discussing the possible vibrations of ethylene glycol we shall start by ignoring possible interactions between skeletal vibrations and hydrogen vibrations and shall use the conventions about methylene vibrations discussed under tetrahydropyran and p-dioxane. Of the 3n-6, or 24, possible vibrations there would, then, be three each of skeletal stretchings and bendings, four C-H stretchings, two each of methylene scissors, rocking, wagging and twisting and two each of O-H stretching, bending and torsion. Only thirteen of these may be expected to have frequencies in the spectral region 700 - 1500 cm.$^{-1}$, in which we are interested, namely the skeletal stretchings, the O-H bendings and the methylene vibrations (see for example, Rasmussen (9) or Beckett, Pitzer and Spitzer (10)). The symmetry classes and activities of these latter vibrations for the C_{2h} and C_2 forms are shown in Table 1.

Table 1

Symmetry Classes and Activities of Some Ethylene Glycol Vibrations for C_{2h} and C_2 Models*

Type of Vibration	C_{2h}	C_2**
Skeletal stretching	$2A_g$(R), B_u(I)	2A, B
O-H bending	A_g(R), B_u(I)	A, B
CH_2 scissors	A_g(R), B_u(I)	A, B
CH_2 rocking	B_g(R), A_u(I)	B, A
CH_2 wagging	A_g(R), B_u(I)	A, B
CH_2 twisting	B_g(R), A_u(I)	B, A

Although the actual symmetry of the ethylene glycol molecule, even with the oxygens in the trans position,

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*For selection rules see Herzberg (11), pp. 252-253

**All vibrations are permitted to be active in both the Raman and infrared.

is probably not greater than C_2, the activities of all except the O-H vibrations are probably given to a fair degree of approximation by Table 1. Thus, if the oxygens are in the trans position we might reasonably expect to find six, or at most seven, infrared bands with any intensity. The twisting band would probably be quite weak, also, so that there would be only five or six bands. Furthermore, we would expect that few, if any, vibrations would show appreciable activity in both the Raman and infrared.

The above predictions may be compared with the infrared spectrum of ethylene glycol as shown in Fig. 2, and the following Raman shifts in cm.$^{-1}$, as given by Ananthakrishnan (12) (polarizations are also given, and relative intensities are included in parentheses): 865(8)P, 900(1)D, 1035(2b)D, 1060(2b)D?, 1090(4)P, 1227(½b), 1260(3b)D, 1450(8b)D. Of the eight Raman shifts given above five are within ten cm.$^{-1}$ of an infrared band. In view of this fact, it seems highly unlikely that the oxygens of ethylene glycol are in the trans position, particularly since some of the coincidences involve moderately intense activity in both the Raman and infrared. Ananthakrishnan takes the presence of depolarized lines in the Raman spectrum as proof that the heavy atoms have a planar configuration, on the basis that the molecule must have symmetry in order for depolarized lines to appear, and that no symmetry can exist unless the heavy atoms are in a plane. Actually, of course, a symmetrical vibration can show as much depolarization as an unsymmetrical line (see, for example, Herzberg (11), pp. 270-271) so that the classification of a line as depolarized does not necessarily mean that it arises from an unsymmetrical vibration. Also, as pointed out above, the molecule can have symmetry C_2 even when the heavy atoms are not in a plane.

Both the number of coincidences between Raman and infrared lines and the dipole moment appear to eliminate the trans form of ethylene glycol, so that we shall assume the C_2 form in making assignments and shall identify the vibrations by their type and C_2 class as shown in Table 1.

The most obvious assignments are 1451 (I) and 1450 (R) to the two scissors vibrations, since these vibrations in general show a remarkably constant frequency in a wide variety of compounds (see Rasmussen (9)); the principal intensity in the infrared probably arises from the B, and that in the Raman from the A vibration. The two strongest infrared bands, at 1089 and 1045 $cm.^{-1}$ probably arise from C-O vibrations, since the C-O bond is by far the most polar in the molecule, and vibrations involving it may therefore expect to show the greatest change in moment. In view of the presence of a strong polarized Raman line at 1090 $cm.^{-1}$ the 1089 $cm.^{-1}$ infrared band should be attributed to an A skeletal stretching vibration, and the 1045 cm.$^{-1}$ band, together with the 1035 cm^{-1} Raman shift, to the B skeletal stretching vibration. The strongest Raman shift, at 868 cm.$^{-1}$, and the 864 cm.$^{-1}$ infrared band probably arise from the other A skeletal stretching vibration, which is probably chiefly a C-C vibration.

A comparison of the infrared spectrum of ethylene glycol with that of the "deuterated" form shows that one of the OH bending bands, probably the B band, is almost certainly that at 1421 cm.$^{-1}$. The absorption decreases materially in this region when H is replaced with D, and the strong new band which appears in the spectrum of the "deuterated" form is displaced from 1421 cm.$^{-1}$ by approximately the square root of two. Identification of the A band is not so obvious, but we shall select the one at 1335 cm.$^{-1}$ because it fits in best with the assignments of the methylene bands.

The rest of the bands may be assigned as follows: 886 (I) and 900 (R), B rocking; 1060 (R), A rocking; 1206 (I), B wagging; 1227 (R), A twisting; and 1256 (I) and 1260 (R), A wagging.

No satisfactory assignment of bands can be made on the basis of the trans structure, even without considering the Raman spectrum; in particular any such assignment would have to be accompanied by a rather labored explanation of the intensity of one of the two very strong infrared bands.

The next question is whether a consideration of the infrared intensities of the symmetrical and unsymmetrical C-O stretching bands in terms of the motion of formal charges will lead to results in agreement with the conclusions we have drawn already about the structure of ethylene glycol. This question is an important one because we shall be using this type of approach to aid us in our discussion of larger molecules later on.

We shall regard each atom as carrying a fixed fractional charge, or formal charge, the magnitude of which depends on the electronegativity differences between the atom and its ligands. We shall then attempt to estimate the order of magnitude of intensities from a consideration of the forms of the normal vibrations. Such an approach cannot be used to calculate quantitative intensities (12a), and in many instances may even give the incorrect order of magnitude when resonance is possible between structures of quite different charge distribution, or when strong interaction between the bond moments is possible, as in water. In ethylene glycol the bond moments in which we are interested are separated by a C-C bond, and chances for resonance are slight also so that we expect that our orders of magnitude will be correct.

First we shall point out that in the symmetrical vibration any change in moment is along the z-axis (the axis of symmetry, in accord with Herzberg's conventions (11)), whereas that of the unsymmetrical vibration is in the xy-plane. Taking the amplitudes of the motions of the oxygens in the two vibrations to be equal, and normalizing them to unity, the expressions for the magnitudes of the change in moment are

$$\mu_A' = \cos 20^\circ \cos \phi = 0.94 \cos \phi$$

$$\mu_B' = \sin 20^\circ + \cos 20^\circ \sin \phi = 0.34 + 0.94 \sin \phi$$

where ϕ is half the angle between the two O-C-C planes, the O-C-C angle is assumed to be 110°, and the motions of the oxygens are taken to be along the C-O bonds. It is apparent that for $\phi = 90^\circ$, i. e. the trans form, the change in moment is zero for the symmetrical vibration, as it should be, and that for $\phi = 0$, the cis form, the symmetrical vibration shows an appreciably larger change in moment than the unsymmetrical vibration. Furthermore, for $\phi = 30^\circ$, the form which we have favored, the changes in moment for the symmetrical and unsymmetrical vibrations are respectively 0.815 and 0.81, which would lead one to expect roughly equivalent intensities for the two vibrations. This result is not cited in support of the C_2 structure, but in support of the treatment of intensities.

The reason for the change in the relative intensities of the above two bands on "deuteration" is not clear. On the basis of the above treatment one would say that ϕ is smaller for the deuterated form than for the untreated form, but this simply substitutes one mystery for another. In any case it is evident that one should not attempt to push our approximate treatment of intensities too far.

b. Higher glykitols

The outstanding feature of the spectra of the glykitols as shown in Figs. 2 and 3 is the concentration of all the strongest bands in or within 0.1 or 0.2 of the spectral region 9 to 10μ. None of the glykitols we have examined shows bands of more than very moderate intensity between 7.6 and 8.9μ. There appears to be no obvious correlation between their spectra and their detailed structure. For example, one of the simplest spectra is shown by D-mannitol, which can show a maximum symmetry of C_2, whereas galactitol, which can have a center of symmetry, shows one of the most complex spectra of the group.

The configurations of the asymmetric carbons are shown by the names of the glykitols. Thus the asymmetric carbons of D-glucitol (sorbitol) have the same relative configurations as the asymmetric carbons in D-glucose, and so on.

The poorly resolved character of the bands of glycerol after exchange with heavy water is rather mystifying. Perhaps a thinner sample would not have shown such a pronounced effect. The spectra shown in Fig. 2 do, however, indicate the general spectral region occupied by O-H bendings, namely 7-8μ, so that we have not investigated further.

B. Tetrahydropyran and p-Dioxane

1. Introduction

Our major purpose in the present section is to identify the bands which arise from the stretching vibrations of the tetrahydropyran ring, since this ring is a distinguishing feature of cellulose and of the pyranose sugars. While it is not expected that these bands will occur unshifted in cellulose and sugar spectra, their identification may be expected to be of assistance in the discussion of such 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 (9)), but in tetrahydropyran and p-dioxane some of the hydrogen frequencies do lie in this spectral region and their consideration is consequently essential to any reasonable assignment of ring frequencies. We therefore include a brief treatment of the methylene vibrations of tetrahydropyran and p-dioxane.

In making vibrational assignments for polyatomic molecules it appears to be generally customary to disregard intensities and to depend principally on normal coordinate treatments of varying degrees of complexity. In this thesis we have placed considerable emphasis on intensities, while at the same time taking into account the results of normal coordinate treatments by others. Our general procedure has been to start from the results of a normal coordinate analysis of cyclohexane by Lu, Beckett and Pitzer (to be published as reported in an article by Beckett, Pitzer and Spitzer (10) and to extend these results to tetrahydropyran and p-dioxane. We have attempted to choose symmetry coordinates for cyclohexane which are probably a reasonable approximation of the normal coordinates 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 consistent with this simplified picture were made. By this procedure we have been able to account for the more intense Raman shifts 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 (13), and Ramsay (14) 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 (10) and by Ramsay (14), both of whom examined the vapor as well as the liquid.

The cyclohexane ring is shown in Fig. 4 with the atoms numbered and with the coordinates indicated which will be used in our discussion of cyclohexane, tetrahydropyran and p-dioxane. The oxygen in tetrahydropyran is taken to be in the 1 position, and the oxygens in p-dioxane in the 1 and 4 positions. The atoms are numbered in the order in which they would appear in position 1 on successive performances of the symmetry operation S_6 in a clockwise direction. The coordinates were adopted for convenience in comparing tetrahydropyran and p-dioxane with cyclohexane although they are not consistent with Herzberg's well-chosen conventions (11). In order to make use of the tables in Herzberg, the reader should permute cyclically one place to the right the coordinates used there for C_s and C_{2h}. Thus Herzberg's α_{xy} becomes our α_{yz}, α_{yz} becomes α_{xz}, etc.

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 (16), and that for p-dioxane by Ramsay (14). We will discuss briefly the spectroscopic evidence for the structure of tetrahydropyran and will present new spectroscopic arguments against the flat D_{2h} and the C_{2v} boat structures for p-dioxane.

As elsewhere in this thesis 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.

2. Experimental part

The spectra of liquid cyclohexane, tetrahydropyran and p-dioxane are shown in Fig. 5. 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. A list of the frequencies in cm.$^{-1}$ of the infrared bands of tetrahydropyran and p-dioxane as shown in Fig. 5 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 line in each spectrum is assigned an intensity of 10. Ramsay (14) assigned somewhat lower relative intensities to the 875 and 1122 cm.$^{-1}$ p-dioxane bands, probably because his samples were thicker than ours.

The cyclohexane was manufactured by the Shell Chemical Company. It was examined in a 0.1 mm. liquid absorption cell. The excellent agreement with previously published spectra (17, 18) shows that its purity is satisfactory.

The sample used by Carpenter and Halford (17) was a standard sample from the National Bureau of Standards, reported to be 99.98 ± 0.02% pure.

The tetrahydropyran was du Pont's Elchem-596. Its boiling point of 88°C., as quoted by du Pont, compares favorably with that of 87.5-88.5°C. 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 (14) (15) is excellent. The "thick" film was obtained in the same way as the tetrahydropyran sample and the thin film was obtained by use of rock salt 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 in 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.

3. Plausible forms for the normal vibrations of cyclohexane

a. Method of setting up symmetry coordinates*

A complete knowledge of the potential function of a molecule is necessary before the exact form of the normal vibrations of a molecule, i. e. its normal coordinates, can be determined unless the symmetry of the molecule is so high that there is no more than one genuine vibration in any given non-degenerate symmetry class or one pair of genuine vibrations in any given degenerate symmetry class (we are not going to consider triply degenerate vibrations). An approximate discussion of intensities does not require such exact knowledge, however, and we shall endeavor to set up symmetry coordinates which satisfy the formal requirements for normal coordinates and which resemble the normal coordinates within the limits of validity of certain assumptions which we shall make, and which will be discussed later. In the present section we shall outline the formal requirements for normal coordinates and the method of setting up symmetry coordinates which satisfy these requirements.

The normal coordinates of any molecule must be mutually orthogonal and must have zero linear and angular

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*See Herzberg (11), Chapter II.

momentum. Furthermore, if the molecule has symmetry, each non-degenerate normal coordinate must be either symmetric or antisymmetric with respect to each element of symmetry other than odd-fold axes and symmetric with respect to the latter. If a pair of normal coordinates is degenerate, they must satisfy certain transformation equations, which, incidentally, automatically ensure orthogonality.

The mathematical expressions of the requirements which can be conveniently so expressed are shown below.

The orthogonality relation between two normal vibrations, k and ℓ :

$$\sum_i m_i \bar{\xi}_i^{(k)} \cdot \bar{\xi}_i^{(\ell)} = 0 \tag{1}$$

or

$$\sum_\alpha m_\alpha \sum_j \bar{\xi}_j^{(k)} \cdot \bar{\xi}_j^{(\ell)} = 0 \tag{1a}$$

where m_i is the mass of the ith atom, $\bar{\xi}_i^{(k)}$ is the vector displacement of the ith atom in the kth normal vibration, m_α is the mass of each atom in the αth set*, and j represents the jth atom in the set α. Equation (1a) is useful when the molecule has one or more sets of atoms of more than one atom each.

