The Dipole Moments of Some Substituted Cyclohexane Compounds by the Solution Method

by

Joseph
John Lander

Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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THEORY

A. INTRODUCTION: The general theory of the dipole moment and its applications to various physical and chemical problems is given in several publications.[1,2,3,4] Molecules may possess dipole moments due to the non-coincidence of the centers of action of the positive and negative charges which are in a state of vibration about certain fixed points in space. This condition of unbalance may be temporary or permanent depending chiefly on the structure and symmetry of the molecule. If the effect is permanent, the molecules are said to be polar in nature and they will have a finite value of the dipole moment. The dipole moment is a molecular constant, designated by the symbol μ, which is equal to the product of the charge multiplied by the distance of seperation. It has the order 1×10^{-18} e.s.u. cms., frequently called the Debye unit.

Since the permanent polarity of molecules is related to their structure, measurements which allow the calculation of μ may be expected to give a more or less definite indication of the structure of molecules. Two general experimental methods are in use for the purpose of obtaining μ: one, the measurement of the polarization of a substance in the gas phase, in which case there is a temperature dependence, if its molecules have a permanent moment, which allows the calculation of μ; and two, the measurement of the polarization of a series of solutions

of the substance in a non-polar solvent, where there is a linear relation with concentration, provided association effects are absent, which also allows the calculation of μ. This thesis is concerned with the solution method.

Calculation of μ may be made by means of equations which follow. These were developed chiefly by Debye! The solar polarization of a mixture of two components is given by:

Eq. 1. $$P_{12} = \frac{\epsilon_{12}-1}{\epsilon_{12}+2} \frac{M_1 N_1 + M_2 N_2}{d_{12}} = P_1 N_1 + P_2 N_2 ,$$

where the subscript 12 refers to the solution, and P_{12} is the molar polarization of the solution, ϵ_{12} and d_{12} its dielectric constant and density, M_1 and M_2 are the molecular weights of the solvent and solute, and N_1 and N_2 are their mole fractions. Evidently the polarization of the solution is an additive property of the polarization times the concentration of the individual species in the solution.

The polarization of the solvent may be determined from the relation of Clausius and Mosotti:

Eq. 2. $$P_1 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2} \frac{M}{d_1} ,$$

where the terms have the same significance for the solvent as those in Eq. 1 do for the solution. This equation was derived without taking into account molecular interaction and is consequently rigorous only for the gas phase where interaction is small enough to be neglected. However, it is found to be applicable to non-polar solvents where the molecular interaction is small. From Eq. 1 it follows that:

Eq. 3. $$P_2 = \frac{P_{12} - P_1(1-N_2)}{N_2} .$$

If P_{12} is determined by measuring dielectric constants and densities for several concentration ranges at constant temperature, then, since P_1 can be determined from Eq. 2, P_2 will also be determined at those concentrations. A plot of the P_2 values vs. N_2 may be extrapolated to the infinitely dilute solution to obtain the quantity P_2^α, which is the molar polarization of the solute in a condition where solute molecules are far enough apart so that they should correspond to the gas phase, i.e., no association effects should be present. Then the equation of Debye for the polarization of a gas should be applicable:

Eq. 4. $$P = \frac{4\pi}{3} N\alpha_E + \frac{4\pi}{3} N\alpha_A + \frac{4\pi}{3} \frac{N\mu^2}{RT} ,$$

or written simply: $P = P_E + P_A + P_0$, where P_E and P_A are the contributions made to the molar polarization by electronic and atomic shifts in the field and P_0 is the contribution made by the orientation of the permanent dipole in the field. Replacing P by P_2^α, Eq. 4 may be solved for μ to obtain:

Eq. 5 $$\mu = 0.01273 \times 10^{-18} \sqrt{[P_2^\alpha - (P_E + P_A)]\, T} ,$$

which is the equation used for the calculation of μ. P_E and P_A may be determined from measurements of the refractive index of the compound, or from the sum of the atomic refractions for the molecule which may be obtained from tables.

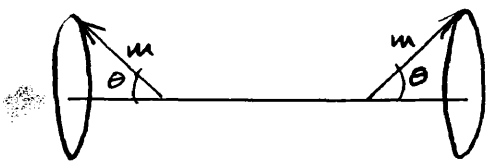
Dipole moments obtained from solution measurements do not usually agree with those obtained from gas phase

measurements. This is attributed to interaction of the solvent molecules with those of the solute under the general term "solvation effects." Various empirical equations have been developed to attempt to bring the two methods into agreement with only partial success.[5] Onsager and Kirkwood[6] have developed an equation which shows that solution measurements should not be expected to agree with gas phase measurements but should lead to higher values of μ. So, the solution method is subject to some uncertainty. In spite of this, a considerable body of experimental data has been built up for solution measurements which shows that the value of μ is the vector sum of all the bond moments in a molecule, and consequently if values for bond moments and their angles can be assigned from solution measurements then μ should be capable of estimation for a supposed structure of a molecule. Comparison of this estimated moment with that determined experimentally, therefore offers a means of determination of the structure of molecules. The method has worked out very well for molecules where angles and bond moments can be estimated with a fair degree of probability. However, in many cases unambiguous structures are not necessarily assignable to a molecule, and the estimation of the dipole moment may be made more complex by such considerations as free rotation of groups and parts of molecules about single bonds, restricted rotation due to a variety

of causes, various kinds of tautomerism, hydrogen bonding, and resonance. Estimated moments may be expected to agree with measured moments in these cases to a degree depending on how completely and quantitatively the various effects which give rise to complexity may be treated. A discussion of the theory of such of these effects as may be applicable to the compounds measured in this work will follow.

B. FREE ROTATION: If a group of atoms in a molecule may be presumed able to rotate freely about a single bond, then by consideration of the magnitude and direction of the vectors associated with the groups, appropriate mathematical treatment should afford equations which should accurately predict the measured dipole moments if such rotation is really free. This should be true provided that this is the only effect necessary to be considered and that the moment estimated from free rotation is different within the limits of experimental error from that which might be estimated from any reasonable configuration of the groups concerned, or combinations thereof.

As an example, consider a molecule which might be described by two vectors of equal magnitude which make the same angle with an axis and which are both able to rotate freely through an azimuthal angle of 360°, as indicated in Fig. 1.



If the vectors are resolved into their components along the axis and perpendicular to it, the components along the axis cancel, and it is only necessary to consider the components rotating in the planes perpendicular to the axis. If one component is held fixed, and the other allowed to rotate through 360°, the possible range of angles between the vectors is 180° and all angles are equally probable. The equation giving the average square moment for this model has been derived[7] to be:

Eq. 6. $\bar{\mu}^2 = 2m^2 \sin^2\theta$,

where m is the partial or group moment and θ is the angle its resultant vector makes with the axis of rotation.

This model has been applied[8] to ethylene dichloride and a value of 1.83 was found in benzene solution. This value is lower than that calculated for free rotation (2.10), probably due to interaction* of the strong C-Cl bond moments which causes them to assume positions such that they are generally in opposition. (It is understood that this rotation is due to thermal motion and is slow enough so that the alternating field will "stop" the molecules so that the average moment will be, in the ideal case, the result of a statistical distribution of vectors through all possible angles.)

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* Interaction of partial moments in a molecule will be considered more completely in a later section.

This equation was also applied to p-xylylene dichloride ($ClCH_2C_6H_4CH_2Cl$), which should behave like ethylene dichloride without temperature dependence because the $-CH_2Cl$ groups are now so far apart that interaction is unlikely. The calculated value is 2.26 which is in striking agreement with an observed value[9] of 2.23.

Eq. 6 applies to a limited case of free rotation where the axes of rotation of the groups are at an angle of 180° to one another, in which case all angles in the whole range are equally probable. Where the angle between the axes of rotation is different from 180°, all angles are not equally probable, as will be shown in the following analysis.

Consider the case of two vectors of equal magnitude which make the same angle with their respective axes of rotation, which axes are at any angle β different from 180° or 0° as illustrated in Fig. 2.

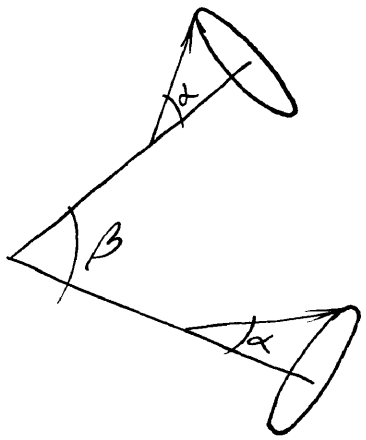

Fig. 2

Let it be assumed further for purposes of simplification that the angles which the vectors make with their axes of rotation are 90° and that the angle β is 60°. In this case, the vectors may be represented as rotating in two circular planes which make an angle of 60° with each other as illustrated in Fig. 3.

It is at once evident that there are only two positions each out of an infinite number which will allow the vectors to be at angles of 0° or 180° to each other, and that the probability of the field catching any molecules in such positions is vanishingly small, and therefore those positions will contribute almost nothing to the average moment of the molecule. As angles greater than 0° or less than 180° are considered their probability increases. (The distribution of probabilities for this model hasn't been worked out with certainty, but probably reaches equal maxima at 60° and 120° with a minimum at 90°). The model also indicates that for the same limitations where the angle $\beta = 120^\circ$ the same average moment would be predicted. The angles $\beta = 60^\circ$ or 120° and $\alpha = 90^\circ$ were selected because these conditions represent to a very good approximation the case of the ortho and meta dihydroxy benzene molecules where α is estimated to be about 88°. They will be discussed in greater detail later.

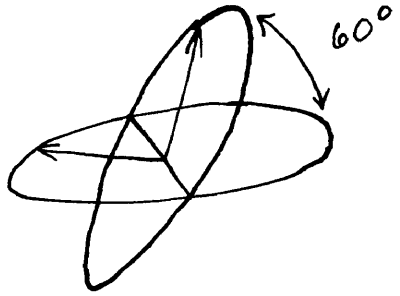

Fig. 3.

It is now proposed to present a vectorial derivation* of an equation based on the model of Fig. 2.