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*A set is a group of identical atoms which can be generated by any one of them by performing the symmetry operations permitted by the point group of the molecule.

The requirements of zero linear and angular momentum:

$$\bar{P} = \sum_i m_i \bar{v}_i = 0 \qquad (2)$$

$$\bar{H} = \sum_i m_i \bar{r}_i \times \bar{v}_i = 0 \qquad (3)$$

where $\bar{v}_i$ is the velocity of the ith atom at a given phase of the normal vibration under consideration and $\bar{r}_i$ is the vector distance of the ith atom from the axis of rotation. The relative velocities and displacements of the atoms in a molecule are the same throughout a given normal vibration, and the relation between displacement and velocity is the same for each atom in a given normal vibration, so that the requirements of zero linear and angular momentum can be expressed in the following more convenient form for computation:

$$\sum_i m_i \bar{\xi}_i^{\,r} = \sum_\alpha m_\alpha \sum_j \bar{\xi}_j^{\,r} = 0 \qquad (4)$$

$$\sum_i m_i \bar{r}_i \times \bar{\xi}_i^{\,r} = \sum_\alpha m_\alpha \sum_j \bar{r}_j \times \bar{\xi}_j^{\,r} = 0 \qquad (5)$$

where $|\bar{\xi}_i^{\,r}|$ is the relative magnitude of the displacement of the ith atom referred to the magnitude of the displacement of some reference atom taken as unity. The actual displacements are small so that the equilibrium value of $\bar{r}_i$ can be used.

Since the only molecules which we shall discuss and which have degenerate vibrations belong to the point-group D_{3d} we shall give the transformation equations specifically for this point-group. Although a pair of degenerate vibrations must satisfy transformation equations for each symmetry operation permitted by the point group of the molecule, these equations are not all independent and it will be sufficient to give the transformation equations for the operation of highest symmetry, namely S_6. It should be noted that for projections in the xy-plane this operation is exactly equivalent to C_6 and that for z-components it is simply a reflection in the xy-plane.

The general transformation equations for the performance of the operation S_6 on a pair of degenerate vibrations ξ_a and ξ_b are:

$$\bar{a}_i' = \bar{a}_i \cos\beta + \bar{b}_i \sin\beta \qquad (6)$$

$$\bar{b}_i' = -\bar{a}_i \sin\beta + \bar{b}_i \cos\beta \qquad (7)$$

where $\bar{a}_i'$ and $\bar{a}_i$ are the transformed and untransformed displacement vectors, respectively, of the ith atom in a given set in the vibration ξ_a and β is $l\pi/3$, $l = 1$ or 2 (see Herzberg (11), pp. 94 ff.). The angle β can also be equal to π, but this value leads to the non-degenerate vibration of class A_{2u}. If, now, the operation $-S_6$ is performed on $\bar{a}_i'$ we will have obtained the displacement vectors of the $(i + 1)$th atom in ξ_a :

$$\bar{a}_{i+1} = \left[a_{ix}' \cos\pi/3 - a_{iy}' \sin\pi/3\right]\bar{i} + \left[a_{ix}' \sin\pi/3 + a_{iy}' \cos\pi/3\right]\bar{j} - a_{iz}'\bar{k} \qquad (8)$$

where $\bar{i}$, $\bar{j}$ and $\bar{k}$ are the usual unit vectors. An exactly analogous equation will hold, of course, for b.

The general equation which expresses the overall process of obtaining the displacement vector of the $(i+1)$th atom from that of the ith atom is somewhat cumbersome, but fortunately it can be simplified considerably. If f pairs of degenerate vibrations are permitted in a given symmetry class the normal coordinates may be represented by linear combinations of f pairs of arbitrary symmetry coordinates provided only that the symmetry coordinates are all mutually orthogonal. We can therefore select first symmetry coordinates which can be determined easily, and then construct more plausible approximations to the normal coordinates, if necessary, by making linear combinations of the original set.

In the case of the X_6 ring of symmetry D_{3d} two pairs of degenerate vibrations are permitted in each of the two degenerate symmetry classes E_g and E_u. For the E_g vibrations it is convenient to let $\bar{a}_1$ and $\bar{b}_1$ be equal to $\bar{j}$ and $\bar{i}$ respectively for one pair and $-\bar{j}$ and $\bar{i}$ for the other pair (note that no genuine vibration with only z displacements is permitted). The second of these pairs turns out to have angular momentum so that equation (5) must be used to calculate z-components.

Of the E_u vibrations one pair is permitted to have all z displacements, so that convenient selections for $\bar{a}_1$ and $\bar{b}_1$ for the E_u vibrations are $\bar{j}$ and $\bar{i}$ for one pair and $\bar{k}$ and 0 for the other pair. The explicit equations relating $\bar{a}_{i+1}$ to $\bar{a}_i$ as simplified by these selections will not be given since they lead simply to the vibrations given by

Herzberg for the plane X_6 ring.

The transformation equations for methylene vibrations of cyclohexane are identical with those for a vibration involving only z-displacements, since, subject to assumptions described later, the motions of the methylene groups in any one vibration differ only in sense.

In constructing new symmetry coordinates from those obtained as described above, combinations of the forms $\xi_{ia} + c\xi_{ja}$, $\xi_{ib} + c\xi_{jb}$, $c\xi_{ia} - \xi_{ja}$, $c\xi_{ib} - \xi_{jb}$ are used provided ξ_{ia}, ξ_{ib}, ξ_{ja} and ξ_{jb} are normalized to the same value, i. e.

$$\sum_i m_i \left(\bar{a}_i \cdot \bar{a}_i - \bar{b}_i \cdot \bar{b}_i\right) = 0 \qquad (9)$$

where $\bar{a}_i$ represents the displacement of the ith atom in one vibration and $\bar{b}_i$ that in the standard vibration. These forms for combinations are derived by straightforward application of the orthogonality condition, equation (1). Combinations such as $\xi_{ia} + \xi_{jb}$ are not considered because we shall later specify that all vibrations shall be either symmetric or antisymmetric with respect to the yz-plane, with "a" indicating the symmetric and "b" the antisymmetric vibrations.

Combinations involving n vibrations, $\xi_{1a} + \xi_{2a} + \ldots . + \xi_{na}$, can be treated analogously, though with considerably more complex results. In general $n^2 - \frac{n}{2}(n-1)$ coefficients may be specified arbitrarily, since the orthogonality requirement supplies $n/2(n-1)$ equations relating the coefficients. In the case of two vibrations we have specified the coefficients 1 and c.

b. 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 coordinates of a flat X_6 ring have been given by Herzberg (11) (p. 93) and have been adopted by Ramsay and Sutherland (16) for the ring vibrations of cyclohexane. We have adapted these to the puckered X_6 ring as shown in Fig. 6, 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. 6 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 (10) for cyclo-hexane are shown in Figs. 6 and 7.

The projections on the xy-plane of the displacements in the A_{1g} vibrations are required by symmetry to have the same magnitude for all atoms, and to be directed radially and in the same sense for all atoms. Symmetry also requires that the z-component of the displacements be alternately positive and negative for alternate atoms, and that it have the same magnitude for all atoms. It seems plausible to assume that the two vibrations will be (1) one which does not change the shape of the ring but alternately expands and contracts it and (2) one which bends the ring without appreciably changing the bond lengths. These conditions are satisfied if the displacement vectors of the stretching vibration make an angle of 35°16' with the xy-plane and if the displacement vectors of the bending vibration make an angle of 54°44' with the xy-plane (assuming tetrahedral bond angles).

Cyclohexane, tetrahydropyran and p-dioxane have only one element of symmetry in common, 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 (16) in choosing for discussion those pairs of degenerate vibrations which meet this condition, so that they may be comparable. There is no loss of generality in doing this, of course, since any possible degenerate vibration can be decomposed into two such orthogonal vibrations. In Figs. 6 and 7 the letters (a) and (b) identify the symmetric and antisymmetric components, respectively. 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 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 E_u vibrations resemble the A_{1g} vibrations in that the forms of the projection on the xy-plane and of the z-component are completely determined by symmetry and the requirement of zero linear momentum, but the way in which these are combined is arbitrary. 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 should not change their orientation.

c. Hydrogen bending vibrations

It is customary in discussing the bending vibrations of methylene hydrogens to speak of bending, rocking wagging, and twisting vibrations*. 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 motions of a pair of methylene hydrogens are termed bending, rocking, wagging or twisting according to whether their motions are perpendicular to the C-C-C plane and symmetrical with respect to that plane, perpendicular and antisymmetrical, parallel and symmetrical, or parallel and antisymmetrical, respectively. Recently the more descriptive term "scissors" has come into use for the perpendicular, symmetrical motion and will be adopted in this thesis.

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. 7. In many of the vibrations, of course, the ring is required

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*See for example R. S. Rasmussen (9) and Beckett, Pitzer and Spitzer (10) to move also, in order to satisfy the requirements of zero angular and linear momentum; the reader can readily supply such motions.

4. The normal vibrations of tetrahydropyran and p-dioxane

a. Plausible forms

Ring vibrations of the exact form of those shown in Fig. 6 are not quite orthogonal for tetrahydropyran and p-dioxane because of the changes in mass distribution, hence independent of other considerations the ring vibrations of the latter cannot be expected to be exactly like those of cyclohexane. Furthermore the relatively greater strength of the C-O bonds as compared with the C-C bonds will tend to cause the motions of the carbons to be somewhat more nearly along or perpendicular to the C-O bonds than would otherwise be the case. A set of vibrations which satisfy the orthogonality requirements of p-dioxane or tetrahydropyran can be drawn which is so closely similar to that shown in Fig. 6 that it would be difficult to show the differences in a figure. We shall assume that the differences are actually small, and that Fig. 6 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 forms of the hydrogen bending vibrations of p-dioxane, as was the case with cyclohexane, are determined by the symmetry of the molecule and the assumptions described under cyclohexane. The motions of the hydrogens alone in the vibrations as so determined may be derived from the cyclohexane vibrations shown in Fig. 7 by simply removing the proper hydrogens. 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 notations 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 vibrations as follows: E_g(a) rocking or scissors with A_{1g} rocking or scissors, E_u(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.

b. Frequencies

We shall make no attempt to predict accurate frequencies, but will discuss only the sign and order of magnitude of the differences from the cyclohexane 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, but of the same sign, 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. Without knowing quantitatively what the bond angles and lengths are in tetrahydropyran, we can outline some qualitative trends as compared with cyclohexane. Almost certainly the distances between the 2 and 6 carbons will be somewhat less than in cyclohexane, the 2, 3 and 5, 6 bonds will not be parallel to each other, and the C-O-C plane will make a somewhat larger angle with the 2, 3, 5, 6 plane than does the 1, 2, 6 plane of cyclohexane, If we assume that any changes in the H-C-H angles are negligible, the net result is to bring the 2 and 6 polar hydrogens closer to each other, possibly into van der Waals contact, but farther from the 4 polar hydrogen, and to spread the 3 and 5 polar hydrogens farther apart. The resultant effect on the separation of the equatorial hydrogens depends on the relative magnitudes of the above trends, but is probably quite small because the z-component of the displacement of all the equatorial hydrogens has the same sign. A simple tinker toy or Hirschfelder model will help the reader to visualize the above changes. In our considerations we have regarded the 2, 3, 5, 6-plane as maintaining a constant orientation with respect to the z-axis and have assumed that C-C $\geqslant$ 1.51 A., C-O $\leqslant$ 1.44 A., $\angle$ C-O-C $\leqslant 116^{\circ}$ and that all carbon valence angles are tetrahedral.

In p-dioxane, on the other hand, both the 2, 6 and

3,5 pairs of polar hydrogens will be brought closer together, probably into van der Waals contact. If Hassel and Viervoll's model* (20) 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** (21) 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 A. (see Pauling (7), p. 189)).

It seems reasonable to expect that the interactions between hydrogens will be greater for p-dioxane than for tetrahydropyran, and in the absence of other effects many of the hydrogen frequencies of p-dioxane would be expected to be higher than for tetrahydropyran. It seems unlikely that all effects would cancel out for more than one or two vibrations at most, so that p-dioxane frequencies should in general be different from corresponding tetrahydropyran frequencies.

5. Rough estimated intensities of tetrahydropyran bands

All tetrahydropyran vibrations are permitted by symmetry to be active in both the Raman and infrared spectrum.

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*C-C = 1.54 A., C-O = 1.42 A., $\angle$ C-C-O = 106°
$\angle$ C-O-C = 108°

**C-C = 1.51 ± 0.04 A., C-O = 1.44 ± 0.03 A., $\angle$ C-C-O = 109.5 ± 5° C-O-C = 112.5 ± 5°, average ring angle = 110.5 ± 2°, $0.94 \leq$ C-O/C-C ≤ 0.98.

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, 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.

a. Intensities of Raman lines

Both classical and quantum mechanical treatments of the molecular scattering of light (see Herzberg (11), Chapter III; also Wu (22) and Breit (23)) attribute this phenomenon to the changing electric moment which is induced in the molecule by the electric field of the incident beam. Under the usual experimental conditions* for detecting the Raman effect the above interaction may be expressed in terms of a symmetric tensor called the polarizability tensor. Insofar as the components, α_{ij}, of the polarizability tensor, α, may be regarded as

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*The important conditions are (1) that the difference between the frequency of the exciting beam and of any absorption band of the molecule be large, (2) that the wave length of the incident beam be sufficiently large that the electric field may be regarded as the same in all parts of the molecule, and (3) that the electric field throughout the molecule due to the incident beam be large compared to that arising from other sources (see the excellent discussion by Mathieu (24)).

linear functions of the normal coordinates, ξ , the change in polarizability associated with a given vibrational transition, $[\alpha]_{nk}$, is

$$[\alpha]_{nk} = \left(\sum_{i,j=x,y,z} \partial\alpha_{ij}/\partial\xi \right) \int \psi_n \, \xi \, \psi_k^* \, d\xi \qquad (10)$$

where n and k represent the quantum numbers of the initial and final states and the ψ's are the eigenfunctions of the unperturbed states n and k. The intensity of the corresponding Raman line is then

$$I_{nk} = I_o \frac{64\pi^4(\nu + \nu_{nk})^4}{3c^3} [\alpha]_{nk}^2 \qquad (11)$$

where I_o is the intensity and ν the frequency of the incident beam and ν_{nk} is the frequency which corresponds to the energy released in the transition. In the harmonic oscillator approximation the integral in equation (10) is the same for all the fundamentals so that the intensity actually depends on the derived polarizability tensor, $\sum_{i,j=x,y,z} \alpha'_{ij}$. Without knowing the numerical values of the components, α_{ij} , of the polarizability tensor, or of their derivatives with respect to the normal coordinates, α'_{ij} *, we can nevertheless indicate by use of well-known principles which derivatives will have

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*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 coordinate ξ about the equilibrium configuration, e, or, briefly, $\alpha'_{ij} = (\partial\alpha_{ij}/\partial\xi)_e$ (Herzberg (6), p. 244).

non-zero values for a given vibration. It seems probable, in any case, that the $A_{1g}(A')$ "breathing" vibration, for which α_{xx}, α_{yy} and α_{zz} are all non-zero, will give rise to the strongest Raman line in the spectral region under consideration. In the absence of further information one might also 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 not only is the polarizability the same in opposite phases so that the value at the equilibrium configuration is an extremal and the diagonal derivatives are zero, but 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, 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.

b. 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_{1u}(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 rest of the ring. Both E_u stretching frequencies should be very strong also, for the same reason. As pointed out above, the two E_u frequencies should be well separated because (a) (A') is essentially a carbon-carbon and (b)(A") a carbon-oxygen vibration.