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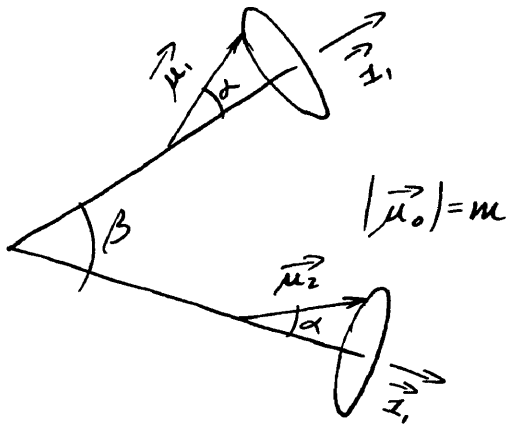
*This derivation was made for us by John RICHARDSON of the Bell Telephone Laboratories, Murray Hill, N.J. The same equation has been derived previously by analytical methods. Fuchs, Zeit. fur Physik. Chem. Ab. B. 14, 342 (1931).



The total instantaneous moment is: $\vec{\mu} = \vec{\mu_1} + \vec{\mu_2}$

$$\overline{\mu^2} = \overline{\vec{\mu}\cdot\vec{\mu}} = \overline{\mu_1^2} + 2\overline{\vec{\mu_1}\cdot\vec{\mu_2}} + \overline{\mu_2^2}$$

$$\overline{\mu_1^2} = \overline{\mu_2^2} = m^2$$

$$\overline{\vec{\mu_1}\cdot\vec{\mu_2}} = \overline{\vec{\mu_1}}\cdot\overline{\vec{\mu_2}},$$

since $\vec{\mu_1}$ and $\vec{\mu_2}$ are independent.

$\overline{\vec{\mu_1}} = \vec{1}_1 m\cos\alpha$ assuming free rotation, and the same holds for $\overline{\vec{\mu_2}}$. $\vec{1}_1$ and $\vec{1}_2$ are the unit vectors indicated in the diagram.

$$\therefore \overline{\mu^2} = 2m^2(1 + \vec{1}_1\cdot\vec{1}_2\cos^2\alpha), \text{ and,}$$

Eq. 7.
$$\overline{\mu^2} = 2m^2(1 + \cos\beta\cos^2\alpha).$$

This equation is general for molecules containing two identical groups which have a fixed angle between their axes of rotation. It is easily extended to include molecules where the groups are different, resulting in vectors of different magnitude having different angles α_1 and α_2 with their axes of rotation:

Eq. 8.
$$\overline{\mu^2} = m_1^2 + m_2^2 + 2m_1m_2\cos\beta\cos\alpha_1\cos\alpha_2.$$

It should be capable of extension to the case where β varies, i.e. for molecules having three degrees of freedom of rotation. It predicts that if the rotating vectors make angles close to 90° with their axes of rotation, then the molecules containing them will show average moments which are very close together in magnitude regardless of the value of β, because of the appearance of $\cos\alpha$ in the second term in the parentheses. This is the case

existing in the diols. It is also evident that where $\beta = 180^\circ$ Eq. 7 reduces to Eq. 6.

The application of the free rotation principle has been made[10] to the ortho, meta, and para isomers of the dimethoxy derivatives of benzene by Fuchs and Wolf. They used the equations:

for ortho: $\overline{\mu^2} = \mu_1^2 + \mu_2^2 + \mu_1 \mu_2 \cos\psi_1 \cos\psi_2$

for meta: $\overline{\mu^2} = \mu_1^2 + \mu_2^2 - \mu_1 \mu_2 \cos\psi_1 \cos\psi_2$

for para: $\overline{\mu^2} = \mu_1^2 + \mu_2^2 - 2\mu_1 \mu_2 \cos\psi_1 \cos\psi_2$

where μ_1 and μ_2 are the magnitudes of the partial moments and ψ_1 and ψ_2 are the angles the vectors make with their axes of rotation. These equations can easily be shown to be special cases of the general form: Eq. 8. Since $\cos\psi$ for the OCH_3 group is close to zero ($\psi = 75^\circ$, by their estimate) the calculated values will be expected to be approximately the same and are: 1.77, 1.71, and 1.69 for the ortho, meta, and para isomers respectively. These may be compared with the experimental values[11]: 1.31, 1.59, and 1.81 in the same order. There is reasonably good agreement for the meta and para isomers, but poor agreement for the ortho. Moreover, the magnitudes increase in opposite directions. The ortho case might be explained qualitatively by steric hindrance or dipolar interaction either of which should tend to keep the dipoles in a generally opposed condition.

Application of the equations of Fuchs and Wolf was made[12] to catechol, resorcinol, and hydroquinone. As

mentioned previously, the equation for free rotation predicts in these cases that the magnitudes of the moments calculated on the basis of free rotation should be about the same, based on an angle α of 68°. The calculated value is 2.21. The experimental values were respectively 2.62, 2.07, and 1.4. Apparently free rotation is not operating here which again may be due at least in the ortho and meta cases, to interaction of groups. In the case of catechol however, intramolecular hydrogen bonding may be acting[13] and in all cases resonance which tends to make the bond have partial double bond character may be acting to tend to keep the H atoms in the plane of the ring.

Recently, Kumler and Fohlen[14] applied the free rotation principle to the interpretation of the experimental moments of sterols and androstane derivatives. They were able to achieve only a limited interpretation, however, their work is indicative of the range of application of the free rotation principle in analyzing molecular configurations.

In general, it is expected that moments of molecules of the types considered should be capable of estimation unless the rotation is prevented or inhibited by steric hindrance, dipole interaction, hydrogen bonding, particularly in the ortho case, or where other complicating factors such as resonance may enter in.

C. RESTRICTED ROTATION DUE TO POLAR INTERACTION: In molecules containing two or more polar groups which might be expected to rotate freely in the absence of steric hindrance, the freedom of rotation might be inhibited by the fields of force they exert on one another. The mean relative orientation of such groups would then depend on their mutual potential energy.

Meyer[15] has used this consideration to develop, for the orientation polarization of a gaseous molecule,

Eq. 9 $$P_0 = \frac{4\pi N}{3} \cdot \frac{2\mu^2 \sin^2\theta}{3kT} \cdot (1-x),$$

which may be compared to Debye's expression:

$$P_0 = \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT}.$$

In Meyer's equation μ is the mean moment in the direction of the field, θ is the angle between the moment vector and its axis of rotation, and x is a complex function of the factors which determine the mutual potential of the dipoles and depends on the geometry of the molecule. x is considered to be negligibly small when the potential energy between two dipoles is less than 1/10 kT. If the energy is of the order kT (at room temperature kT 4×10^{-14} erg. per molecule) then the resultant moment may be expected to be seriously reduced. The mutual potential energy of two moments m_1 and m_2 at a distance d is about $m_1 m_2/d^3$ and consequently the energy is about equal to kT when m_1 and $m_2 = 1 \times 10^{-18}$ and $d = 3 \times 10^{-8}$ cm. This means that if the distance between the partial moments is much greater than 3×10^{-8} or if the moments are much less than 1×10^{-18}, x

may be neglected and in Eq. 9, $2\mu^2\sin^2\theta$ becomes equivalent to μ^2 in Debye's expression. Also x decreases with increasing temperature so that at high temperatures Meyer's expression approaches Debye's as a limiting case. For larger m_1 and m_2, the separation must be greater in order that polarization may not be affected. Thus if m_1 and m_2 are 2×10^{-18} the separation must be between 4 and 5×10^{-8} cm.

Application of these conclusions by Meyer[15] to hydroquinone dimethyl ether where the separation of the dipoles is about 6×10^{-8} cm. and their magnitudes about 1.23×10^{-18} resulted in a mutual potential energy of the dipoles small enough to admit completely free rotation. This is apparently justified by the agreement of the measured moment with that calculated by Eq. 6 as previously mentioned.

Thus, an estimation of the magnitude of the mutual potential energy between two dipoles in a molecule by the foregoing method offers a qualitative means of judging whether or not rotation of these groups should be free or inhibited by dipole interaction.

F. <u>STERIC HINDRANCE</u>: Steric hindrance may be expected to have an effect on the moment when it blocks free rotation. The effect will not be general and consequently each case would have to be examined individually for its effect on the moment. Consideration of steric hindrance may even

be somewhat useless if the groups concerned have large moments and are close together, because in such a case the interaction energy should be sufficient to prevent free rotation.

For purposes of this paper, only a qualitative estimate of the possibility of free rotation is desired and steric effects shall be judged by means of Fischer-Herzfeld models.

5. THE STRUCTURE OF CYCLOHEXANE AND TAUTOMERISM OF THE OF THE RING IN CYCLOHEXANE AND CERTAIN OF ITS DERIVATIVES: Cyclohexane, on the basis of the molecular models, could exist in two configurations, a "chair" and a "boat" form, as illustrated in Fig. 4. For some years the presence or absence of the two configurations was subject to controversy. The fact that isomers were never isolated even led to the postulation of a rapid tautomerism between the two forms which would give the molecule an average flat form. In recent years electron diffraction measurements[16], spectroscopic work[17], infra-red absorption spectra[18], and calorimetric methods in conjunction with spectroscopic data[19] have shown that substantially all of the molecules exist in the chair form even at ordinary temperatures.

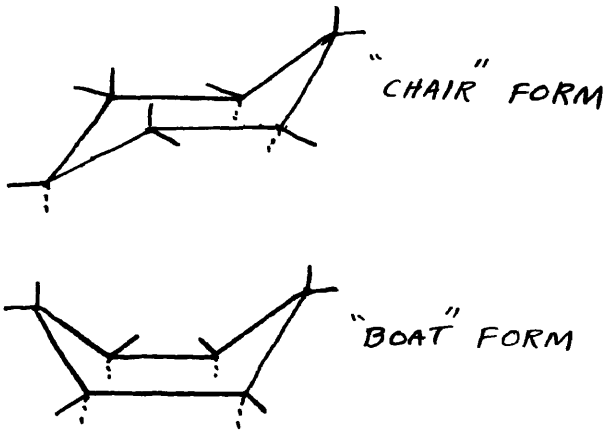


Fig. 4

From a study of the infra-red spectrum of cyclohexane, Pitzer, et. al.[18] have estimated that vibration of the bonds which allow passage of the chair form to the boat form involves a potential energy maximum of 14 kcal., while that type of vibration which allows the chair form to pass through a planar configuration into the opposite chair form involves an energy hump of 31 kcal. Kumler[20] estimated that the boat form should have a higher energy than the chair form by about 7-10 kcal. Thus, two kinds of tautomerism are possible in the cyclohexane molecule: chair $\rightleftarrows$ chair and chair $\rightleftarrows$ boat, although the amount of boat form must be very small. Kumler estimated about 0.001% on the basis of the energy difference at room temperature.