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, 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. As pointed out earlier, we cannot predict the activity of twisting vibrations on the basis of the motions of fractional formal charges, but if any 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.

6. 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 show 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, as with tetrahydropyran, will be expected to yield the strongest shift. We might expect also that the $E_g(b)(B_g)$ ring stretching band will be somewhat stronger than the corresponding tetrahydropyran band because the intensity of this band 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 bands 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 arise from the attraction of the positively charged nuclei for the valence electrons 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).

7. Assignment of bands

The assignments which we have made on the basis of the highly simplified picture described above are summarized in Fig. 8. The reasons for these assignments are given briefly below. The specific assignment of methylene frequencies is not unique, particularly for tetrahydropyran in view of the uncertainty of the forms of the vibrations, but the assignment of ring frequencies seems reasonable so that our major purpose has been achieved.

In Fig. 8 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.

a. Ring bands

The first step in assigning ring frequencies was to combine the above intensity considerations with Ramsay's approximate calculations (14) 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 (10), 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 are repeated below in cm.$^{-1}$ together with their intensities: Raman 835(10), 852 (0), 1014(6), 1111(3) and 1125(3); infrared 875(10), 890(7), 1020(0s), 1052(5), 1086(6) and 1122(10). 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.$^{-1}$ instead of the predicted 55 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*. 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**. 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 straight-forward, but we favor the $E_u(a)(B_u)$ over the $A_{1u}(A_u)$ stretching vibration because it appears to fit

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*The ring stretching frequencies calculated by Ramsay and Sutherland (7) 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.

**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.

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.

If the above ring assignments for p-dioxane are accepted, the ring assignments for tetrahydropyran as shown in Fig. 8 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.

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. 6 and obtained by adding the ring stretching and bending E_g vibrations chosen by Ramsay, 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 form 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 vibrations.

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.

b. 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. 8 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 is 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 bands to vibrations of the same symmetry raises the question of the possibility of the former "borrowing" some intensity from the latter. The other assignments in this region have little significance except to show that the number of bands is satisfactory.

8. 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 usual approach is to count the number of fundamentals which are permitted to be active in each of the Raman and infrared spectrum by the symmetry of the structures to be compared. Structures which require less than the number of bands found experimentally are then eliminated unless the extra band or bands can be explained plausibly as a combination frequency or overtone. In many cases, for example that of cyclohexane (25) or of p-dioxane (14), the permitted frequencies can be grouped into distinct spectral regions with little loss in rigor.

The estimation of relative intensities by the rough methods of the present paper can hardly compare in rigor with the above, 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 infra-

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.

C. Cyclitols

Any interpretation of the infrared spectra of the cyclohexanehexols may be expected to be of direct use in a discussion of the infrared spectra of the pyranose sugars. Both groups of compounds probably have the chair-form ring, both have a multiplicity of hydroxyl groups, and the members of both groups differ among themselves principally in the arrangement of hydroxyls about the ring. From the point of view of interpreting their spectra, however, the cyclitols have the advantage of greater symmetry. The symmetry of scyllitol is undoubtedly a good approximation to D_{3d} and that of meso-inositol to C_s, whereas the sugars show no symmetry. A discussion of the spectra of some cyclitols, then, would seem to be a desirable preliminary to a consideration of sugar spectra.

In our preceding discussions we have shown that OH bending bands probably lie at frequencies above 1200 cm.$^{-1}$, and have found that stretching bands involving carbon and oxygen lie below this frequency. In sugar spectra only one other type of fundamental can possibly fall in the stretching region, namely tertiary hydrogen bending. In the present discussion we shall attempt to show that the principal infrared absorption bands of the cyclitols in the region 8.5 to 12.5μ and therefore, by inference, of the sugars, can be accounted for in terms of skeletal stretchings. In order to do this we shall assume that the forms of the skeletal vibrations can be related to those of cyclohexane and, as in the preceding discussion, shall make use of D_{3d} symmetry classes to identify them.

1. Experimental part

The infrared absorption spectra of mineral oil mulls of scyllitol (the all-trans cyclohexanehexol), meso-inositol and pinitol (a methyl ether of d-inositol) are shown in Fig. 9 for the spectral region 7.6 to 14μ. The scyllitol was kindly supplied by Dr. R. Christian Anderson (26) and the pinitol by W. W. Pigman. The meso-inositol was Eastman White Label.

A list of the frequencies in cm.$^{-1}$ of the bands shown in Fig. 9 are shown below, with relative intensities in parentheses:

Scyllitol 730 (4b), 800 (0b), 900 (2s), 985 (9), 1004 (9), 1070 (2s), 1088 (4s), 1105 (10), 1121 (9), 1208 (0s), 1220 (1), 1241 (1), 1280 (1), 1305 (5).

meso-Inositol 736 (3), 894-900 (unresolved pair) (5), 930 (3) 1002 (6), 1014 (5), 1053 (10), 1117 (8), 1151 (8), 1199 (3), 1222 (1), 1250 (3).

Pinitol 752 (3), 861 (2), 903 (2), 962 (5), 1002 (6), 1025 (6), 1055 (6), 1074 (10), 1085 (6s), 1106 (5), 1129-1138 (unresolved pair) (8), 1193 (1), 1209 (0s), 1248 (2), 1277 (2), 1309 (0).

meso-Inositol has also been examined by Kuhn, (2), in the form of a film evaporated from water. In contrast to the sugars when examined in this form, meso-inositol yielded well-resolved bands, though the intensities differ from ours below 100 cm.$^{-1}$.

2. Scyllitol

a. Structure

Scyllitol may be regarded as derived from cyclohexane by replacing one set* of hydrogens by hydroxyl groups. In principle either the polar or equatorial set might be replaced, but steric considerations favor the equatorial; we shall assume the latter form, which is also favored by the spectroscopic evidence, as is pointed out below. If, now, the hydroxyl hydrogens alternately point up and down, the full symmetry of cyclohexane is retained. The carbons, the hydrogens attached to carbon, and the oxygens each constitute a set, which we shall hereafter refer to as the C, H and O sets, respectively.

The symmetry of the carbon-oxygen skeleton may in any case be though of as D_{3d}, with small distortions introduced by a lack of symmetry in the force field in the crystal. That there will be such distortions is shown by the fact that scyllitol crystallizes in the monoclinic system (27) and cannot therefore have an overall symmetry greater than C_{2h}.

Fig. 4 can be used to help visualize the all-equatorial structure which we have assumed. The 1, 3 and 5 oxygens are in approximately the same plane as the 2, 4 and 6 carbons, while the 2, 4 and 6 oxygens are in approximately the same plane as the 1, 3 and 5 carbons. We will not

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*See definition above.

attempt to locate the hydroxyl hydrogens.

b. Forms of vibrations

As pointed out above we shall be concerned in this discussion only with tertiary hydrogen bendings and skeletal stretchings. As far as these types of vibrations are concerned the symmetry of the molecule is probably D_{3d} to a fairly high degree of approximation, and we shall assume this symmetry in our discussion.

The vibrations of the tertiary hydrogens can be obtained directly from Fig. 7 by considering only the interior arrows. It is immediately apparent that only the E_u vibrations can be active, in accord with the selection rules, so that there should be only two hydrogen bending frequencies of any intensity, with the reservation that the E_u vibrations may be split by the deviations from D_{3d} symmetry. It is highly unlikely that the deviations would be great enough to cause any other vibrations to be active with appreciable intensity.

The forms of the skeletal vibrations present an entirely different problem from that of cyclohexane, since we now have two sets of heavy atoms. Appreciable amplitudes of relative translation must now be included in a consideration of the forms of the vibrations of each set. Also carbon-oxygen and carbon-carbon frequencies are not greatly different so that we may expect interaction between the vibrations of the two sets.

It seems reasonable to expect that the principal motion of the oxygens in skeletal stretching vibrations will be along the carbon-oxygen bonds. Such a motion may readily be worked out for the O set in the infrared-active A_{2u} and E_u vibrations by combining the motions shown in Fig. 6* with the appropriate translations. The translation of the O set must, of course, be accompanied by the opposite translation of the C set. The A_{2u} vibration of the C set is a bending vibration and therefore of relatively low frequency so that the motion of the ring in the A_{2u} skeletal stretching vibration will probably be simple translation in the z direction. In the E_u vibrations, however, we may expect the stretching vibrations of the C set to interact strongly with those of the O set. Suitable A_{2u} and E_u skeletal stretching vibrations may be represented in terms of the motions shown in Fig. 6 as follows: A_{2u}, $(A_{2u} - T_z)_O + (T_z)_C$; E_u, $(E_u(a) + T_y)_O + (E_u(a) - T_y)_C$ and $(E_u(b) - T_x)_O + (E_u(b) + T_x)_C$, where T_x, T_y and T_z reprent the translations and O and C indicate the sets. The motions of the carbons are not directly along any bonds since each carbon is attached to three heavy atoms. It is not at all obvious which of the two sets of E_u vibrations should be expected to have the lower frequency.

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*In this discussion the bonds shown in Fig. 6 are disregarded and only the atoms and symbols considered.

If the carbon bond angles are all tetrahedral and the amplitudes of the motions of the oxygens are about the same in all the above vibrations, the change in moment in the two E_u vibrations will be about the same and roughly three times that in the A_{2u} vibration (i. e. sin 70.5°/cos 70.5°). Infrared intensity varies as the square of the change in moment so that this highly simplified treatment indicates that the E_u vibrations will give rise to substantially stronger bands than will the A_{2u} vibration.

c. Discussion of spectrum

The outstanding features of the scyllitol spectrum are the two very strong double bands at about 1000 and 1100 cm.$^{-1}$. There seems little doubt that these two pairs correspond to the two E_u skeletal stretching vibrations, split by the distortion introduced by the unsymmetrical crystalline force field.

Independent of steric considerations, the presence of these two very strong doublets rules out the possibility of an all-polar structure for scyllitol. The all-polar form would indeed have two infrared-active skeletal stretching bands, but only one of these would be degenerate and therefore capable of splitting to form a doublet, namely the ring stretching band. Furthermore there would be much less interaction between ring and oxygen vibrations since they have different symmetries and any interaction would have to arise from the deviation from D_{3d} symmetry.

As a consequence we would expect the infrared spectrum of the all-polar form to show only one band of much greater intensity than all the rest, and this one band could not be a doublet.

The strongest shoulder on the 1100 cm.$^{-1}$ doublet, at about 1088 cm.$^{-1}$, might be the A_{2u} skeletal stretching frequency. We are reluctant to attempt assignments for the rest of the bands without first making a study of the 6.5 to 7.5μ region because tertiary hydrogen bendings in the hydrocarbons are reported by Rasmussen (9) to fall in the region 1300-1350 cm.$^{-1}$, or 7.4 to 7.7μ. We might, however, tentatively assign the four weak bands from 1220 to 1305 cm.$^{-1}$ to hydrogen bendings.

The broad band at about 730 cm.$^{-1}$ is either complex or involves a transition between poorly defined energy levels, such as might be the case for torsional oscillations of the hydroxyls. The frequency is very high for torsional vibrations, however, so that if they are involved it would have to be as a combination band, probably with the A_{2u} carbon-oxygen bending vibration*. If this is correct we might expect to find a very intense fundamental in the far infrared.

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*Translation of the O set along the z-axis with C (and H) set moving in opposite direction.

It is exceedingly unfortunate that Raman data are not available for scyllitol, since we could almost certainly identify a few more bands which would be very useful in our discussion of the other cyclitols and, eventually, the sugars.

3. meso-Inositol and pinitol

If one of the hydroxyls of scyllitol is moved to the polar position (without moving it to a different carbon), the resulting molecule is that of meso-inositol. If, then, the process is repeated on a neighboring hydroxyl group, we obtain d- or l-inositol, depending on which neighbor is selected; d-inositol is obtained if, with the meso-inositol molecule oriented so that the polar hydroxyl is nearest the reader, and above the plane of the ring, the left-hand neighbor is selected. Pinitol is monomethyl ether of d-inositol, but it is not known which one of the three possible isomers.

meso-Inositol has a potential symmetry of C_s and pinitol C_1*, so that all vibrations are permitted to be active in both the Raman and infrared. As might be expected, then, the infrared absorption spectra of these compounds are appreciably more complex than that of scyllitol.

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*d-Inositol has a potential symmetry of C_2, but since the methyl group cannot lie on the C_2 axis pinitol cannot have any symmetry.

In discussing these spectra we shall regard the vibrations as derived from scyllitol vibrations, and shall identify them in terms of the symmetry class of the related scyllitol vibrations.

Obviously the increased dissymmetry of the molecules will cause additional splitting of the vibrations which are related to the E_u vibrations of scyllitol. We might tentatively assign these to the 1002, 1014, 1117 and 1151 cm cm.$^{-1}$ bands of meso-inositol and to the 1002, 1025, 1106 and 1129 or 1138 cm.$^{-1}$ bands of pinitol. The A_{2u} vibration, with greatly increased infrared intensity because of the presence of polar hydroxyls, might then be assigned to the strong 1053 and 1074 cm.$^{-1}$ bands of meso-inositol and pinitol, respectively.

If we limit skeletal stretching frequencies to the spectral region 800 to 1150 cm.$^{-1}$ and hydrogen bendings to higher frequencies, three more meso-inositol and six more pinitol bands must be accounted for in terms of skeletal stretchings. Meso-Inositol has a total of twelve and pinitol thirteen skeletal stretching vibrations.

Three of the remaining unassigned pinitol frequencies are in the upper part of the stretching range. One of these is probably the C-O stretching band of the methoxy group, perhaps the unassigned member of the 1129-1138 cm.$^{-1}$ pair. The other two, at 1055 and 1085 cm.$^{-1}$ can then be assigned to vibrations derived from the E_g vibrations of scyllitol.

The remaining three bands in the stretching regions of the meso-inositol spectrum, at 930, 900 and 894 cm.$^{-1}$, and the pinitol spectrum, at 962, 903 and 861 cm.$^{-1}$, may be assigned to the breathing vibration of the oxygens and to the two remaining "E_g" vibrations, respectively.

We shall not attempt to assign the bands lying outside the spectral region which we have selected as the skeletal stretching region, namely 800 to about 1150 cm.$^{-1}$.

Part III. Pyranose Sugars

A. Structure

The arrangement of substituents about the asymmetric carbons of the sugars has been known for years, but very little detailed information about the structure of the sugars is available. Atomic parameters have been obtained by means of x-ray diffraction for only two sugars or sugar derivatives, namely α-glucosamine hydrobromide (28) and sucrose sodium bromide dihydrate (29); in both cases the pyranose ring was shown to have a chair-type conformation, but the accuracy of the parameters is not sufficient to show how closely it approximates the theoretical strainless trans ring.

Discussions of the structures of the sugars have been given in recent years by Cox, Goodwin and Wagstaff (30), Pacsu (31) and Hassel and Ottar (32). In the two latter discussions a strainless ring is assumed, whereas in the former a flattened, strained form of the ring is proposed. Apparently the latter authors were not aware of the existence of the first article because no attempt is made to answer the carefully formed arguments advanced by Cox, Goodwin and Wagstaff in favor of the strained ring. In our discussion of the spectra of the sugars we shall assume a modified chair-form ring, but first we shall attempt to justify this assumption as far as is possible in the absence of detailed x-ray data.

Cox, Goodwin and Wagstaff base their case primarily on the observation that the smallest unit cell dimension of each of eight pyranose sugars and derivatives lies between 4.6 and 5.0 A. and that the smallest unit cell dimension* of eleven methylated sugars and derivatives lies between 4.4 and 4.9 A.. Six furanoid compounds, whose rings are presumably very nearly flat, show a smallest unit cell dimension between 4.4 and 4.75 A.. They state that these observations are incompatible with any form of Sachse ring, by which they no doubt mean any strainless ring, but would be in excellent agreement with a form in which the five ring carbons are approximately in a plane and the oxygen is tipped up out of the plane. The coplanarity of cis C-O bonds 2 and 3, and of 3 and 4 of such a model would give a ready explanation for the ease of formation of isopropylidene compounds with cis hydroxyls in the case of the sugars, whereas attempts to form such compounds with quercitol or inositol, which probably have the chair-form ring, have been unsuccessful. Since the carbon-oxygen bonds of the 1 and 2 hydroxyls are not coplanar in the above model we also have an explanation of the fact that attempts to form 1,2-isopropylidene compounds often yield the furanose form, in which the 1 and 2 carbon-oxygen bonds would be coplanar, or very nearly so.

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*This dimension places an upper limit on the thickness of the molecule.

They also suggest that the existence in solution of two isomeric "flat" forms with the oxygen tipped opposite ways and with relatively small difference in energy might explain the complex mutarotation behavior of many sugars.

The x-ray exidence cited by Cox, Goodwin and Wagstaff shows clearly that the molecules of many pyranose sugars and their derivatives pack in the crystal in such a way that the distance along a normal to the mean plane of the ring from any point in one molecule to the equivalent point in an adfacent molecule is too small to correspond to a structure based on a strainless trans ring. We shall attempt to show, however, that these observations can be satisfactorily explained on the basis of a less strained structure than their "flat" pyranose ring.

In our discussion the thickness of the molecule will be understood to be the distance along a normal to the mean plane of the ring between corresponding atoms in two adjacent molecules; the packing is to be such that the centers of both atoms lie on the same normal. This type of packing is very nearly the closest possible for both the strainless Sachse trans form and the CGW form. In making our calculations we have assumed the van der Waals radii given by Pauling (7) and have used the results given by Beevers and Cochran (29) for the average values of the ring parameters of the glucose unit of sucrose, namely 1.50 A.. Pauling's value for the van der Waals radius of the methyl group has been used for the sugar methylene group. The terms polar and equatorial (10) will be used to identify both the atoms and bonds associated with the positions of substituents above or below and in the region of the mean plane of the ring, respectively, in the strainless Sachse trans form.

The thickness of a pyranose sugar which has a strainless trans ring is then 4.62, 5.18, or 5.74 A. according to whether there are no polar hydroxyls at all, polar hydroxyls on only non-adjacent carbons, or polar hydroxyls on adjacent carbons, respectively. If the hydroxy-methyl group is in a polar position, 0.74 A. must be added to the above figures, but we shall assume with Pacsu (31) and Hassel and Ottar (32) that this form is the less probable of the two possible trans form for any sugar. The thickness of the CGW structure is 4.63 or 4.91 A. for any pyranose sugar depending on whether the hydroxymethyl group is cis or trans to the oxygen*.

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*The apparent discrepancy between our figures and those cited by Cox, Goodwin and Wagstaff is purely the result of a difference in the definition of thickness. The CGW value of 1.5 A. for the extreme variation in thickness for trans forms appears to refer to the thickness obtained by taking the distance between two impenetrable planes parallel to the mean plane of the ring and touching the outermost atom on either side of the mean plane.

The relative positions of the hydroxyls and the terminal hydroxymethyl group for each of the sixteen* aldohexoses is shown below on the assumption of a strainless trans ring with the hydroxymethyl group in the equatorial position. The number 2 refers to the equatorial region and 1 and 3 to the two polar regions; the positions are given consecutively for the nonhydrogenic substituent on each carbon from 1 to 5 so that the configuration appears as a five-digit number made up of one's, two's and three's.

α-Glucose 32222, β-glucose 22222, α-mannose 31222, β-mannose 21222, α-allose 32322, β-allose 22322, α-altrose 31322, β-altrose 21322, α-talose 31212, β-talose 21212, α-galactose 32212, β-galactose 22212, α-idose 31312, β-idose 21312, α-gulose 32312, β-gulose 22312.

The configuration of xylose, lyxose and arabinose may be obtained by dropping the fifth number from the configurations of glucose, mannose and galactose, respectively, with the exception that the and forms of arabinose are interchanged with respect to those of galactose. The stable form of ribose appears to be the furanose form (1). The configurations of xylose, lyxose and arabinose

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*We are not concerned here with the differences between D- and L- sugars since their spectra must necessarily be identical.

could in principle be derived from those of idose, gulose and altrose, respectively, but their properties show much more resemblance to glucose, mannose and galactose. The configurations of β-fructose and α-sorbose are probably 1223 and 3222, respectively, where the hydroxymethyl group has been assumed to be equatorial and has not been included in the configuration since it is attached to the same atom as the first hydroxyl group listed. The corresponding configurations of some cyclitols would be scyllitol 222222, meso-inositol 122222 and d- or l-inositol 132222, where the form with the smallest number of polar hydroxyls has been given.

The pyranose compounds cited by Cox, Goodwin and Wagstaff include the free sugars or derivatives of α- and β-glucose, β-mannose, α- and β-galactose, α- and β-arabinose, and xylose. Six of the nineteen compounds have no polar substituents and none have polar substituents on adjacent carbons. A comparison of the smallest unit cell dimensions cited by Cox, Goodwin and Wagstaff with our calculated thicknesses for the strainless trans form shows that at least thirteen of these compounds must deviate appreciably from the strainless trans form. In the absence of far more detailed x-ray data, however, it is apparent that the deviation is not required to be as great as that proposed by Cox, Goodwin and Wagstaff.

To explain the difference in behavior between the sugars and the cyclitols with respect to the formation of alkylidene compounds we must consider the effect of the ring oxygen. The six ring carbons of the cyclitols are probably equivalent, to a high degree of approximation, with respect to the dependence of potential energy on C-C-C angle. Any deformation of the ring, then, which must take place when an alkylidene compound is formed, may be expected to be such that all C-C-C angles change in the same direction and by the same amount. The C-O-C angle of the pyranose ring, however, can probably be decreased more easily than it can be increased since oxygen tends to form p bonds (7). Consequently when the pyranose ring is deformed it will tend to be deformed in such a way that the carbon bond angles are increased and the oxygen bond angle is decreased. This leads to a far greater ease of deformation for the pyranose ring than for an all-carbon ring as is shown by the fact that a CGW "flat" ring with the bond lengths and C-O-C angle which we have assumed above would have ring C-C-C angles of more than 118°, whereas with a C-O-C angle of 90° the C-C-C angles would be about 115°. Furthermore if the C-O bond lengths were 1.42 instead of 1.50 A., as we assumed above, and the C-O-C angle 90° instead of 109.5°, the other ring angles would be only about 113.5°. It is apparent, then, that whatever the equilibrium configuration of the sugars may be, they can assume the deformed configuration which is required for forming alkylidene compounds far more readily than the cyclitols can. The type of deformation which we have discussed above cannot, however lead to a configuration in which the 1 and 2 C-O bonds are coplanar, so that the relative difficulty of formation of 1,2-alkylidene compounds is also explained.

B. Monosaccharides

1. Experimental part

The infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of twenty-four monosaccharides and derivatives are shown in Figs. 10-14. The positions of the bands in cm.^{-1} are shown below with relative intensities in parentheses. Due to the variation in thickness between samples, as well as within each crystalline sample, little can be said about absolute intensities.

α-D-Glucose monohydrate 720 (2), 772 (3), 855 (3), 917 (3), 927 (0s), 1015 (10), 1030 (9), 1052 (7), 1072 (2), 1098 (2), 1112 (3), 1156 (6), 1209 (1), 1233 (0), 1248 (0).

α-D-Glucose 778 (3), 841 (4), 917 (2), 996 (8), 1027 (10), 1054 (7), 1081 (2), 1114 (7), 1152 (7), 1206 (1), 1227 (2), 1277 (0s), 1299 (1).

β-D-Glucose 740 (1), 902 (4), 916 (1s), 1017 (10), 1037 (9), 1086 (8), 1116 (7), 1157 (5), 1205 (1), 1229 (1), 1250 (1s), 1274 (2).

β-D-Mannose 700 (1), 734 (5), 773 (7), 858 (2), 901 (1), 936 (2), 1010 (4), 1036 (8s), 1046 (10), 1065 (9), 1076 (9), 1091 (10), 1124 (4), 1171 (5), 1220 (1), 1242 (3), 1264 (1).

α-D-Galactose 708 (1), 767 (5), 840 (6), 957 (5), 975 (2), 995 (1s), 1046 (8), 1071 (10), 1083 (6s), 1106 (6), 1140 (2s), 1152 (5), 1242 (2), 1297 (1).

α-D-Talose 710 (1), 768 (3), 803 (6), 818 (6), 876 (3), 907 (2), 950 (8), 985 (8), 1014 (7), 1054 (9), 1085 (10), 1114 (2), 1144 (6), 1235 (6), 1261 (2), 1272 (1s), 1318 (3).

α-D-Xylose 762 (4), 904 (5), 934 (6), 1018 (5), 1041 (10), 1060 (3s), 1082 (1), 1110 (2s), 1129 (5), 1151 (4), 1191 (2), 1205 (1s), 1238 (1).

β-D-Lyxose 710 (1), 755 (4), 773 (0), 843 (4), 854 (1), 884 (4), 954 (1), 1006 (8), 1036 (8), 1046 (8), 1067 (10), 1099 (8), 1110 (2s), 1133 (5), 1163 (4), 1220 (2), 1250 (0s), 1285 (0).

L-Arabinose·CaCl$_2$ 774 (4), 836 (2), 863 (2), 875 (2), 890 (0), 937 (4), 996 (5), 999 (9), 1015 (5), 1037 (9), 1049 (10), 1082 (8), 1111 (7), 1155 (8), 1193 (1), 1212 (1), 1263 (1), 1309 (1).

β-D-Arabinose 787 (9), 845 (5), 895 (4), 944 (2), 997 (9), 1055 (10), 1067 (6s), 1094 (8), 1106 (4s), 1136 (9), 1226 (3), 1244 (3).

D-Ribose 730 (3), 750 (2s), 763 (0s), 807 (2), 869 (2), 891 (2), 911 (2), 923 (2), 949 (6), 957 (4s), 1015 (7s), 1037 (10), 1083 (4), 1119 (6), 1133 (4), 1147 (3s), 1159 (7), 1215 (0s), 1239 (1), 1277 (3).

Methyl Glucoside·CaCl$_2$ 725 (2s), 739 (3), 774 (2), 824 (3), 874 (4), 915 (1), 952 (1), 1013 (8), 1043 (10), 1055 (6s), 1073 (9), 1102 (6), 1113 (5), 1148 (4), 1193 (1), 1220 (1s), 1231 (2), 1268 (2), 1278 (2), 1303 (0).

Methyl α-D-Mannoside 725 (2), 816 (6), 849 (3), 889 (1), 915 (1), 971 (9), 1029 (10), 1056 (8), 1070 (7), 1102 (7), 1119 (7), 1132 (7), 1200 (3), 1219 (3), 1245 (1), 1256 (1).

α-L-Rhamnose (6-desoxy α-L-mannose) 805 (3), 835 (3), 879 (1), 910 (1), 976 (5), 1035 (10), 1075 (8), 1086 (3s), 1120 (5), 1142 (2), 1223 (2), 1285 (2).

α-L-Fucose (6-desoxy α-L-galactose) 773 (4), 820 (6), 879 (2), 916 (2), 963 (3), 999 (6), 1032 (6s), 1042 (10), 1073 (7), 1091 (4s), 1112 (4), 1129 (4), 1168 (5), 1221 (2), 1250 (1), 1297 (2).