Pitzer,[18] following an analysis due to Hassel,[16] developed the consequences that may be expected as a result of the chair $\rightleftarrows$ chair tautomerism and his conclusions, explained and amplified, will be discussed and applied to this work in the following pages. The boat form will be considered to contribute negligible effects.

With the cyclohexane molecule in the chair form the hydrogen atoms in cyclohexane may be divided into two types called polar and equatorial. If the carbon ring is viewed as horizontal there are three polar hydrogens markedly above and three markedly below the ring while six hydrogen

atoms lie in an equatorial belt around the carbons. If the two hydrogen atoms on each carbon, one is polar and the other equatorial. If the molecule passes from one chair form to another, all polar hydrogens become equatorial and vice versa. As long as all are identical hydrogen atoms nothing new is obtained by such tautomerism, but with one different nucleus or group attached, tautomers become possible where the two forms may have the substituent in either the polar or equatorial position. By studying models of methylcyclohexane Pitzer found that due to steric interaction the polar form has an energy of from 1.6 to 2.4 kcal./mole higher than the equatorial form, the value being supported by experimental results.

If molecules are considered which have two substituent groups, tautomerism is still possible and in addition so is cis-trans isomerism and sometimes optical activity. For example, the 1,2 substituents could have the following possibilities: one, both substituents polar (p); two, both substituents equatorial (e); three, substituent one polar up with two equatorial; and four, substituent one equatorial with two polar down. Cases one and two represent trans forms of the molecule, while cases three and four are both cis forms. Chair $\rightleftarrows$ chair tautomerism will convert one trans form to the other trans form and one cis form to the other cis form.

In the following discussion the cis and trans forms of 1,2 and 1,4 disubstituted cyclohexane will be considered in greater detail and the discussion will be limited to the case where the substituents are the same.

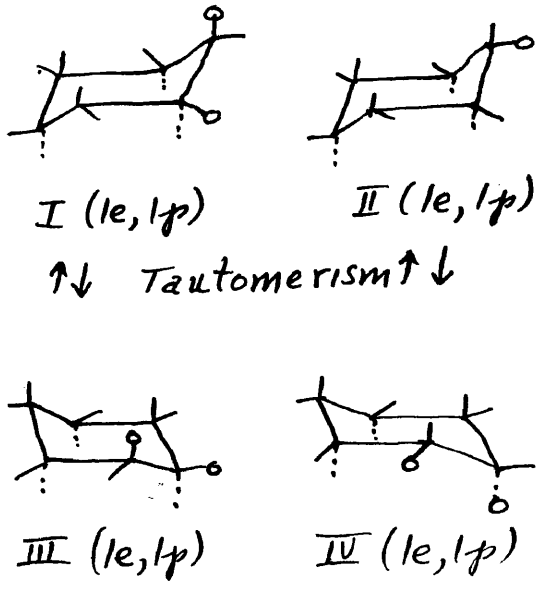


Fig. 5

In Fig. 5 all possible configurations for the chair form of the cis 1,2 case are illustrated. (In these and following drawings, the dotted lines indicate polar down substituents, solid lines pointing toward the top of the page represent polar up groups, while the others represent equatorial groups.) It can be seen that I and II are identical as are III and IV, while I and III are mirror images and hence optical isomers. These two configurations will result in the same dipole moment.

In the case of trans 1,2 the situation is somewhat different. Reference to Fig. 6 in which all possible configurations are illustrated will show that none of them are identical. The tautomer of I is the mirror image of II and the tautomer of II is the mirror image of I.

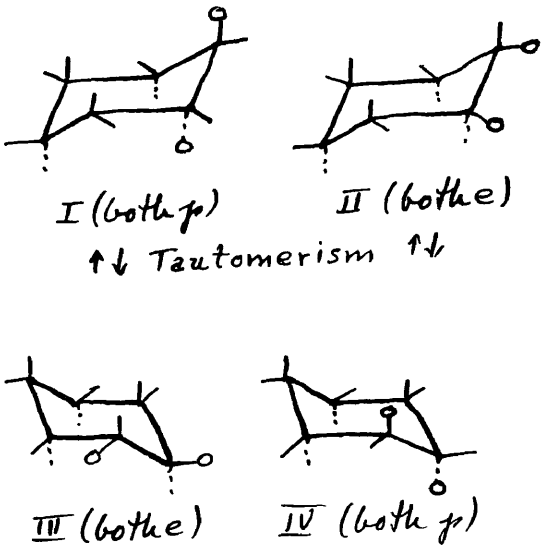


Fig. 6.

Thus in trans 1,2 compounds four configurations are possible, two of which are optical isomers of the other two. For purposes of estimation of dipole moments then, two forms must be considered one with both substituents (p) the other with both substituents (e).

In the case of the cis 1,4 compounds all four configurations when illustrated as for the previous cases are immediately seen to be identical.

Reference to Fig. 7, where all possible configurations for trans 1,4 derivatives are illustrated, shows that I and IV are identical as are II and III, with no optical isomers possible, so that trans 1,4 disubstituted compounds will have two possible configurations which are in tautomeric equilibrium.

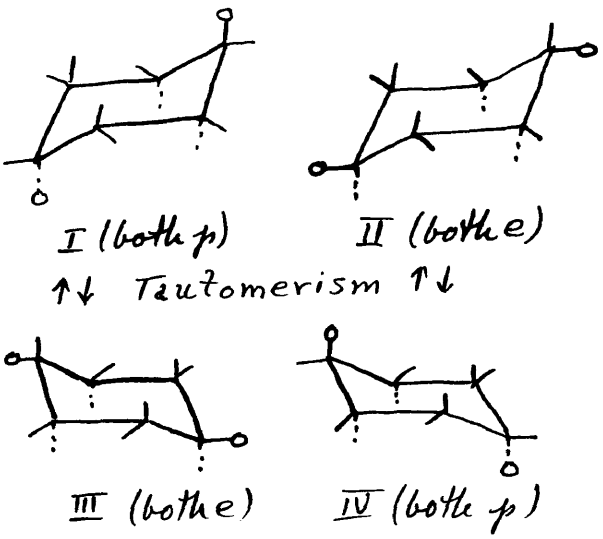


Fig. 7.

Both of these may have to be considered in making dipole moment estimates.

α -Hydroxycyclohexanone can be treated in the same fashion as will be shown in the discussion. The 1,2 cyclohexanedione molecule has optical isomers in tautomeric equilibrium if it exists in a rigid chair form. The energy of both configurations should be identical in this case.

The geometry of the cyclohexane ring is difficult when it comes to figuring the angles between the dipole moment vectors of the substituted groups, even if the molecule is considered to be held in a rigid chair form. As an approximation the angles could be estimated from the models allowing suitable limits for error. Measurement of moments of compounds where only one atomic nucleus is connected to a ring C (no possibility of free rotation complicating the calculations) would allow an estimate of the angles between the pairs of C-substituent bonds in the molecules, and these values could be used for compounds where free rotation is possible. However, where more than one configuration is possible a knowledge of the distribution of the molecules among the configurations would be necessary in order to use such a scheme. For the case of dihydroxy derivatives the estimation of moments regardless of the number of configurations is considerably simplified for free rotation because Eq. 7

predicts that for dihydroxy compounds where the angle β is fixed the magnitude of the moments should be very close. Furthermore, for the trans 1,2 (both p) and the trans 1,4 (both p, or both e) the models indicate that the angles between the axes of the C atoms of the ring and the attached nuclei are close to 180°. In such a case, if the vectors of the substituent groups lie along the C-substituent bond, the resultant moments would be very close to zero, if a rigid chair form for the cyclohexane nucleus can be assumed. Thus, measurements of the trans 1,4 dichloro compound, for example, should give a resultant moment close to zero. If such were found to be the case, then the model adopted could reasonably be assumed to be qualitatively correct, and measurements of the 1,2 trans compound should enable the distribution of this compound between its two configurations to be calculated. Indeed, a knowledge of this distribution should enable an estimate to be made of the difference in energies between the two configurations.

Pitzer and co-workers have found that polar methyl cyclohexane has a higher energy than the equatorial form by from 1.8 - 2.4 kcal./mole. On this basis they show that for the dimethyl substituted cyclohexanes those tautomers containing polar groups have higher energies by amounts which may range as high as 5.4 kcal./mole in one case. An energy difference of such a magnitude would

result in a small percentage of the higher energy form at the lower temperatures. For example, Sumler has calculated 99.999% of the chair form of cyclohexane at 25C. for an energy difference of 7 to 10 kcal./mole between the boat and chair forms.

Thus the calculation of moments for the disubstituted cyclohexane derivatives is rendered difficult by the ring tautomerism in most cases, even if a knowledge of the energies of the different configurations were available. It might be expected that those configurations having polar substituents would exist to a smaller extent than those having equatorial substituents. Again, each case must be examined individually for these effects on the dipole moment.

F. THE HYDROGEN BOND: The hydrogen bond, in which the hydrogen atom serves as a link between two other atoms, is different from other bonds in magnitude if not in essence. The nature of the forces involved have not been definitely ascertained, but may be adequately explained by electrostatic interaction and consequently, the bond is expected to be formed between strong electronegative groups where one contains a covalently bonded hydrogen atom. The energies of hydrogen bonds are estimated to be from 5 to 10 kcal. per mole. Existence of the hydrogen bond between strong electronegative groups is indicated

by studies of association, solubility, spectra, and other properties.[21]

Two general types of hydrogen bonding may occur: intermolecular, which is responsible for association in alcohols, water, and acids; and intramolecular, where the bond exists between two atoms within a molecule. The latter type may lead to a supression of the characteristics which are dependent on the hydroxyl or other group carrying a bonded hydrogen atom; for example, the solubility of ortho isomers are increased in non-polar solvents and molecular association may be decreased or inhibited, leading to increased volatility. Many other examples of these effects have been quoted.[22]

One of the most fruitful experimental methods for studying hydrogen bonding has been the study of the infrared absorption of molecules. In the following discussion, this type of bonding shall be limited to molecules containing hydroxyl groups. Phenol and other alcohols exhibit a strong, sharp absorption peak at about 7100 $cm.^{-1}$ (wave nos.). If the hydroxyl group is located in a molecule where it may be bonded through a hydrogen atom to another nucleus either within or outside the molecule, the absorption peak will be shifted to lower wave numbers. The magnitude of the shift is a measure of the strength of the bonding, while the height of the peak is a measure of the amount of bonding. For example in a molecule such as catechol which

contains two hydroxyls, one of which may be bonded to the other, two peaks are observed; one at about 7100 cm.$^{-1}$, the other shifted to a lower wave number, with both peaks having equal magnitude. This is interpreted[23] as meaning that catechol exists in a configuration such that one hydroxyl is free while the other is completely bonded to the oxygen atom of the free hydroxyl. Evidence for this configuration has recently been obtained from a measurement of the dipole moment of catechol.[12] If the internal bonding is complete, only a single shifted peak equal in magnitude to the usual peak should be obtained. Orthochlorophenol closely approaches this type. The infrared absorption spectrum of this molecule shows a peak of low magnitude at the usual position and a strong peak shifted to a lower wave number. This is interpreted as meaning that the compound exists in solution with most molecules exhibiting intramolecular hydrogen bonding.