α-D-Isorhamnose (6-desoxy α-D-glucose) 805 (5), 835 (5), 879 (2), 911 (2), 975 (5), 1035 (10), 1068 (4s), 1075 (9), 1085 (5s), 1122 (7), 1143 (4), 1222 (5), 1285 (3).

α-D-Glucosamine 774 (3), 855 (2), 889 (1), 913 (2), 1004 (4), 1035 (10), 1064 (4), 1094 (6), 1117 (2), 1139 (2), 1182 (3), 1218 (1), 1247 (2).

6-Methyl α-D-Glucose 774 (4), 790 (1s), 858 (4), 913 (2), 949 (2), 1011 (8), 1046 (9), 1058 (10), 1080 (8), 1099 (5s), 1116 (5s), 1126 (8), 1144 (8), 1196 (3), 1253 (1), 1304 (1).

3-Methyl α-D-Glucose 754 (4), 770 (0s), 845 (2), 919 (4), 955 (1), 1002 (8), 1024 (9), 1037 (10), 1057 (8), 1085 (5), 1100 (7), 1114 (5), 1141 (7), 1199 (1), 1228 (1), 1290 (1).

2-Methyl β-D-Glucose 700 (1), 770 (1b), 904 (4), 955 (6), 1018 (9), 1064 (10), 1088 (8), 1124 (8), 1130 (6s), 1159 (6), 1214 (3), 1264 (2).

Levoglucosan (1,6-anhydro β-D-glucose) 790 (1), 834 (2), 860 (7), 894 (6), 921 (7), 949 (5), 989 (6), 996 (5), 1013 (8), 1045-1053 (unresolved pair) (10), 1079 (8), 1091 (4), 1111 (2), 1142 (6), 1185 (1), 1229 (2), 1258 (2) 1290 (5).

Sorbose 725 (2), 821 (4), 883 (3), 901 (1s), 992 (3), 1013 (3s), 1028 (3s), 1049 (10), 1065 (4s), 1083 (4s), 1110 (6), 1129 (3s), 1149 (3), 1190 (3), 1256 (3).

Fructose 784 (5), 820 (2), 864 (1s), 876 (3), 923 (1), 978 (7), 1027 (4s), 1053 (10, 1065 (6s), 1079 (10), 1095 (8), 1133 (3s), 1149 (7), 1172 (3), 1227 (0s), 1245 (1s), 1264 (2).

$(\text{Fructose})_2 \cdot CaCl_2 \cdot 3H_2O$ 786 (6), 825 (2), 861 (3), 879 (2), 919 (1), 982 (5), 1036 (8), 1050 (5), 1070 (7), 1085 (10), 1114 (6), 1144 (3), 1168 (8), 1178 (1s), 1250 (2), 1267 (1).

The β-D-glucose ($[\alpha]_D = +24°$) was prepared according to the method of Hudson and Dale (33) by precipitating it from hot concentrated acetic acid, then taking up the crude product in ice water and reprecipitating by addition of absolute alcohol. α-D-Glucose monohydrate was prepared by recrystallizing commercial anhydrous glucose from water. The L-arabinose calcium chloride compound, methyl α-D-mannoside, α-L-rhamnose, α-L-fucose, α-glucosamine hydrochloride, 6-methyl α-D-glucose, 3-methyl α-D-glucose, 2-methyl β-D-glucose, levoglucosan and α?-L-sorbose were supplied by Dr. C. M. McCloskey; and the α-D-talose, methyl guloside calcium chloride compound, α-D-isorhamnose, and $(\text{fructose})_2 \cdot CaCl_2 \cdot 3H_2O$ by Dr. W. W. Pigman. The remaining samples were obtained from the chemical stockroom.

The arabinose calcium chloride compound was prepared as the α variety, but does not have the properties of any previously reported calcium chloride compound of arabinose. No mutarotation could be detected in solution.

α-D-Glucose, β-D-mannose, α-D-galactose, α-D-xylose, β-arabinose, D-ribose, methyl α-D-mannoside, α-L-rhamnose, α-L-fucose, α-glucosamine hydrochloride, 3-methyl α-D-glucose, levoglucosan and α?-L-sorbose have been examined also by Kuhn (2), but as stated earlier his resolution is not as good as ours and many of his samples show excessive absorption.

The very limited amount of previous work on the infrared spectra of sugars may be found in references (34) to (36). Wiemann (37) has examined the Raman spectra of several sugars, but unfortunately he does not define his symbols and since "f" could equally well mean strong or weak his work is not very helpful to us.

2. Infrared spectra

If the bands lying between about 800 and 1150 cm.$^{-1}$ are to be attributed solely to skeletal stretching vibrations, as is suggested by our study of the cyclitols, the hexoses may be expected to show a maximum of thirteen bands in this region and the pentoses eleven. Since the sugars have a methylene group, however, we might perhaps expect one or two additional weak bands in this region arising from rocking and wagging of the methylene group. A count of the number of bands in this region shows that the actual number ranges from only 7 for β-glucose to fourteen for levoglucosan and the arabinose calcium chloride compound. The latter compound may well be a mixture, however, and need not be considered.

Most of the spectra show about the same number of bands in this region, but the intensity distribution shows a fairly large variation. A very high proportion of the absorption in the β-glucose spectrum is concentrated in the spectral region from 8.5 to 10μ whereas the absorption of levoglucosan (1,6-anhydro-β-D-glucopyranose) is relatively evenly distributed over the spectral region from 8.7 to 12μ. Levoglucosan must have the configuration 13131, i. e. with all polar substituents, whereas β-glucose has all equatorial substituents so that these two compounds also represent the extremes with respect to the distribution of substituents among polar and equatorial positions. The spectrum of α-talose, which probably has three polar hydroxyls, has an intensity distribution approaching that of levoglucosan.

These observations lead us to investigate whether the intensity distribution can be correlated more closely with configuration. If β-mannose is excepted, the correlation is fairly good, with the proportion of absorption below 1000 cm.$^{-1}$ increasing with the number of polar hydroxyls. meso-Inositol and pinitol show about the same proportion although the latter has one more polar substituent than the former.

The above rough correlation appears to be useful in determining whether a derivative of a sugar is of the α or β form. The five derivatives of glucose shown in Fig. 13 can be readily classified from their spectra by this means. Rhamnose and fucose also follow this correlation fairly well.

A consideration of the forms of the cyclohexane vibrations shows that the effect of moving a large bond moment from an equatorial to a polar position is to reduce the intensity of the E_u skeletal stretching vibrations and to increase the intensity of all other skeletal stretching vibrations. Although the vibrations of the sugars are not expected to resemble those of cyclohexane at all closely, it is apparent that this general effect of distributing the intensity among more vibrations as the number of polar hydroxyls is increased is retained in the sugars. The effect of two polar hydroxyls on cyclohexane-type vibrations is smaller when the two are on adjacent carbons, as has been noticed experimentally for pinitol. It is interesting that methyl α-mannoside also shows little effect of the additional polar substituent compared with β-mannose.

It is not at all clear what types of vibration are responsible for the strong absorption of β-mannose, α-galactose, β-arabinose and fructose below 800 cm.^{-1}.

C. Di- and Tri-saccharides

1. Experimental part

The infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of thirteen di- and tri-saccharides are shown in Figs. 15 to 17. The positions of the bands in cm.^{-1} are given below with relative intensities in parentheses.

β-D-Maltose 779 (1), 850 (2), 907 (3), 1002 (8), 1014 (10), 1075 (10), 1106 (9), 1136 (7), 1149 (4s), 1206 (1), 1248 (1), 1271 (3), 1306 (1).

Cellobiose 743 (2), 896 (2), 975 (1s), 993 (5), 1030 (5s), 1048 (10), 1058 (6s), 1085 (9), 1102 (5s), 1130 (5), 1168 (5), 1211 (2), 1267 (2), 1287 (2).

α-Gentiobiose·$2CH_3OH$ 776 (1), 855 (0), 905 (1), 959 (0s), 997 (5s), 1027 (10), 1058 (9), 1079 (9), 1105 (7), 1134 (5s), 1148 (4s), 1168 (3s), 1200 (0s), 1250 (0).

Hydrol 774 (1), 846 (1), 918 (1), 1030 (10), 1083 (9), 1111 (8s), 1151 (8), 1205 (0s), 1250 (1).

α,α-Trehalose 806 (1), 843 (1), 855 (1), 879 (0s), 912 (1), 954 (2), 996 (10), 1011 (7), 1031 (8), 1062 (5), 1085 (6), 1101 (7), 1127 (6), 1149 (5), 1214 (1), 1239 (2).

α-D-Lactose hydrate 761 (3), 781 (5), 880 (4), 902 (3), 919 (1), 990 (5), 1007 (4s), 1024 (6s), 1038 (10), 1063 (7), 1076 (9), 1098 (9), 1120 (7), 1146 (6), 1171 (5), 1205 (2), 1264 (2), 1302 (1).

β-D-Lactose 739 (1), 770 (2), 879 (3), 893 (3), 948 (1), 989 (6), 1018 (4s), 1037 (8), 1048 (8), 1072 (10), 1099 (8), 1107 (3s), 1117 (7), 1159 (6), 1192 (1), 1211 (0), 1223 (0), 1252 (2), 1266 (0), 1285 (0), 1307 (2).

β-Neolactose 685 (0s), 715 (2), 780 (5), 794 (4), 850 (1), 869 (1), 882 (2), 903 (3), 912 (1s), 928 (0), 948 (0s), 962 (3), 1003 (3s), 1019 (7), 1033 (7), 1055 (10), 1091 (6), 1120 (3s), 1133 (8), 1163 (5), 1221 (2), 1256 (2), 1284 (2)

β-Melibiose 739 (1), 803 (4), 839 (1), 876 (2), 907 (1), 923 (1), 939 (1), 971 (3), 1017 (10), 1054 (10), 1075 (10), 1087 (3s), 1125 (7), 1134 (3s), 1153 (6), 1186 (1), 1220 (1), 1252 (2), 1277 (0).

Raffinose 735 (1), 758 (0s), 775 (2), 837 (2), 864 (2), 876 (2), 892 (0), 938 (4), 966 (5), 1000 (9), 1016 (4), 1034 (6), 1049 (10), 1082 (7), 1112 (5), 1155 (8), 1195 (0), 1212 (0), 1261 (1).

Sucrose 695 (1), 733 (2), 797 (0), 851 (2), 868 (3), 910 (6), 921 (4s), 942 (2), 986 (8), 1009 (6), 1040 (3s), 1054 (7), 1070 (10), 1106 (4), 1124 (5), 1161 (2), 1208 (1), 1236 (3), 1277 (1).

Turanose 698 (2), 713 (3), 747 (2), 806 (1), 840 (3), 865 (4), 899 (4), 909 (1s), 917 (0s), 934 (1), 969 (5), 1018 (8), 1041 (6s), 1059 (10), 1070 (5s), 1085 (7), 1109 (8), 1129 (4s), 1143 (7), 1202 (3), 1245 (2), 1274 (2), 1300 (0s).

Melezitose 717 (2), 784 (1), 831 (2), 852 (1), 873 (2), 916 (5), 930 (3), 996 (10), 1028 (8), 1048 (5s), 1057 (6s), 1066 (8), 1098 (5), 1112 (6), 1148 (5), 1223 (1), 1258 (2), 1292 (1s).

β-Cellobiose was supplied by Dr. L. Zechmeister; gentiobiose, hydrol, α,α-trehalose, β-lactose, raffinose, β-melibiose and melezitose by Dr. C. M. McCloskey; and β-neolactose and turanose by Dr. W. W. Pigman. β-Maltose, α-lactose and sucrose were obtained from the chemical stockroom.

β-Maltose, β-cellobiose, α,α-trehalose, α-lactose, raffinose and β-melibiose have also been examined by Kuhn (2).

2. Infrared spectra

The spectra of the di- and tri-saccharides have the same general characteristics as the monosaccharides except that they are somewhat more complex, as might be expected. Also, the individual bands below 1000 cm.$^{-1}$ are weaker relative to those in the 1000-1150 cm.$^{-1}$ region, probably because the higher frequency bands are spaced so close together that they overlap and add intensities.

By applying the correlation mentioned in the preceding section between intensity distribution and number of polar hydroxyls one might expect that of the glucose disaccharides whose spectra are shown in Fig. 15 the cellobiose is all β; maltose, gentiobiose and hydrol are mixed α and β; and trehalose is all α. This is correct for all except hydrol, of which the composition is not positively known. Wolfrom (38) has indicated that it contains a good proportion of isomaltose, which he believes to be 6-D-glucose α-D-glucopyranoside. Our prediction would be that it is the β form.

The glucose tri- and tetra-saccharides cellotriose and cellotetraose, whose spectra are shown in Fig. 18, also show a good correlation. The cellotetraose would be expected to be all β, whereas the complexity of the cellotriose spectrum indicates a mixture, which requires it to be α-cellotriose. These predictions were indeed made before it had been determined which forms had been examined.

The spectra of the mixed oligosaccharides are not nearly so clearcut, although α- and β-lactose appear to follow the correlation fairly well.

Part IV. Polysaccharides

A. Animal Cellulose

1. Experimental part

Suitable samples of native cellulose for examination in the very strongly absorbing 8 to 10μ region are difficult to obtain, which no doubt partially accounts for the lack of published data on the infrared spectrum of cellulose. Fortunately we have found the dried test of the tunicate Ciona intestinalis, which is very common off the Southern California coast, to be very satisfactory.

The cellulose is considerably swollen with water and on drying decreases in thickness from about 0.2 to about 0.002 mm., which gives about the right amount of absorption. The latter figure was estimated by comparing the infrared absorption of an average Ciona test with that of cellophane samples of known thickness supplied by Rayonier, Inc.. The dried test is as highly crystalline as ramie, as is shown by its x-ray diffraction pattern (39).

The Ciona tests were freed of the minute amount of protein material present by treatment for two days at 30°C. with each of the following successive solutions, as suggested by Professor Carl Niemann: 0.01f hydrochloric acid, 2 percent of pepsin in 0.01f hydrochloric acid, and 2 percent of pancreatin in a citrate-phosphate buffer of pH 7.8. This treatment does not affect the spectrum of the tests, but improves their keeping qualities. No attempt has been made to remove the small amount of pigment which is present. For examination the treated tests are placed on a brass ring about an inch and a quarter in diameter and are dried in an oven for one hour at 70°C.

The water-white, jelly-like inner casing of Ciona appears to be somewhat purer than the test in that it lacks the pigment; however, the pigment does not appear to affect the spectrum, and the test is more convenient to work with because of its greater tensile strength.