In molecules containing two hydroxyls located on adjacent carbon atoms there may be some question as to whether or not the bonding is intra or intermolecular. The question may be partially resolved by studying the absorption spectrum versus dilution, where the amount of absorption will decrease with dilution if the bonding is purely intermolecular. The method would break down if association were so strong that it persisted to dilutions below the limit of measurement, or if intramolecular

bonding were so strong as to exclude association, or if association existed, but at lower dilutions as association became less complete the intramolecular bonding takes over. These cases do not necessarily correspond to any real types, but are only postulated as possibilities where a constant amount of bonding should be indicated by the absorption spectrum, unless the strengths of the intra and inter bonds were so different as to give different absorption peaks, which is quite possible. In these cases, measurements of the molecular weights at higher concentrations might provide a qualitative criterion for the bond type. For example, if association were found at high concentrations by molecular weight methods and decreased within the limits of concentration by that method, while at considerably lower concentrations the infra-red absorption spectrum showed a constant amount of bonding, it might reasonably be concluded that the bonding is of the intramolecular type at the lower concentrations. On the other hand, extremely strong bonding of the intermolecular type might possibly not be shown up by either method.

A further distinction might be made on the basis of amount of bonding as determined by the infra-red spectrum. For example, the molecular weight method would not indicate in the case of the dihydroxy compounds how many of the groups are bound in the association. On the other hand, if all groups were bound in a "lock and key" configuration,

the infra-red spectrum should show half free hydroxyls and half bonded as evidenced by the position of the peaks and their equal magnitudes, while if one molecule were associated to the other through one hydroxyl only, the absorption spectrum should show three unbound hydroxyls to one bound as evidenced by two peaks, the one having three times the height of the other.

From the previous discussion, it can be seen that the infra-red method could be a powerful tool in determining the configuration of the types of molecules considered.

Hydrogen bonding should have an effect on the dipole moment of these kinds of molecules because it would be expected to inhibit the free rotation of these groups and hold the hydrogen in a rather fixed position in the molecule. This of course, would lead to a fixation of the OH vector in space, so that its angle with respect to other vectors in the molecule could be calculated with some degree of probability, which should make estimation of the dipole moments of such molecules considerably simpler. This would be true for molecules with complete intramolecular hydrogen bonding. Consequently, agreement between the estimated value and that determined experimentally could be considered as evidence for that type of hydrogen bonding, provided that the moment so estimated is different within experimental error from that estimated from any other reasonable configuration.

If association occurs, the situation might be considerably more complex, depending on whether or not the dimer would be symmetrical. If symmetrical, the resulting measured moment should be close to zero; if otherwise, the moment might take on a value impossible to check because of the variety of possible configurations. In this regard however, if the amount of association changes in the range of concentrations wherein the moment is measured, the result should be a non-linear dependence of the solute polarization on concentration. The nature and extent of this variation might give a clue as to the configuration of the dimer. For example, if it were such that the P_2 values decreased with concentration, then the association would probably be tending toward a symmetrical dimer, or at least a dimer with a lower average moment. However, it is unlikely that a dimer of higher average moment would be formed.

In general, it may be concluded that measurement of moments for molecules of types described above, may give more or less definite indications of the configurations of the molecules, where the extent of probability assigned to the configurations may depend on several factors in each different case, so that each case must be decided individually, if it is possible at all, with the help of such available evidence as may be obtained from experimental work of other types.

3. KETO-ENOL TAUTOMERISM AND RESONANCE IN CONJUGATED SYSTEMS:

Tautomerism is that property of a molecule whereby it may pass from one configuration of its atomic nuclei to another. These may be expressed by different structural formulae when the tautomerism is of that kind known as prototypy or anionotropy and is to be distinguished from that kind previously considered for the cyclohexane ring. In this instance, the migration of a nucleus from one position of attachment in the molecule to another is involved.

The existence of this kind of tautomerism may be inferred from the chemical properties of molecules which show it, but it may be demonstrated conclusively by the infra-red absorption spectrum of the substances, where the spectrum will show peaks characteristic of the different forms. Some indication of the distribution of the substance among the forms should be obtainable from the amplitude of the peaks characteristic of each form.

The reason for tautomerism must lie in the similarity of energies of the different forms; if their magnitudes are close together, then the distribution should be about the same, neglecting other effects. If the energies are considerably different, then the distribution should be preferentially to that form having the lowest energy and consequently the greatest intrinsic stability. However, the position of equilibrium may be affected by such factors

as resonance, hydrogen bonding, and, if in solution, the nature of the solvent.

This thesis is particularly concerned with the type known as "keto-enol" tautomerism which may be expressed in the general fashion: $>C-C=O \rightleftarrows >C=C-OH$, where a hydrogen atom has migrated from an adjacent carbon to the oxygen of the carbonyl, establishing a double bond between carbons during the process. A good example of this type exists in the acetylacetone molecule, which may be represented by the formulae: $CH_3COCH_2COCH_3$ and $CH_3C(OH)=CHCOCH_3$. This substance is found[24] to exist to the extent of 91-93% enol in the gas phase, the enol form probably being stabilized by hydrogen bonding and resonance. The β-diketones and β-ketonic esters provide the best known examples of keto-enol tautomerism, however, the phenomenon is well-established in the case of α-diketones,[25] especially if they have a cyclic structure.

If the substance is in solution, the solvent may have an important effect on its distribution between the forms. The equilibrium constant (K) may be defined as the ratio of the concentration of the enol form to that of the keto. Values of K for acetylacetone range from 0.24 in water to 5.7 in benzene and 12.0 in hexane. K can thus be roughly correlated with the polarity of the solvent, the keto form

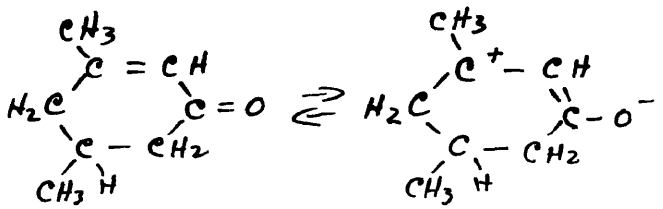
being favored in strongly polar solvents.

Resonance has been discussed completely in various works[26] and more recently in the papers of Smyth.[27] It will be sufficient here to point out that resonance in conjugated double bonds will in general be expected to contribute to the stability of structures by amounts ranging from 2 to 6 kcal. per mole, and consequently resonance of this type may be an important factor in determining the distribution between the keto and enol forms.

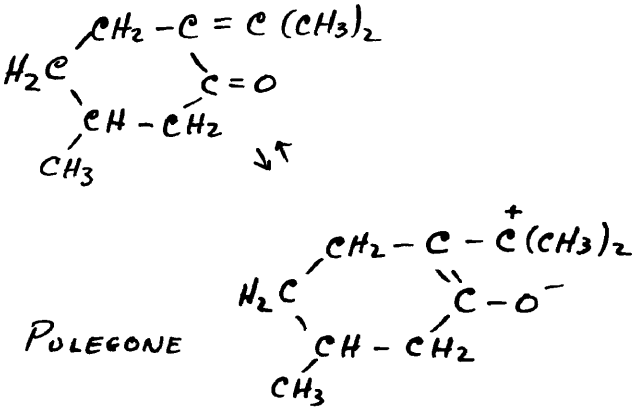
Neglecting the resonance effect for the moment, let us consider what effect the keto-enol tautomerism should have on the dipole moment. It is evident that since the moment associated with a hydroxyl group (about 1.7) is considerably smaller than that for a carbonyl (about 2.8) the effect should be appreciable. In spite of this perhaps no more than a qualitative estimate of the effect may be made in any case because the estimation might depend on a knowledge of the distribution of the substance between the two forms, on the configuration of the molecule in each of these two forms, and the possibility of dimerization as discussed previously for the diols. Certain simplifying effects might possibly exist; for example, a cyclic α-diketone might be expected to exist in a non-polar solvent with one ketone group fully enolized because all three of the effects previously considered would favor

that form. In such a case then, hydrogen bonding might be expected to fix the resultant vector of the C-H group with respect to the C = O group vector so that a definite estimate of the moment could be made. Agreement with experiment would be strong evidence for the enol form and the bonded configuration, provided a similar moment cannot be estimated for any other reasonable configuration.

In the above example, the picture is further complicated by the effect of resonance on the dipole moment, where however, a reasonable estimate might still be made by adding the effect due to resonance to the result already calculated. The resonance contribution might be estimated by comparison with similar molecules where the effect has been evaluated. For example, α,β unsaturated aldehydes and ketones usually give a moment of about 0.9D unit higher than the corresponding saturated compounds if the vector representing the ionic contribution of resonance is approximately in full support of the ketone vector. For example, crotonaldehyde ($CH_3CH = CH\ CHO$) has a moment of 3.67D, while saturated ketones run about 2.8. This explanation of the effect of resonance of this type is supported by the moments of 3,5 dimethylcyclohexanone and pulegone. For the former molecule, the resonance form supports the C = O group moment, while in the latter case it is more nearly neutral, as shown in Fig. 8. The moments



3,5 DIMETHYLCYCLOHEXENONE



POLEGONE

Fig. 8.

are 3.79 and 2.95 for 3,5 dimethylcyclohexenone and pulegone, respectively.

It may be concluded that the estimation of moments of compounds which involve enolization and resonance of this type should in general be difficult, and it is expected that little more than a qualitative picture can be obtained unless the system is simplified by complete enolization of one or both groups. If a definite moment could be assigned to the forms and configurations possible and if only two need be considered, then a distribution of the substance between the enol and keto forms could be calculated from the measured moments. Such would not be expected to be the general case. Infra-red absorption studies should be a powerful tool in elucidating the structures of these molecules.

THE EXPERIMENTAL METHOD

A heterodyne beat apparatus was used to measure the dielectric constants. This apparatus and the methods and techniques have been described in detail previously.[28,29]

Molecular weights were determined by the Rast method.[30]

The infra-red absorption spectra were obtained by methods which have already been described.[31]

PREPARATION AND PURIFICATION OF MATERIALS

Benzene: The method of purification of benzene has already been described.[28,29]

Cis- and trans- 1,2 cyclohexanediol: The crude mixture of isomers was prepared[a] by hydrogenating catechol in ethanol over Raney nickel at about 195-200°C. The crude mixture melted at 72-75°C. The trans form was crystallized nicely from the mixture in benzene solution by slow cooling and removal of successive amounts of the solid until the melting point began to drop sharply. This solid material was recrystallized several times from benzene to a constant melting point of 103-104°C. (uncorr.). This value checks a literature value of 104°C.[32]

The remaining solution was recrystallized about ten times from benzene according to a method previously used.[33] The resulting solid had a constant melting point for the last few recrystallizations of 98.0 to 99.0°C (uncorr.), which may be compared with a literature value of 98-99°C.[32,33]

Because the melting point of catechol is 104-105°C. and those of the isomers lie so close together, mixed melting points were determined for all combinations, using a roughly 50-50 mixture. All gave large depressions: the cis-trans mixture melted at 72-75°C; the trans-catechol

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We are indebted to various members of the Chemistry Department for suggestions, discussions and assistance in the preparation of some of these compounds. We particularly wish to acknowledge the aid given by Dr. H. L. Drake, Dr. Sidney Melamed, Dr. W. Reeve, Dr. G. F. Woods, and Dr. S. B. Tuemmler.

[a] One batch of this crude material was prepared by Dr. T. V. Roe of the Naval Research Laboratory to whom we are duly grateful.

mixture melted at 72-76°C; the cis-catechol mixture softened during mixing to the extent that it could not be introduced into the melting point tube.

Cis- and trans 1,4 cyclohexanediol: Hydroquinone in ethanol was hydrogenated over Raney nickel at a temperature of 170°C. The crude material, after removal of the solvent under vacuo, melted at 98-100°C. The trans isomer was separated by slow recrystallization from a 50-50 benzene-acetone mixture. The first recrystallization gave a solid melting at about 125°C. Two or three more recrystallizations were sufficient to bring this material to a constant melting point of 141-141.5°C. (uncorr.). This is comparable to a literature value of 142°C.[34]

The cis isomer was originally prepared by making the diacetates of the cis-rich diol mixture, separating out as much of the trans form as possible by recrystallization from ether, then recrystallizing the cis-rich diacetate mixture to a melting point of 53°C. This was trans esterified using a 10 mole excess of methyl alcohol. After refluxing for three hours the methyl acetate was slowly fractionated off. After removal of the solvent, the product was vacuum distilled (B_{2-3} 128°C.). The distillation product was recrystallized four times to a constant melting point of 111-112°C. (uncorr.). This may be compared with literature values of 107°C.[34], 112°C.[35], and 112.4-112.8°C.[36]

Two subsequent preparations were made* and their dipole moments measured. Both were carried through the diacetate separation. Cis-diacetate melting at 33°C., upon $Ba(OH)_2$ hydrolysis yielded an impure diol with melting point range 103-105°C., which could not be raised by rectystalligation from acetone or benzene. Ether was employed in the separation of the diacetates and when a cis-rich mixture was slowly evaporated, very large crystals of the cis isomer were formed. These were picked out by hand and recrystallized to a melting point of 39°C. $Ba(OH)_2$ hydrolysis yielded the cis diol, which upon recrystallization from acetone gave a constant melting point of 108-109°C.

The recent work of Perrine and White[36] indicates that the cis-diacetate must have a melting point of 41.25°C. to give a diol completely free of the trans isomer. The trans-diol content of cis-rich material melting at 109°C. may be roughly estimated to be 5-7%, based on their work.

1,2 Cyclohexanedione: This compound was obtained from G. Frederick Smith of the University of Illinois. It was prepared by the oxidation of cyclohexanone using SeO_2. It was marked of uncertain purity and had a yellow to orange color. It was fractionated** into four parts through a

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*We are indebted to Dr. W. Beaver of the Naval Research Laboratory for these preparations.
**We are indebted to Dr. W. Reeve for this fractionation.

small column:

Fraction	B.P. °C.	Press. (m.m.)	Weight (g.m.)
1	63-67	19	3.06
2	82-83	19	4.38
3	84.5-85	19.5	6.66
4	85	18.75	1.43

All fractions had a greenish color. Fractions 2 and 3 were mixed and refractionated:

1	79.5-81	19.5	1.42
2	81.5-83	19.25	7.80
3		19.25	1.23

Fraction #2 was used for the dipole moment measurements. It had a pale green tint and when poured into a weighing bottle a slushy white solid was formed. This was warmed over a very low flame to liquify it for weighing purposes.

Fraction #2 was analyzed** for carbon and hydrogen:

	Found		Theoretical for $C_6H_8O_2$	
	C	H	C	H
1	62.36	7.28	64.28	7.19
2	62.38	7.13		

<u>α -Hydroxycyclohexanone Preparation #1</u>: This material was prepared[38] by chlorinating freshly distilled cyclohexanone using SO_2Cl_2 and hydrolyzing the product in strong K_2CO_3 solution. The hydrolysis was carried out immediately, using efficient stirring. The cream-colored, waxy hydrolysis product was filtered, leached with water, triturated with ether, and filtered. Repeated crystallizations from benzene with large losses brought the white

**We are indebted to Miss E. Werble and Mrs. M.H. Aldridge of the Chemistry Department, University of Maryland, for these and subsequent analyses.

substance to a constant melting point of 137.8-138.8° C. (uncorr.). This may be compared with literature values of: 90° and 113° C.[39], 132° C.[40], and a vacuum distilled product, M.P. 130° C.[41] This material was analyzed to give:

	Found		Theoretical for $C_6H_{10}O_2$	
	C	H	C	H
1	63.11	9.00	63.13	8.83
2	63.24	8.80		

It was allowed to stand in two bottles for a year, one glass-stoppered, the other with a screw-top with a tin-foil lining. At the end of this time, the glass stoppered bottle had a definite yellow color at the bottom and an odor like that of the 1,2 cyclohexanedione. No color was observed in the other bottle, although the odor was present. The melting point of the material in the second bottle had dropped to 112-114° C. One recrystallization from benzene brought it up to 121-126° C. This was subsequently allowed to stand in air. After two months, the melting point had dropped back to 112-114° C. No odor was present. The material in the second bottle was re-analyzed after drying in a stream of air:

	Found		Theoretical for $C_6H_{10}O_2$	
	C	H	C	H
1	63.05	8.73	63.13	8.83
2	62.90	8.76		

The first two runs of those reported were made on the solid melting at 112-114°C.

<u>α-Hydroxycyclohexanone, Preparation #2</u>: A new preparation was made by chlorinating cyclohexanone with chlorine gas, in glacial acetic acid. The reaction mixture was fractionated and the product taken off at 85-100°C. (16 mm.). This was combined with fractions from other runs and refractionated to give a product boiling at 78-80° at 8mm. After standing at low temperature overnight, this material was hydrolyzed in strong K_2CO_3 solution. A waxy white solid was obtained which melted at 67-73°C. This substance was vacuum distilled. A watery fore-run came over at 42°C. (19 mm.). A second fraction came over at 82-85°C. (13-15 mm.). This may be compared with a literature value[44] of 83-86° (13 mm) (solid, 130°C.). This clear, colorless liquid was used immediately for the dipole moment measurements (Run #3). After standing for a few hours in a glass vial, the distillation product became milky, and after a few days it became completely solid. Both the liquid and the solid had the characteristic odor previously noted. This solid melted over the wide range: 112-130°C. Extracting with boiling ether narrowed the range but did not raise the top limit. The liquid from the distillation was quite soluble in both water and benzene. The benzene solutions from the dipole moment

measurements were allowed to stand in glass-stoppered flasks and after a few days a yellow solid was precipitated which melted at 148-152°C.

After standing one day in a tightly stoppered bottle, at which time it was in a semi-solid condition, the material from the distillation was analyzed to give:

	Found		Theoretical for $C_6H_{10}O_2$	
	C	H	C	H
1	62.59	8.80		
2	62.12	8.85	63.13	8.83

Apparently the substance was somewhat impure, although there is some question about the analysis because the sample lost weight during the weighing procedure.

Attempts were made to purify this material by other means. First, the semi-solid obtained from the original distillation was re-distilled at about 1 mm. pressure, where it came over at 42-45°C. and solidified in the distillation apparatus. It is believed that the pot must be maintained at about 140°C. and the substance distilled fairly hot-with no solid in the condensing apparatus-and caught in a cooled receiver in order to get the material in the liquid condition.* Second, the crude material was extracted with water and ether and dissolved in benzene and the benzene-water azeotrope distilled off until no more water was present. This was crystallized from the benzene and vacuum desiccated for 48 hours to give a substance

*These were the conditions for the original distillation which gave a completely liquid product.

melting at 100-103°C. Further attempts to recrystallize this from benzene were abandoned because of the poor yield, the length of time it took to get even a small amount of solid out, and because the melting point was raised only very slightly. Third, an attempt to purify by sublimation in a molecular still, using the vacuum desiccated solid (M.P. 100-103°C.) resulted in a waxy solid which melted at 98-104°. This was dried under vacuum overnight at a temperature of 78°C. and melted at 102.8-104.8°C.

Evidently, melting points given in the literature for this compound are at considerable variance, as indeed are our own, and the difficulties encountered in the preparation and purification of this substance lead to doubt about the nature and the purity of this compound. An attempt will be made to explain this later in the thesis.

CALCULATIONS AND DATA

The dipole moments were calculated using the pertinent equations in the general theory. These calculations are amply described elsewhere. Sometimes an extrapolated value for the dielectric constant for the pure solvent was used instead of the measured value, as has been done previously. In these cases the measured value of ϵ_1, and the P_1 value calculated from it are given in their usual position in the tables while the extrapolated values of ϵ_1 and P_1 are given below the table proper. The P_2 values were calculated using the extrapolated ϵ_1 value. An averaging process was used to obtain the P_2 values at infinite dilutions, except in the case of the trans 1,2 cyclohexane diol because polarization for this compound showed a slight upward slope with increasing dilution.