Mercerized samples are prepared by clamping the test firmly on a brass ring, then allowing it to stand for half an hour at room temperature in 20 percent sodium hydroxide; it is then washed two or three times in dilute acetic acid and repeatedly with distilled water. The thickness of the mercerized sample may be controlled roughly by the tightness with which it is stretched on the ring. During mercerization an unstretched sample decreases in linear dimensions by a factor of about three and increases in thickness so that it gives complete absorption between 8.3 and 10μ.

The infrared absorption spectra between 7.6 and 13μ of native and of mercerized animal cellulose (tunicin) are shown in Fig. 18 together with those of mineral oil mulls of some cellulose degradation products. The spectra of cellophane, starch and some starch degradation products are shown for comparison in Fig. 19. The positions of the bands in cm.$^{-1}$ are shown below with relative intensities in parentheses.

α-Cellotriose 777 (1), 850 (1), 890-898 (unresolved pair) (1), 933 (1), 979 (3s), 999 (8), 1020 (10), 1031 (8s), 1050 (9), 1075 (9), 1093 (9), 1119 (7), 1130 (3s), 1147 (5), 1163 (4), 1200 (1), 1224 (1), 1264 (2).

β-Cellotetraose 725 (1), 770 (0), 896 (2), 1101 (6), 1032 (10), 1053 (8s), 1088 (9), 1122 (8), 1164 (5), 1202 (1), 1229 (0), 1272 (0).

Tunicin 1014 (5s), 1037 (9), 1063 (10), 1116 (5), 1164 (4), 1210 (1), 1239 (1), 1269 (0s), 1319 (1), 1337 (1).

Mercerized tunicin 897 (1), 970 (3s), 998 (6s), 1033 (9), 1070 (10), 1119 (7), 1160 (5), 1209 (1), 1241 (1), 1267 (1s), 1321 (0), 1341 (0).

Cellophane 895 (1), 960 (2s), 992 (5s), 1024 (9), 1064 (10), 1112 (6s), 1155 (4), 1196 (1).

Maltose film 759 (0), 789 (0), 854 (1), 1114 (0s), 924 (1), 996 (4s), 1038 (10), 1079 (9), 1112 (7), 1153 (7), 1208 (0), 1248 (0).

Starch 765 (1), 855 (1), 930 (1), 997 (5s), 1036 (10), 1050 (8s), 1081 (8), 1115 (5s), 1153 (6), 1203 (0), 1241 (0).

α Schardinger dextrin 712 (1), 763 (0), 846 (0), 866 (0), 901 (0s), 938 (1), 953 (2), 1001 (5s), 1035 (10), 1060 (8), 1081 (8), 1101 (4s), 1157 (7), 1206 (0s), 1245 (0).

β Schardinger dextrin 709 (1), 762 (1), 858 (1), 943 (1), 999 (5s), 1031 (10), 1058 (8s), 1082 (8), 1107 (5s), 1156 (7), 1209 (0s), 1252 (0), 1302 (0).

α-Cellotriose was supplied by Dr. L. Zechmeister; β-cellotetraose and an additional sample of α-cellotriose by Dr. M. L. Wolfrom; and α- and β-dextrin by Dr. C. M. McCloskey. The thin sample of cellophane was obtained through the courtesy of Dr. O. Goldschmid of Rayonier, Inc., in Shelton, Washington; it was specially prepared without plasticizer by Dr. R. L. Mitchell and Mr. E. Mead. The starch is so-called soluble starch, obtained from the chemical stockroom. The maltose film was prepared by evaporation of a solution of maltose in 40% alcohol-water and was supported on silver chloride.

Impure samples of native plant cellulose have been examined by Stair and Coblentz (40), and Rowen, Hunt and Plyler (41) have published a curve for cellulose regenerated from cellulose acetate, but otherwise there is nothing in the open literature on the infrared spectrum of cellulose between 8 and 13μ.

2. Infrared spectra

The chemical and structural identity of animal cellulose with plant cellulose has been shown by Zechmeister and Toth (42), Gross and Clark (39), and others (43-45). These experiments do not, however, exclude the possibility of small differences which might show up in the spectrum. The spectrum of native animal cellulose, shown in Fig. 18, resembles reasonably well the spectra obtained by Stair and Coblentz (40) from unpurified samples of plant cellulose, but to be significant, such a comparison would have to be made with purer samples.

The cellulose absorption spectrum resembles that of the sugars in that most of its absorption occurs in the spectral region from 8.5 to 10μ and it resembles the spectra of β-cellobiose and β-cellotetraose in its lack of absorption beyond 10μ. As with the cyclitols and the sugars, it seems probable that the bands in the strongly absorbing 8 to 10μ region arise from skeletal stretching vibrations.

Aside from the resemblances mentioned above, however, the cellulose spectrum is quite different, even from those of its own degradation products. There is scarcely a trace of the strong band at about 9.2μ, for example, or the secondary band at about 11.1μ, both of which are present in the spectra of the degradation products. The relative simplicity of the cellulose spectrum compared with the spectra of cellulose degradation products might well be related to the fact that the cellulose molecules are long straight chains of glucose units. The infrared spectrum of starch, which has coiled molecules, shows a much closer resemblance to those of its degradation products as shown in Fig. 19. A study of the nature of the interactions along straight and coiled chains might shed some light on the matter.

Mercerization of animal cellulose decreases the resolution of the spectral bands between 8.5 and 10μ, eliminates the weak 9.85μ shoulder, considerably strengthens the 10.0 and 10.3μ shoulders, and introduces a weak 11.1μ band. The spectrum of a somewhat thicker sample of mercerized tunicin than that shown in Fig. 18 is almost identical with that obtained by Rowen, Hunt and Plyler (41) with a cellulose film regenerated from cellulose acetate and agrees well also with the cellophane spectrum shown in Fig. 19. The band at 11.1μ appears to be somewhat weaker than the corresponding cellophane band and there are small differences below 8.3μ, but the possibility that mercerization was not complete cannot be excluded.

B. Cellulose Derivatives

1. Experimental part

The infrared absorption spectra from 7.6 to 14μ of evaporated films of some nitrocelluloses, cellulose acetate, and methyl and ethyl cellulose are shown in Figs. 20 and 21. The positions of the bands in cm.$^{-1}$ are shown below together with relative intensities in parentheses.

Nitrocellulose, 10.93% nitrogen 753 (2), 845 (9), 921 (0s), 944 (0s), 998 (7), 1071 (9), 1125 (6), 1164 (5), 1211 (0), 1284 (10).

Nitrocellulose 12.55% nitrogen 753 (1), 845 (7), 921 (0s), 944 (0s), 998 (5), 1026 (5), 1071 (7), 1125 (4), 1164 (3), 1211 (0), 1284 (10).

Nitrocellulose 13.46% nitrogen 753 (2), 845 (8), 921 (0s), 944 (0s), 998 (6), 1026 (6), 1071 (8), 1125 (4), 1164 (4), 1211 (0), 1284 (10).

Ramie cellulose acetate 839 (0), 878 (0), 905 (1), 951 (0), 989 (2s), 1053 (10), 1127 (4), 1164 (4), 1233 (10), 1323 (0).

Methylcellulose 948 (2), 1020 (5s), 1075 (10), 1121 (9), 1156 (6s), 1201 (2s), 1314 (2s).

Ethylcellulose 886 (1), 923 (1), 977 (1s), 1030 (5s), 1060 (10), 1089 (10), 1114 (10), 1159 (5s), 1183 (2s), 1205 (0s), 1282 (0), 1314 (1).

All except ethyl cellulose have been examined by Kuhn (2), cellulose acetate has been examined by Rowen, Hunt and Plyler, and nitrocellulose by Freymann and Freymann (47).

2. Infrared spectra

As might be expected the infrared bands of films of cellulose derivatives are not as well resolved as those of native animal cellulose. The spectra of nitrocellulose and methyl and ethyl cellulose appear to resemble that of mercerized more than that of native cellulose, but the spectrum of cellulose acetate bears somewhat more resemblance to that of native cellulose.

The bands of nitrocellulose in the cellulose region, 8 to 10μ, sharpen up appreciably with increases in the nitrogen content and it seems likely that the "new" band which appears in the spectra of nitrocelluloses with higher nitrogen content at about 9.8 is present but unresolved in the spectrum of the nitrocellulose with the lowest nitrogen content.

The nitrocellulose band at about 11.9μ appears to shift about 0.1μ to longer wave lengths in going from 12.55 to 13.46 % nitrogen.

It is interesting that the positions of the nitrate bending bands correspond fairly closely to those of the nitrate ion (48), whereas the stretching bands correspond better with those of nitric acid.

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Appendix

Table 2

Conversions from Microns to Reciprocal Centimeters

μ	cm.$^{-1}$	μ	cm.$^{-1}$	μ	cm.$^{-1}$
7.6	1316	10.1	990	12.6	794
7.7	1299	10.2	980	12.7	787
7.8	1282	10.3	970	12.8	781
7.9	1266	10.4	962	12.9	775
8.0	1250	10.5	952	13.0	769
8.1	1235	10.6	943	13.1	763
8.2	1220	10.7	935	13.2	758
8.3	1205	10.8	926	13.3	752
8.4	1191	10.9	917	13.4	746
8.5	1177	11.0	909	13.5	741
8.6	1163	11.1	901	13.6	735
8.7	1149	11.2	893	13.7	730
8.8	1136	11.3	885	13.8	725
8.9	1124	11.4	877	13.9	719
9.0	1111	11.5	870	14.0	714
9.1	1099	11.6	862	14.1	709
9.2	1087	11.7	855	14.2	704
9.3	1075	11.8	848	14.3	699
9.4	1074	11.9	840	14.4	694
9.5	1053	12.0	833	14.5	690
9.6	1042	12.1	826	14.6	685
9.7	1031	12.2	820	14.7	680
9.8	1020	12.3	813	14.8	676
9.9	1010	12.4	807	14.9	671
10.0	1000	12.5	800	15.0	667

Figure 1. Reproduction of tracing of the infrared absorption spectrum from 2 to 12μ of a film of mineral oil on a silver chloride plate. Note shape of background curve, approximate linearity of wave length scale and weakness of atmospheric absorption.

Figure 2. Infrared absorption spectra from 6.5 to 14μ of liquid ethylene glycol and glycerol, before and after exchange with D_2O. The ordinate is transmission.

Figure 3. Infrared absorption spectra from 7.6 to 14.5μ of mineral oil mulls of higher glykitols: erythritol (meso-erythritol), D-arabitol, ribitol (adonitol), D-mannitol, D-glucitol (sorbitol) and galactitol (dulcitol). The ordinate is transmission.

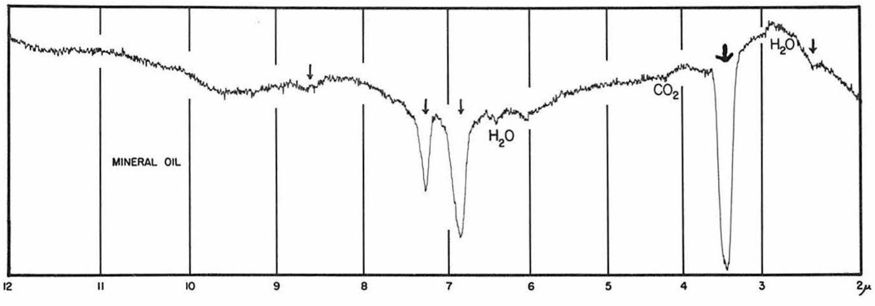


Figure 1.

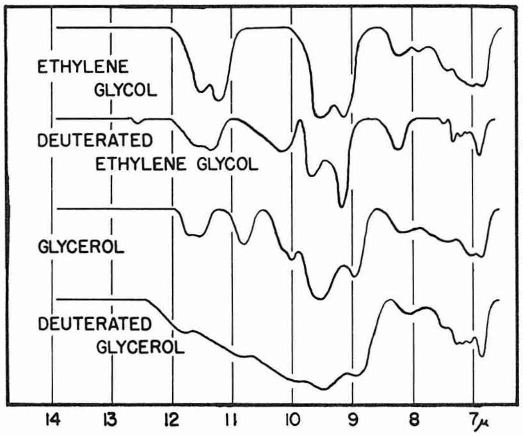


Figure 2.

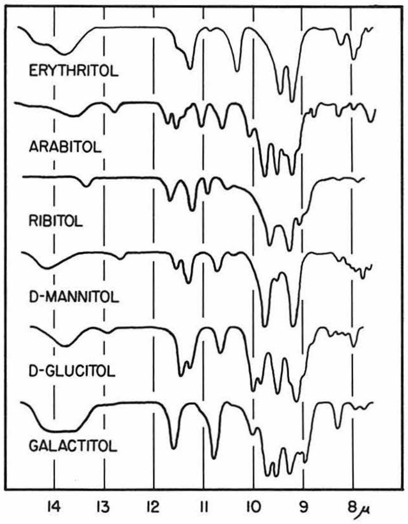


Figure 3.

Figure 4. Coordinates and numbering of ring atoms as adopted in this thesis for the staggered six-membered ring. The coordinates used by Herzberg (11) for six-membered rings of the indicated symmetry are also shown.

Figure 5. Infrared absorption spectra from 6.5 to 13μ of liquid cyclohexane (0.1mm.), tetrahydropyran, and thick and thin films of p-dioxane. The ordinate is transmission.

Figure 9. Infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of the cyclitols meso-inositol, pinitol (methyl ether of d-inositol) and scyllitol. The ordinate is transmission.

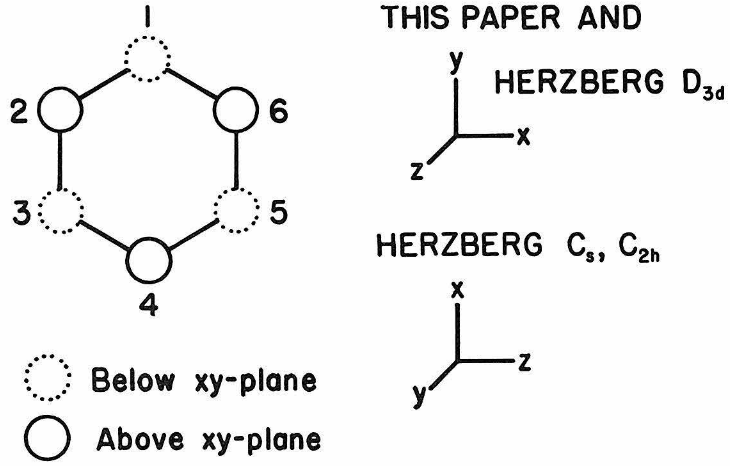


Figure 4.