Densities were not determined for every solution due to the amount of time involved. Two or three solutions were measured and the density values for the others determined from the curve. The latter are in parentheses in the tables.

The polarization vs. mole fraction curves for the trans 1,2 cyclohexane diol are shown.

Dipole moment data is also included for the compound: monobromodiethylmalonate, which was furnished by Dr. E.S. Ames of Louisiana State University. It boiled over

a range 131 to 139°C. at 33 mm. This was fractionated and a fraction boiling over the range 135-138°C. (uncorr.) was used for the dipole moment measurements. This compound was measured only for its dipole moment and there will be no discussion concerning it.

A table is shown presenting the apparent molecular weight of some of these compounds in camphor as their concentration is changed.

The infra-red absorption spectra for cis-1,2 cyclohexane diol, trans-1,2 cyclohexane diol, and catechol in the 2.8 micron region is shown, and a table is presented giving the positions of absorption peaks, for all the compounds studied, which are pertinent to this work.

Estimates of the moments based on free rotation were made using equations 7 or 8, wherein the value for the resultant vector of the COH group is considered to be the same as that for cyclohexanol (1.7), and the angle it makes with the C-O bond is estimated to be 36°, on the basis of a bond moment of 0.7D for the C-O bond and 1.6D for the O-H bond.

To determine qualitatively the possibility of free rotation both the models and a calculation of interaction energy for the couple was estimated from the expression $m_1 m_2/d^3$. 2.8 was used for the group moment of C=O and 1.7 for COH. d was considered as the distance from the carbon in C=O to the oxygen in COH in the hydroxy ketone molecule.

In the diols the distance d was taken as that between oxygen atoms. When possible, these distances were calculated using bond distances given by Pauling[42], otherwise they were estimated from the molecular models.

TRANS-1,2 CYCLOHEXANEDIOL

Run #1 at 45.25°C.

No.	N_2	d	ϵ	P_{12}	P_2
0	——	0.84927	(2.2277)	(26.708)	——
1	2.2416×10^{-3}	(0.84990)	2.2427	26.948	142
2	4.4624	(0.85046)	2.2591	27.209	143
3	5.6800	(0.85082)	2.2674	27.340	141
4	6.0111	(0.85088)	2.2696	27.375	141
5	6.2200	0.85094			
6	7.8326	(0.85139)	2.2813	27.560	139

ϵ_1 (extrap.) = 2.2265 P_1 (using ϵ_1 extrap.) = 26.689 $P_\infty + P_A$ 32.296

P_2^∞ 145.5 ± 3.5 μ 2.41 ± 0.03D

Run #2 at 44°C.

0	——	0.85163	(2.2256)	(26.601)	——
1	1.7344×10^{-3}	0.85202	2.2385	26.809	143
2	3.0789	0.85227	2.2490	26.965	143
3	4.6322	(0.85273)	2.2594	27.144	143
4	6.1777	0.85306	2.2687	27.294	138
5	7.6894	(0.85341)	2.2810	27.489	141

ϵ_1 (extrap.) = 2.2260 P_1 (using ϵ_1 extrap.) = 26.607

P_2^∞ 144.7 ± 1.7 μ = 2.40 ± 0.02D

Run #3 at 44°C.

0	——	0.85216	(2.2303)	(26.657)	——
1	1.5909×10^{-3}	(0.85258)	2.2411	26.830	140
2	3.1074	(0.85301)	2.2516	26.997	139
3	4.6154	(0.85343)	2.2626	27.170	139
4	6.3257	0.85389	2.2736	27.343	136
5	7.3118	(0.85417)	2.2806	27.454	137

ϵ_1 (extrap.) = 2.2298 P_1 (using ϵ_1 extrap.) = 26.649

P_2^∞ 141 ± 1.0 μ = 2.36 ± 0.01D

avg. μ = 2.39 ± 0.03D

CIS-1,2 CYCLOHEXANEDIOL

Run #1 at 36.3°C.

No.	W_2	d	e	P_{12}	P_2
0	—	0.86018	2.2397	26.551	—
1	0.8294 10	(0.86042)	2.2460	26.650	146
2	2.0726	(0.86080)	2.2535	26.786	131
3	4.2345	0.86144	2.2691	27.009	135

avg. $P_2 = 137 \pm 6$ $\mu = 2.29 \pm 0.07$D $P_E + P_A = 32.296$

Run #2 at 44°C.

0	——	0.85214	(2.2319)	(26.682)	——
1	0.7811×10^{-3}	(0.85236)	2.2365	26.756	138
2	1.5595	(0.85252)	2.2417	26.841	138
3	1.7005	(0.85258)	2.2431	26.862	141
4	2.3038	(0.85270)	2.2473	26.930	140
5	3.3784	0.85298	2.2542	27.041	137

e_1 (extrap.) = 2.2310 P_1 (using e_1 extrap.) = 26.668

avg. $P_2 = 139 \pm 2$ $\mu = 2.34 \pm 0.02$D

Run #3 at 44°C.

0	——	0.85213	2.2297	26.648	—
1	2.1952×10^{-3}	(0.85271)	2.2444	26.884	134
2	2.9991	(0.85288)	2.2508	26.988	140
3	3.9149	(0.85311)	2.2567	27.082	137
4	4.9424	0.85345	2.2638	27.192	137
5	6.3790	(0.85373)	2.2732	27.344	136

avg. $P_2 = 137 \pm 2$ $\mu = 2.32 \pm 0.02$D

avg. $\mu = 2.32 \pm 0.02$D

TRANS-1,4 CYCLOHEXANEDIOL

Run #1 at 46.1° C.

No.	W_2	d	e	P_{12}	P_2
0	—	0.85018	(2.2287)	(26.694)	—
1	1.7062×10^{-4}	(0.85025)	2.2291	26.700	99
2	3.2573	0.85030	2.2297	26.710	94
3	4.7700	(0.85039)	2.2302	26.717	87
4	6.4590	0.85048	2.2312	26.732	93

$P_E + P_A = 32.296$

e_1 (extrap.) = 2.2283 P_1 (using e_1 extrap.) = 26.688

avg. $P_2 = 93 \pm 3$ $\mu = 1.77 \pm 0.05$D

Run #2 at 46.1° C.

0	—	0.85075	2.2265	26.642	—
1	1.6377×10^{-4}	(0.85077)	2.2271	26.653	95
2	4.7570	(0.85083)	2.2283	26.673	92
3	6.2080	0.85096	2.2291	26.687	98
4	7.7481	(0.85089)	2.2297	26.698	93

avg. $P_2 = 96 \pm 2$ $\mu = 1.82 \pm 0.03$

avg. $\mu = 1.80 \pm 0.03$

CIS-1,4 CYCLOHEXANEDIOL

Run #1* at 46.1° C.

0	—	0.85024	(2.2279)	(26.677)	—
1	3.5854×10^{-4}	(0.85038)	2.2299	26.711	152
2	4.8704	(0.85044)	2.2309	26.726	150
3	6.6347	0.85050	2.2324	26.750	155
4	7.9416	(0.85055)	2.2336	26.768	156
5	11.7840	(0.85070)	2.2368	26.818	155

$P_E + P_A = 32.296$

e_1 (extrap.) = 2.2270 P_1 (using e_1 extrap.) = 26.666

avg. $P_2 = 153 \pm 2$ $\mu = 2.50 \pm 0.02$D

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*M.P. - 111° C.

Run #2** at 46.1° C.

No.	N_2	d	e	P_{12}	P_2
0	——	0.85026	(2.2266)	(26.659)	——
1	1.6079×10^{-4}	(0.85033)	2.2283	26.685	147
2	4.8917	(0.85047)	2.2307	26.722	142
3	8.1193	(0.85061)	2.2331	26.759	142
4	10.0254	(0.85069)	2.2344	26.779	140
5	12.6482	0.85080	2.2367	26.814	144

e_1 (extrap.) = 2.2270 P_1 (using e_1 extrap.) = 26.666

avg. P_2 = 143 ± 2 μ = 2.39 ± 0.02

Run #3*** at 46.1° C.

0	——	0.85038	(2.2268)	(26.659)	——
1	2.4983×10^{-4}	(0.85046)	2.2286	26.687	126
2	4.1220	(0.85052)	2.2298	26.707	133
3	6.2087	(0.85059)	2.2310	26.725	128
4	9.9627	0.85071	2.2333	26.761	126
5	13.9375	(0.85086)	2.2359	26.802	126

e_1 (extrap.) = 2.2271 P_1 (using e_1 extrap.) = 26.663

avg. P_2 = 128 ± 2 μ = 2.23 ± 0.02

** M.P. - 108-109° C.
*** M.P. - 103-105° C.

1,2 CYCLOHEXANEDIONE

Run #1 at 46.1° C.

No.	N_2	d	e	P_{12}	P_2
0	——	0.85014	2.2271	26.671	——
1	5.7626×10^{-3}	0.85176	2.2835	27.546	179
2	7.5756	(0.85244)	2.3034	27.843	181
3	9.2218	(0.85263)	2.3115	27.966	184
4	11.2410	0.85362	2.3421	28.420	182

avg. P_2 181 2

dione structure: $P_E + P_A = 29.12$ ($\mu = 2.80 \pm 0.02$D)

mono enol " : " 29.17 ($\mu = 2.80 \pm 0.02$D)

di enol " : " 31.32 ($\mu = 2.78 \pm 0.02$D)

Run #2* at 46.1° C.

0	——	0.85070	2.2275	26.659	——
1	1.1133×10^{-3}	(0.85107)	2.2376	26.816	169
2	2.5257	0.85155	2.2510	27.023	171
3	4.4313	(0.85226)	2.2689	27.294	170
4	5.6097	0.85271	2.2809	27.474	172

avg. $P_2 = 170 \pm 1$

μ (dione structure) $= 2.70 \pm 0.01$D

avg. $\mu = 2.75 \pm 0.05$D

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*This run was made about 1½ years after the first run on the same material which had become slightly darker in color. The first run is probably more reliable.

α-HYDROXYCYCLOHEXANONE

Run #1* at 46.1°C.

No.	N_2	d	e	P_{12}	P_2
0	——	0.85082	(2.2268)	(26.645)	——
1	0.9037 x 10^{-4}	(0.85083)	2.2272	26.653	155
2	1.7208	(0.85083)	2.2277	26.660	155
3	2.4278	(0.85084)	2.2286	26.675	169
4	3.2368	(0.85085)	2.2291	26.683	157
5	4.0221	0.85087	2.2297	26.693	155

e_1 (extrap.) = 2.2265 P_1 (using e_1 extrap.) = 26.641 $P_E + P_A = 30.71$

avg. $P_2 = 154 \pm 8$ $\mu = 2.5 \pm 0.1$D

Run #2* at 46.1°C.

0	——	0.85071	2.2282	26.670	——
1	4.7872 x 10^{-4}	(0.85086)	2.2330	26.746	185
2	7.1816	0.85088	2.2360	26.793	198
3	9.5766	(0.85101)	2.2380	26.822	186
4	14.3680	0.85121	2.2443	26.918	200

avg. $P_2 = 192 \pm 6$ $\mu = 2.88 \pm 0.05$D

Run #3** at 25.3°C. (B_{P3-15} – 82-85°C)

0	——	0.87210	(2.2553)	(26.421)	——
1	2.9820 x 10^{-3}	(0.87285)	2.2855	26.880	207
2	5.4020	(0.87345)	2.3151	27.321	208
3	8.3712	0.87412	2.3522	27.869	208
4	10.4952	(0.87465)	2.3761	28.218	205

e_1 (extrap.) = 2.2500 P_1 (using e_1 extrap.) = 26.342

avg. $P_2 = 207 \pm 1$ $\mu = 2.92 \pm 0.01$D

avg. μ 2.8 ± 0.2

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*Runs 1 & 2 on material M.P. 112-114°C.
**Run 3 on vac. dist. liquid.

MONOBROMODIETHYLMALONATE

Run #1 at 36.8°C.

No.	N_2	d	ϵ	P_{12}	P_2
0	—	0.86022	2.2485	26.683	—
1	1.4197×10^{-3}	(0.86163)	2.2643	26.955	218
2	2.8385	(0.86310)	2.2800	27.225	214
3	4.5619	0.86464	2.2992	27.555	218
4	6.8832	0.86712	2.3243	27.977	215

avg. $P_2 = 216 \pm 2$ $\mu = 2.90 \pm 0.02$D

Run #2* at 36.8°C.

0	—	0.86052	2.2466	26.645	—
1	1.4708×10^{-3}	(0.86202)	2.2637	26.937	225
2	2.0817	(0.86265)	2.2718	27.072	232
3	2.3930	(0.86295)	2.2752	27.131	230
4	3.8292	0.86448	2.2917	27.408	226
5	7.4704	0.86815	2.3344	28.124	225

avg. $P_2 = 228 \pm 3$ $\mu = 3.00 \pm 0.02$D

avg. $\mu = 2.95 \pm 0.05$D

*Run #2 made on same material as Run #1 about 1½ years later.

POLARIZATION vs. CONCENTRATION

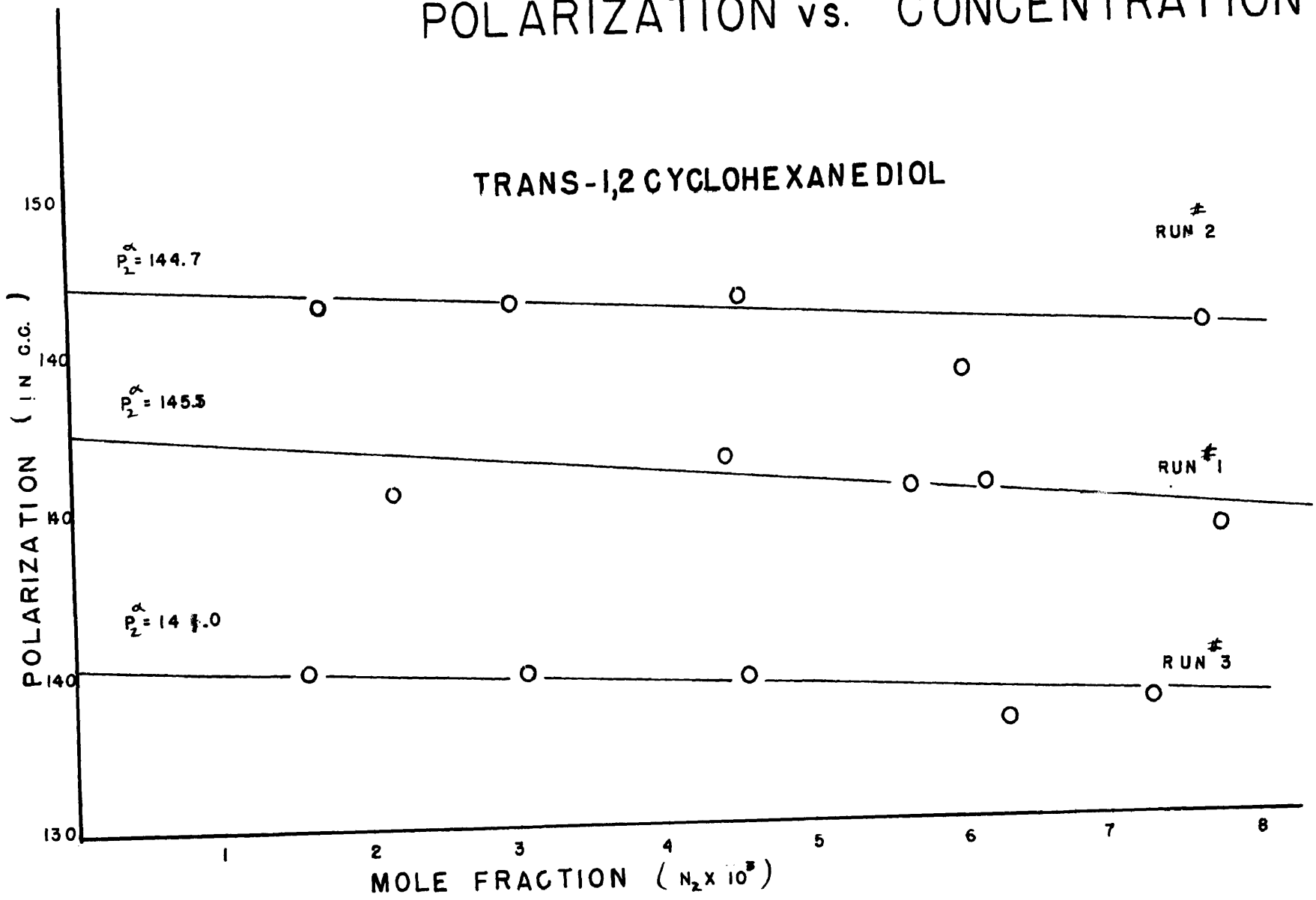


PLATE I

RAST MOLECULAR WEIGHT DATA

M.P. Camphor - 179.0°C

Benzoic acid (M.W. 121)

No.	wt solute	wt camphor	M.P.	M_2	M.W.
1	0.0174 gm.	1.1279 gm.	174.0		122.4
2	0.0329	1.1469	156.6		128.1

Trans 1,2 diol (M.W. 116.2)

1	0.0122	1.1669	176.9	0.014	198
2	0.0213	1.0201	174.4	0.027	180
3	0.0487	0.6109	164.0	0.096	193
4	0.0822	0.5465	149.0	0.166	199

Cis 1,2 diol (M.W. 116.2)

1	0.0366	1.5068	172.0	0.031	138
2	0.0371	1.2851	171.7	0.037	157
3	0.0445	1.0688	169.7	0.053	178
4	0.0512	0.5815	161.6	0.105	201

Trans 1,4 diol (M.W. 116.2)

1	0.0122	1.1305	175.9	0.014	132
2	0.0241	1.2905	173.9	0.024	144
3	0.0514	0.9021	165.8	0.071	149
4	0.0536	0.6294	158.5	0.102	166

Cis 1,4 diol*(M.W. 116.2) M.P. 109 C.

1	0.0146	0.7091	175.0	0.0262	204
2	0.0276	0.6510	169.7	0.0524	191
3	0.0521	1.1666	169.7	0.055	190
4	0.0449	0.6900	162.5	0.068	177

α-Hydroxycyclohexanone.** (M.W. 114)

1	0.0215	1.1064	175.5	0.025	206
2	0.0421	0.5990	165.5	0.085	210
3	0.0616	0.5630	159.9	0.127	218
4	0.0643	0.4681	154.0	0.149	238

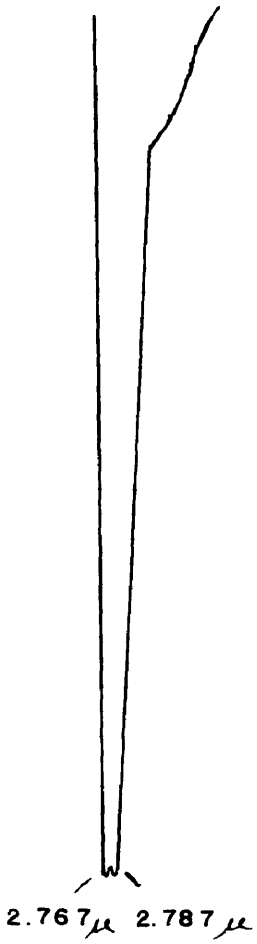
* Runs 2 and 3 on material melting at 103-105°C.
**Runs 1 and 2 on material melting at 112-114°C. Runs 3 and 4 on material from vacuum distillation (M.P. 112-130°C.)