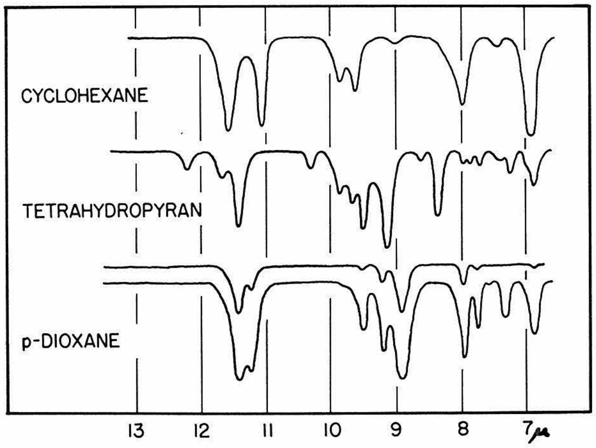


Figure 5.

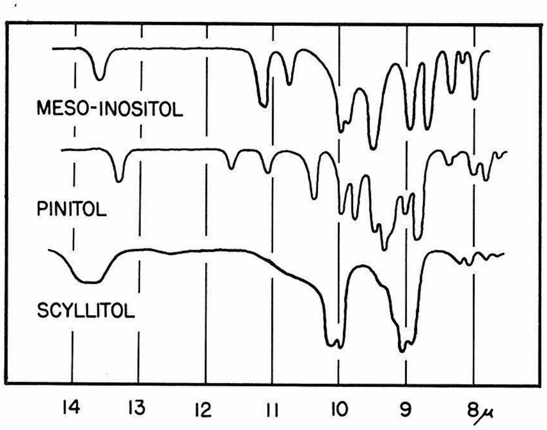


Figure 9.

Figure 6. 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 (10). 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.

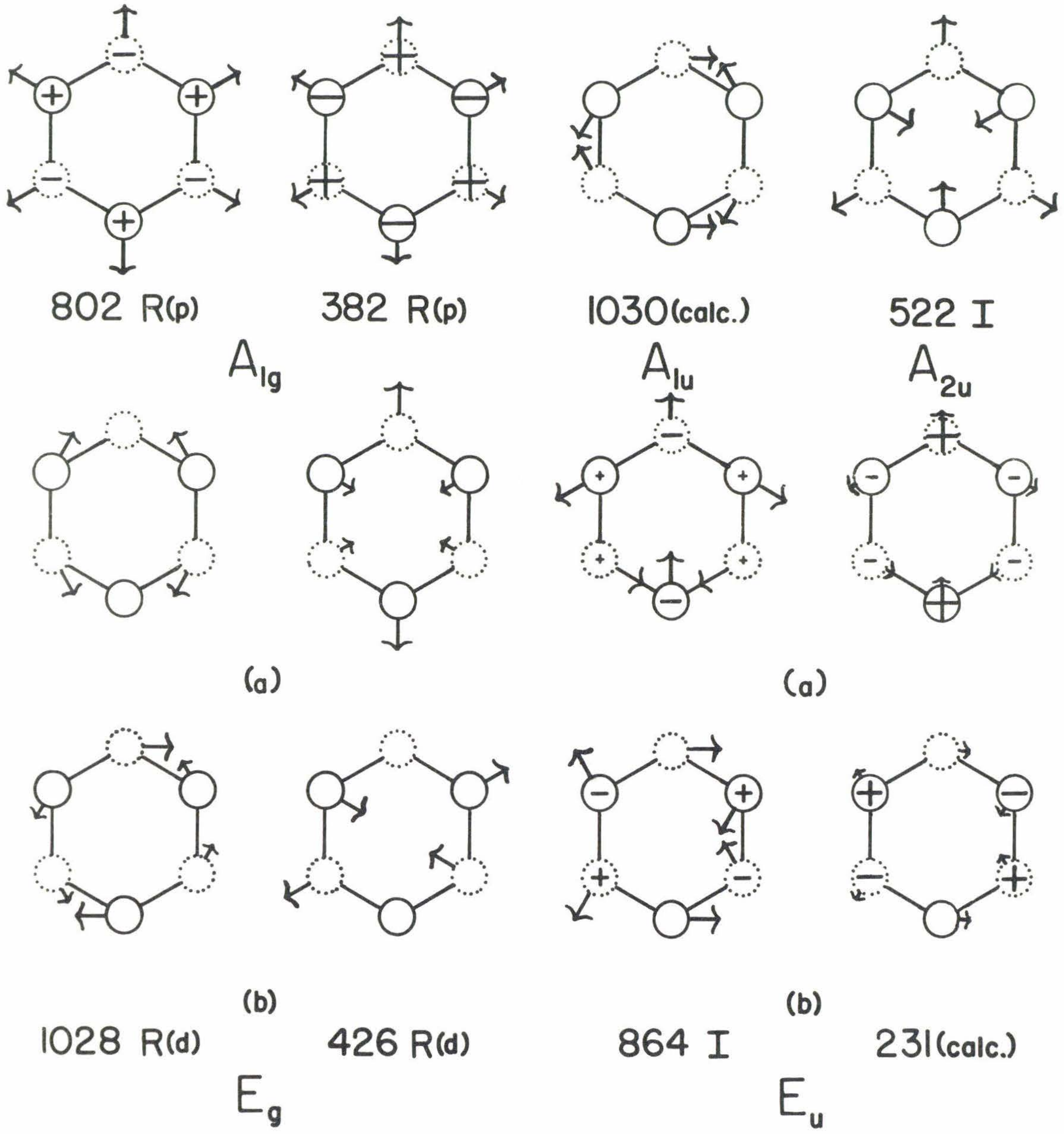

802 R(p)
382 R(p)
1030(calc.)
522 I
A_{1g}
A_{1u}
A_{2u}
(a)
(a)
(b)
(b)
1028 R(d)
426 R(d)
864 I
231(calc.)
E_g
E_u

Figure 6.

Figure 7. 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 (10). 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.

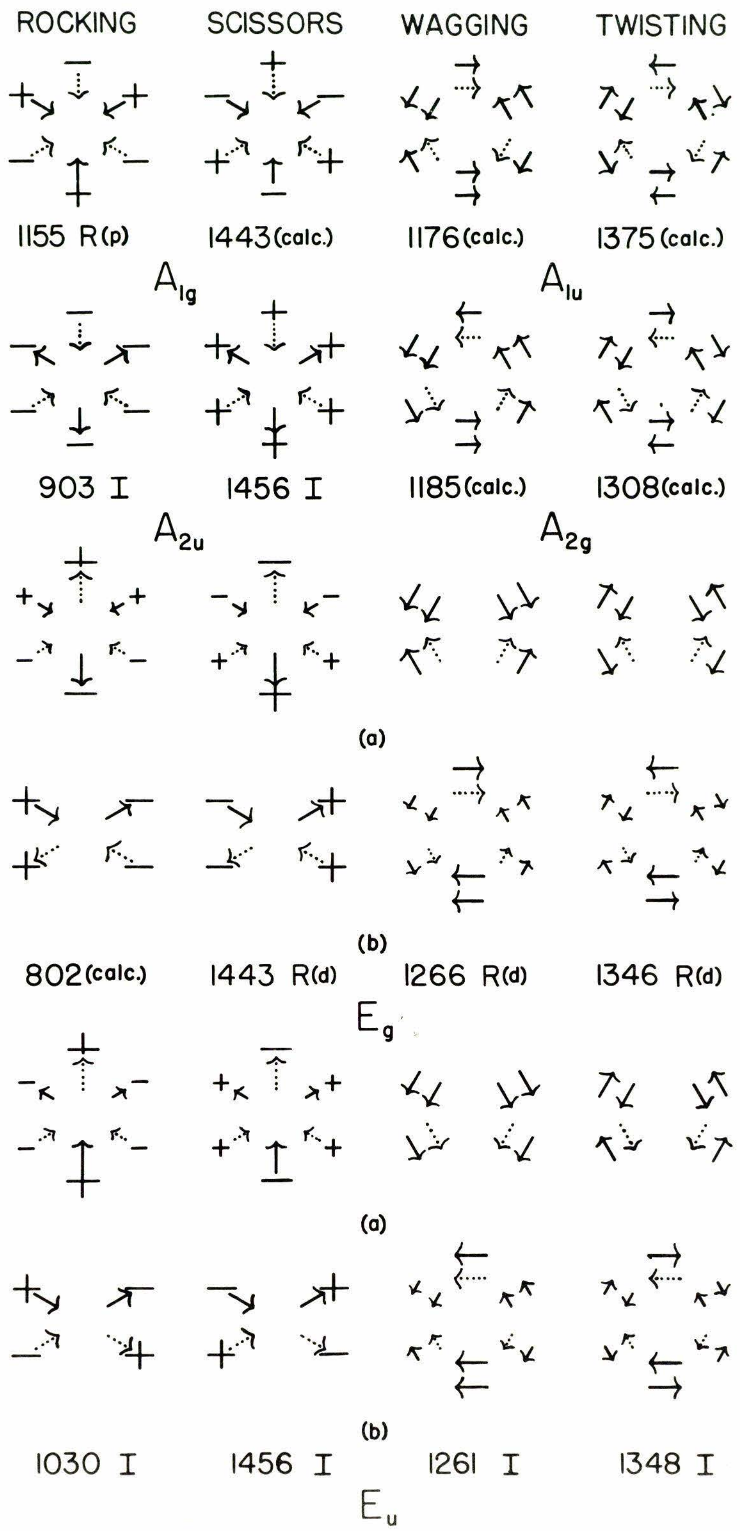
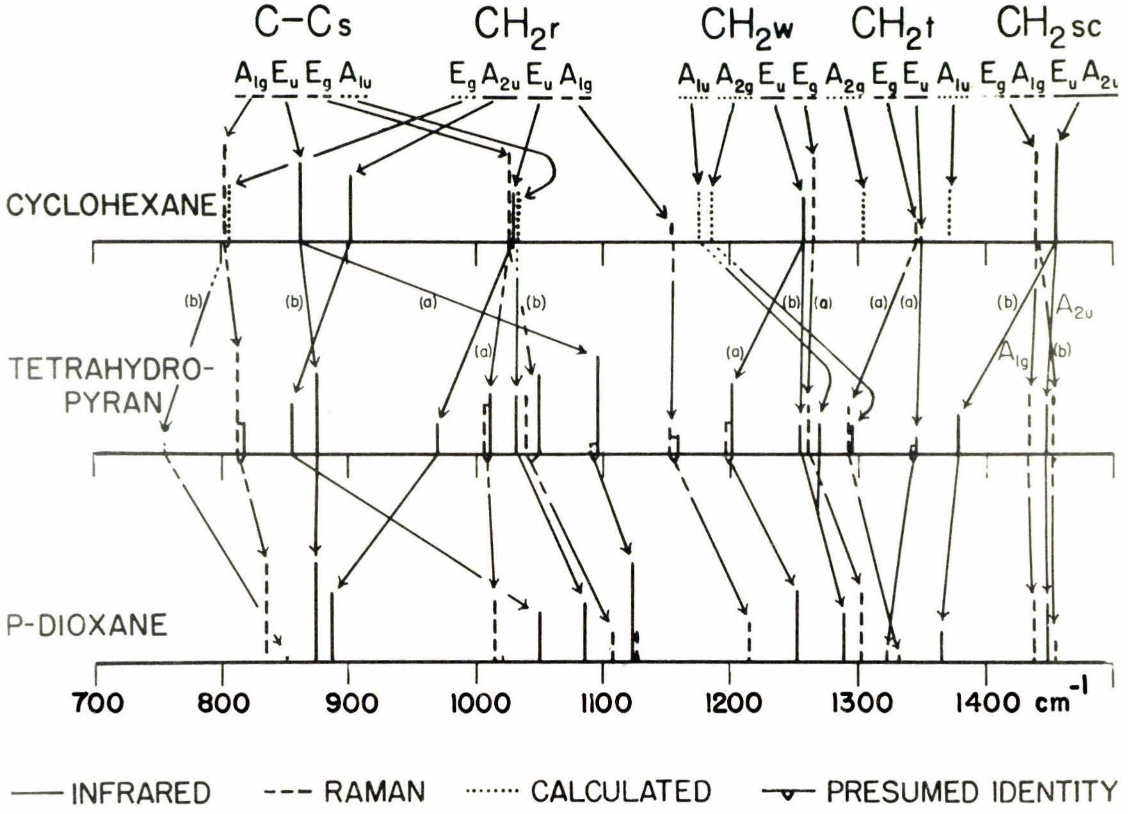

ROCKING
SCISSORS
WAGGING
TWISTING
1155 R(p)
1443 (calc.)
1176 (calc.)
1375 (calc.)
A_{1g}
A_{1u}
903 I
1456 I
1185 (calc.)
1308 (calc.)
A_{2u}
A_{2g}
(a)
(b)
802 (calc.)
1443 R(d)
1266 R(d)
1346 R(d)
E_g
(a)
(b)
1030 I
1456 I
1261 I
1348 I
E_u

Figure 7.

Figure 8. 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 (10) 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 (13). The letter (a) or (b) near some of the arrows identifies the number of the degenerate pair which the arrows represent; where space permits the identifying letter is placed to the left of its arrow.



C–Cs
CH2r
CH2w
CH2t
CH2sc
A1g Eu Eg A1u
Eg A2u Eu A1g
A1u A2g Eu Eg
A2g Eg Eu A1u
Eg A1g Eu A2u
CYCLOHEXANE
TETRAHYDRO-PYRAN
P-DIOXANE
(a)
(b)
A2u
A1g
700
800
900
1000
1100
1200
1300
1400 cm-1
INFRARED
RAMAN
CALCULATED
PRESUMED IDENTITY

Figure 8.

Figures 10-14. The infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of some hexoses, pentoses and derivatives. Rhamnose, isorhamnose and fucose are the 6-desoxy derivatives of mannose, glucose and galactose, respectively. The ordinates are transmission.

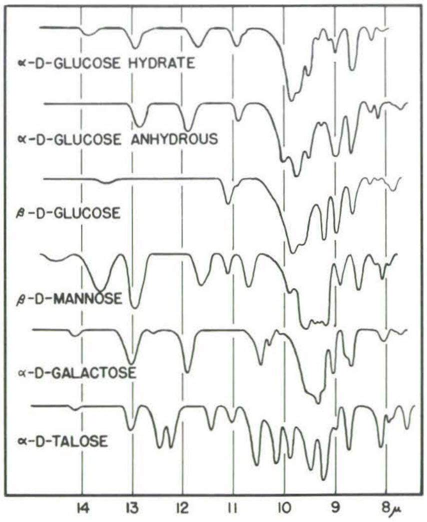


Figure 10.

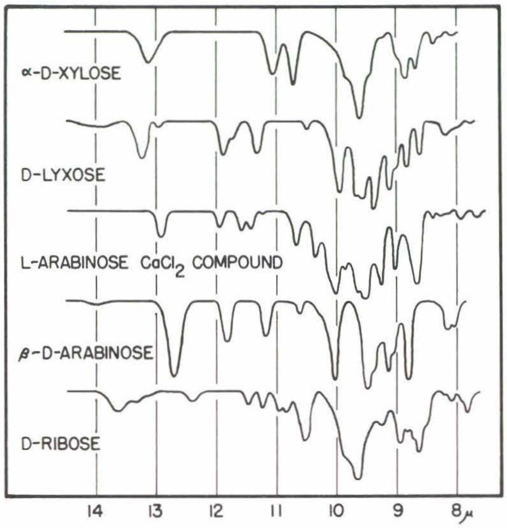


Figure 11.

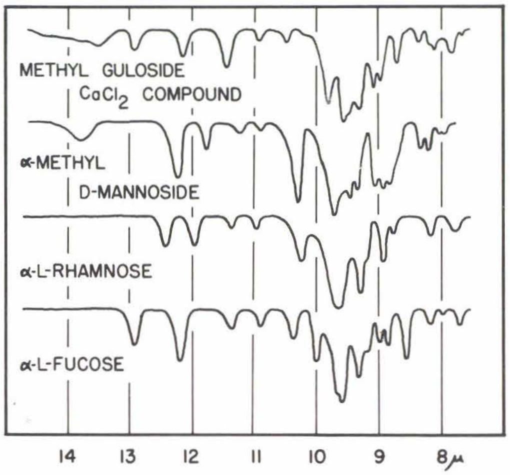


Figure 12.

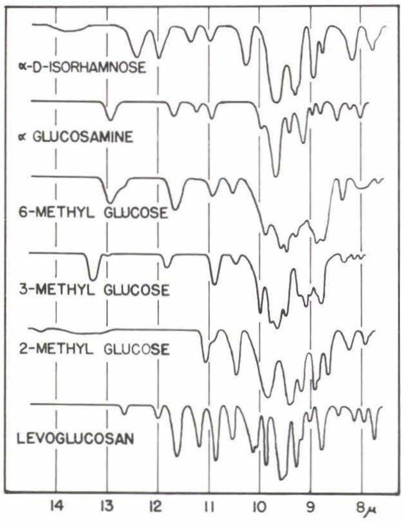


Figure 13.

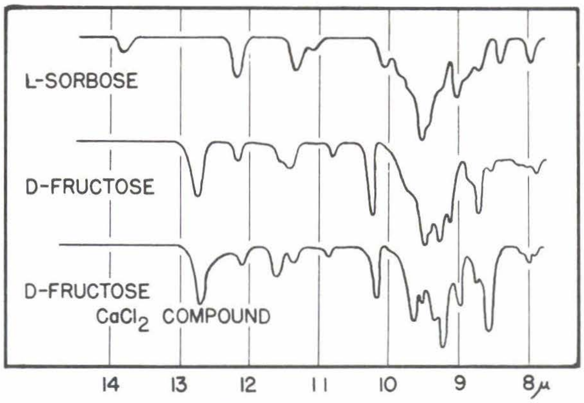


Figure 14.

Figure 15. Infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of some disaccharides which contain only glucose units: β-maltose monohydrate (4-β-D-glucose α-D-glucopyranoside), β-cellobiose (4-β-D-glucose β-D-glucopyranoside), hydrol (probably mostly isomaltose, or 6-D-glucose α-D-glucopyranoside (38)) and α,α-trehalose (1-(α-D-glucopyranose) α-D-glucopyranoside). The ordinate is transmission.

Figure 16. Infrared absorption spectra from 7.6 to 14μ of mineral oil mulls of some disaccharides which contain galactose: α-lactose monohydrate (4-α-D-glucose β-D-galactopyranoside), β-lactose, and β-neolactose (4-β-D-altrose β-D-galactopyranoside). See also melibiose in Fig. 17. The ordinate is transmission.

Figure 17. Infrared absorption spectra from 7.6 to 14 of mineral oil mulls of some trisaccharides and related disaccharides: raffinose pentahydrate (1-[6-(α-galactopyranosyl)-α-D-glucopyranose] β-D fructofuranoside), β-melibiose dihydrate (6-β-D-glucose α-D-galactopyranoside), sucrose (1-α-D-glucopyranose β-D-fructofuranoside), turanose (3-D-fructose α-D-glucopyranoside) and melezitose dihydrate (2-[3-(α-glucopyranosyl)-β(?)-D-fructofuranose α-D-glucopyranoside). The ordinate is transmission.

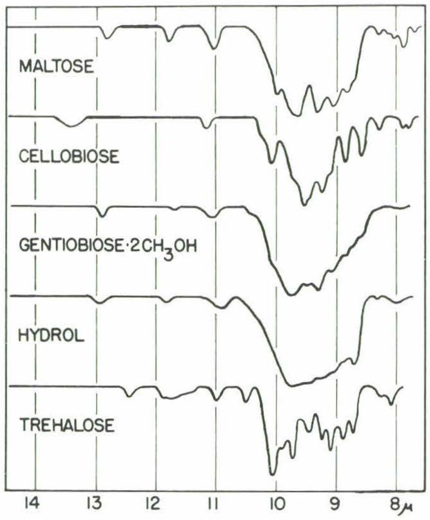


Figure 15.

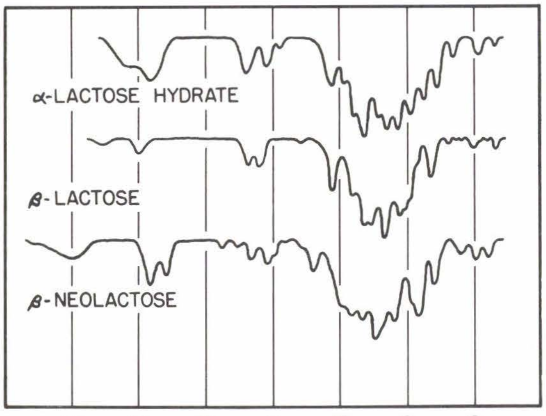


Figure 16.

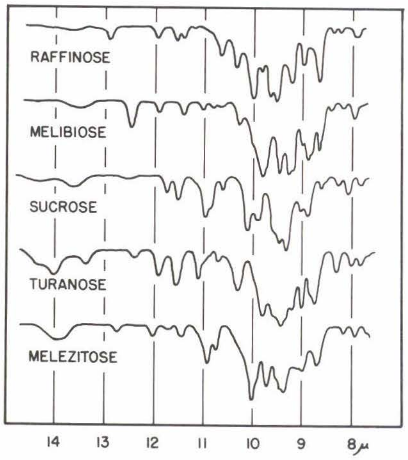


Figure 17.

Figure 18. Infrared absorption spectra from 7.6 to 14μ of mercerized and unmercerized animal cellulose (tunicin) and of mineral oil mulls of some degradation products of cellulose. The ordinate is transmission.

Figure 19. Infrared absorption spectra from 7.6 to 14μ of cellophane (0.001 mm.), a film of soluble starch evaporated from 60% alcohol-water, and some degradation products of starch: maltose film (evaporated from 60% alcohol-water) and mineral oil mulls of the Schardinger dextrins (α- and β-dextrins probably cyclohexaamylose and cycloheptaamylose, respectively, after French and Rundle (49)). The ordinate is transmission.

Figures 20 and 21. Infrared absorption spectra from 7.6 to 14μ of films of some cellulose derivatives: cellulose nitrate containing 10.96, 12.55 and 13.46% nitrogen, cellulose acetate, methyl cellulose and ethyl cellulose. The ordinates are transmission.

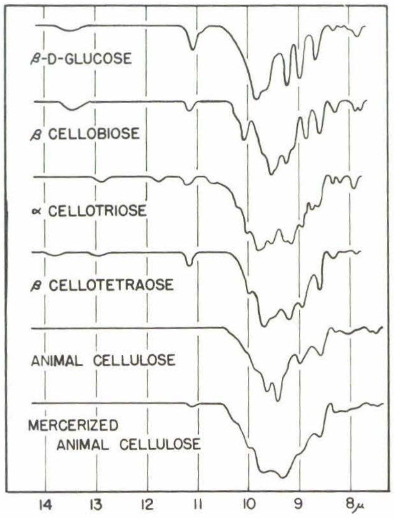


Figure 18.

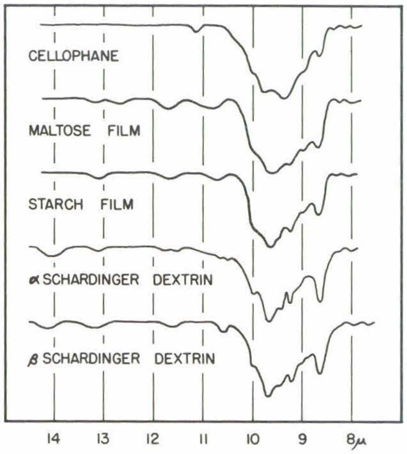


Figure 19.

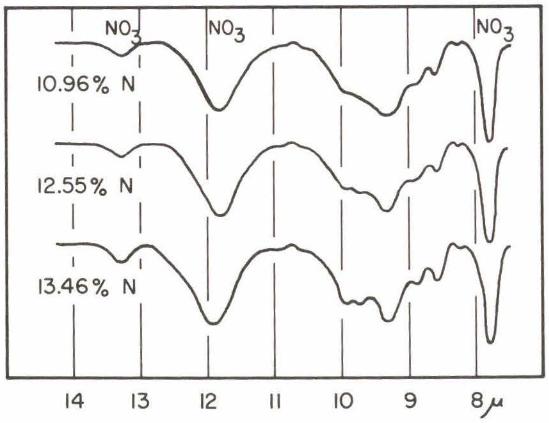


Figure 20.

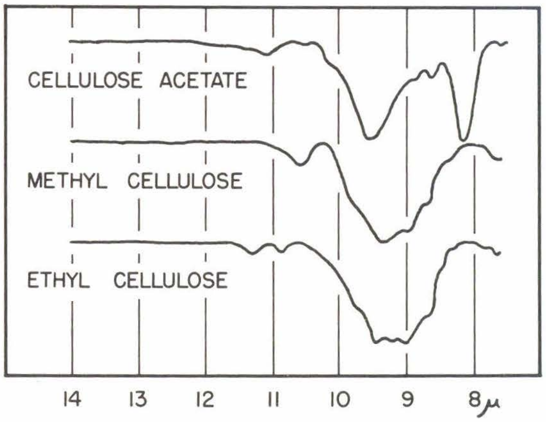


Figure 21.

Propositions

1. Sodium dithionite has long been used in industry as a reducing agent. It is proposed that sodium dithionite itself is only a rather weak reducing agent and that sulfoxylic acid is the active agent in acid solutions of dithionite.

2. Cox, Goodwin and Wagstaff (1) have observed that the crystals of many pyranose sugars and derivatives show a smallest unit cell dimension which is remarkably independent of configuration and is incompatible with a strainless trans pyranose ring. They explain this observation and some others in terms of a flattened, strained conformation of the pyranose ring. In part III of this thesis it is shown that equally satisfactory explanations can be given in terms of a modified chair-form ring which is less strained than the CGW model.

3. a. The phenomenon of retrograde condensation is often observed in binary systems at temperatures above the critical temperature of one of the components. A discussion in terms of the differential equations of the equilibrium lines of a P vs. x diagram is proposed.
b. It is suggested that the compositions of the two phases in such systems be studied by use of untraviolet

or visible spectrophotometry.

4. In view of the demonstrated stability of the chair-type six-membered ring the decalins and their substitution products should be rediscussed. A consideration of melting points raises the question as to whether the isomers of 2-decalol have been properly identified.

5. Recently a complete vibrational assignment has been made for ethylene imine (2) on the assumption that its moments of inertia are not much different from those of ethylene oxide. An at least equally satisfactory assignment may be made if one assumes that the least and intermediate axes of inertia have been interchanged with respect to ethylene oxide; such a model is not in disagreement with existing electron diffraction results (3). A microwave investigation of ethylene imine such as that carried out on ethylene oxide by Gwinn and co-workers (4) will be necessary to resolve this question.

6. One might expect that samples which are being examined at the focus of an infrared microscope would heat up excessively, but experimentally such is not the case. It is proposed that samples which are too thick to be

suitable for examination in the infrared would indeed heat up excessively, but that for the thin samples actually used much of the absorbed energy is re-radiated.

7. a. It has long been recognized that a consideration of spectral intensities should be very helpful in making vibrational assignments for polyatomic molecules, but no one appears to have attempted it so far. It is suggested that for molecules in which resonance between structures with different charge distributions is not important, the intensities of infrared bands may be discussed in terms of the motions of formal charges.
b. By means of this approach it is possible to show that scyllitol, the all-trans cyclohexanehexol, must have all equatorial rather than polar hydroxyl$. The above and other examples are described in this thesis.

8. It is suggested that the infrared spectra of dilute solutions of water in sulfuric and in nitric acid be examined to determine whether bands characteristic of H_3O^+ can be observed. By analogy with NH_3 a low frequency band which does not appear with H_2O might be expected if H_3O^+ exists in appreciable concentration.

9. In discussing the isomerism of cyclohexane derivatives it is always assumed that the potential barrier between the two possible chair-forms is sufficiently low that equilibrium is attained too rapidly to permit isolation of either form. It is suggested that this may not be so for the cyclohexanehexols and related compounds and that epi-meso-inosose, for example, might be resolvable into d- and l- forms.

10. It is suggested that abstractors of French articles for Chemical Abstracts be informed that "l'" and "d'" are not necessarily synonymous with "l-" and "d-" (5).

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