INFRA-RED ABSORPTION DATA

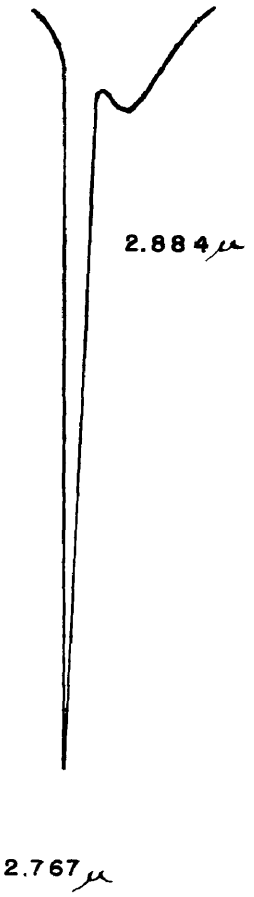
Compound	Condition of Measm't	Position of Absorp. Band (microns)	Structure & Remarks
Catechol	CCl_4 solu.	2.767	free hydroxyl } No variation
		2.797	internally bound hydroxyl } of intensity with concentration
		2.94	Intermolecularly bound hydroxyl?
Trans-1,2 diol	CCl_4 solu.	2.767	free hydroxyl
		2.884	intermolecularly bound hydroxyl? Intensity varies with concentration.
Cis-1,2 diol	CCl_4 solu.	2.767	free hydroxyl } no variation
		2.787	internally bound hydroxyl } of intensity with concentration.
Trans-1,4 diol	solid	3.08	bound hydroxyl
	CCl_4 solu.	2.768	free hydroxyl
Cis-1,4 diol	solid	3.05	bound hydroxyl?
		3.10	bound hydroxyl
1,2 Cyclohexanedione	liquid	2.92	bound hydroxyl
		5.99	carbonyl
		6.22	carbon double bond carbon
	CCl_4 solu.	2.90	strong, internally bound hydroxyl?
		3.00	very weak, intermolecularly bound hydroxyl?
α-Hydroxycyclohexanone	solid (M.P. 112-114)	2.98	bound hydroxyl
		6.02	very weak carbonyl bond
	CCl_4 solu.	2.776	free hydroxyl?, no change of
		2.86	intensity with dilution weak, bound hydroxyl?
		2.92	bound hydroxyl?, apparent increase of intensity with dilution.

PLATE II

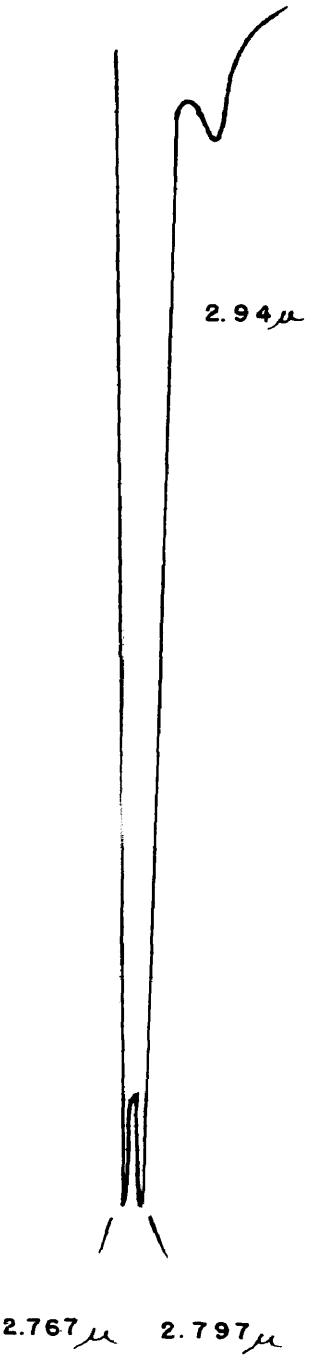
CIS-1,2CYCLOHEXANEDIOL



TRANS-1,2 CYCLOHEXANEDIOL



CATECHOL



HYDROXYL ABSORPTION

DISCUSSION OF RESULTS

The molecular weight data determined by the Rast method is good to within 6% for a single determination as indicated by the check runs on benzoic. Where more than one run is involved it may be somewhat better. The accuracy obtainable by this method is certainly good enough to show the presence of association.

The curves which are plotted from the data show that association in camphor solution is strong in all cases for concentrations above $N_2 = 0.1$. This strong association persists to lower concentrations for α-hydroxycyclohexanone, the trans 1,2 diol, and the cis 1,4 diol. The cis 1,2 diol shows a definite inflection indicating that the association is becoming rapidly smaller in extent as concentrations below $N_2 = 0.06$ are approached. The trans-1,4 diol has a slighter tendency toward association than any of the other compounds, and the association falls off gradually with decreasing concentration.

Thus, the tendency of these compounds toward association is quite strong for the relatively more concentrated solutions in camphor. It might be expected from the data, that the cis 1,2 diol and the trans 1,4 diol should be substantially monomeric in the benzene solutions used for the measurement of the moments if they were to act in benzene as they do in camphor. No conclusion can be drawn as to the extent of association in benzene of the

other compounds.

The infra red absorption spectrum of catechol and of all the compounds studied here have been recorded under certain conditions and in certain ranges of the spectrum in an attempt to determine the existence of hydrogen bonding and/or enol-keto tautomerism. The results obtained for each compound are given below.

The data were obtained for catechol, cis-1,2 cyclohexanediol, and trans-1,2 cyclohexanediol in the 2.8 micron (μ) region in carbon tetrachloride solutions of different concentration to determine the existence and type of hydrogen bonding. For each of these compounds the concentration was varied from about 0.1 to 1.0 gm./l. in cells from 5 to 50 m.m. in thickness and the effect of concentration on the intensity of the bonds was studied. Plate II shows the absorption bonds at one concentration for each compound. No attempt has been made to indicate the change in intensities of the bonds with concentration but such changes will be described qualitatively below.

Catechol gives absorption maxima at 2.767, 2.797, and 2.94 μ. The 2.767 bond is due to free hydroxyl while the 2.797 bond may be ascribed to intramolecularly bound hydroxyl, because its intensity does not change with concentration. This interpretation is in agreement with that of Pauling[13]. The change in intensity of the 2.94

μ bond was not determinable because the bond was too weak to study the dilution effect, but the bond may be due to intermolecularly bound hydroxyls as discussed for the trans-1,2 diol below.

Trans-1,2 cyclohexanediol exhibits a single sharp absorption peak at 2.767 μ and a much weaker, broader peak at 2.884 μ which varies in intensity with concentration. The 2.767 μ peak is the normal free hydroxyl bond, while the 2.884 peak has been ascribed* to intermolecularly bound hydroxyls because of the variation in intensity with concentration, although there is some doubt about this interpretation. If correct, however, it indicates that some association takes place. No intramolecular hydrogen bonding is indicated.

Cis-1,2 cyclohexane diol shows a broad band which is barely resolved into equal maxima at 2.767 and 2.787 μ, the intensities of which do not appear to change with concentration, indicating a high degree of internal bonding. This band has a shoulder toward the higher wavelengths which may be an unresolved maximum due to intermolecularly bound hydroxyl groups. If this is so, then some association is present in this case also.

The trans-1,4 diol was investigated both in the solid state and in solution. The solid exhibited a single

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*Private communication from Dr. D.C. Smith of the Naval Research Laboratory.

absorption peak at 3.08 μ, indicating that all hydroxyls are strongly bound. A saturated solution of this substance showed a single sharp absorption peak at 2.76θ, indicating no hydrogen bonding of either type, consequently no dilution studies were run.

The cis-1,4 diol was investigated in the solid state and showed absorption peaks at 3.10 μ and 3.05 μ. The latter peak was ascribed to bound hydroxyls. It is suggested that the former is also due to bound hydroxyls. Two peaks might be expected because the hydroxyl configurations are different in this compound, provided the chair form is maintained in the solid. In the case of the trans-1,4 diol both hydroxyls are the same, if the molecule retains completely either the 2p or the 2e configuration, the latter being more probable on energy grounds. The solution study on the cis-1,4 diol hasn't been run due to instrumental difficulties.

For the 1,2 cyclohexanedione a supposedly pure sample was used.* This material exists as a yellowish-white, solid-liquid mixture. Some of the liquid was pipetted off and absorption maxima were found at 2.92, 5.89, and 6.22 μ. These positions are due to bonded hydroxyl, the C=O group, and the C=C group respectively. The intensities of the 2.92 and 5.89 μ peaks were such as to indicate that

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* This sample supplied by Dr. W. Weaver.

approximately half of the ketone groups were enolized. This is not inconsistent with a complete mono-enolized form, but could correspond to a mixture of dione, mono-enolized, and di-enolized forms. A solution study on this compound showed a strong peak at 2.90 μ and a very weak peak at 3.00 μ. The former showed no change in intensity with dilution while the latter exhibited a slight decrease with increasing concentration. This may be interpreted as indicating that almost all hydroxyls present are bound internally, with a small fraction in an associated condition. The internal hydrogen bonding in this case may be quite strong if the position of the bound hydroxyls can be compared with those of the 1,2 diols.

α -Hydroxycyclohexanone was run in both the solid condition and in very dilute solution. The solid material showed a single absorption peak at 2.93 μ and a very weak C=O peak indicating that the solid is almost completely enolized and that all hydroxyls are bound. In CCl_4 solution, the C=O absorption peak became quite strong, showing that a considerable amount of the ketonic form is present. Absorption peaks were also found at 2.776, 2.86, and 2.92 μ. The former showed no change with dilution. The latter increased in intensity. This is an anomalous phenomenon, and may be due to the fact that the solubility

range is so dilute that it was working very close to the constants of the instrument. Any attempt at interpretation of these results may be questionable, but if the 2.770 peak is due to free hydroxyl, then the other two may be of two different bond types and quite a mixture of forms and configurations may be present. This compound should be studied further. The spectrum of the freshly distilled liquid and its change on aging, the spectrum of various dilutions of the freshly distilled substance and their change on aging, and studies of the solids with various melting points are suggested.

A complete analysis of the Debye equation for the effect of errors in the various measured quantities has already been made and applied[28,29] to extremely dilute solutions such as have been measured in this work. It indicates that moments measured in this order of dilution ($N_2 = 10^{-2}$ to 10^{-4}) are precise to $\pm$ 0.1D or better. The results obtained here show precision well within these limits, except in the case of α-hydroxycyclohexanone, where the first run (made in very dilute solutions) leads to a value about 0.4D less than the other two runs.

It will now be of interest to attempt to determine the structure and/or configuration of these molecules from the dipole moment, infra-red, and molecular weight data, in the light of the theory which has been presented.

In order to facilitate the discussion a table has been drawn up to present at a glance the information which can be obtained by examination of the Fisher-Herzfeld models and calculation of interaction energies. Two types of steric hindrance are encountered in these molecules: interference of hydroxyl hydrogens, and interference of polar hydroxyl hydrogens with polar hydrogens attached to carbons twice removed from the hydroxyl carbon. The latter is indicated as C^3H in the table. 1,2 cyclohexanedione and -hydroxycyclohexanone have not been included in the table. Such of these characteristics as are pertinent to these molecules will be included in the discussion.

TABLE I

Compound	Config.	Internal H Bonding Possible?	Steric Hindrance? Type?	d	$m_1 m_2/d^3$
Cis-1,2 diol	1e,1P	Yes	both	2.86°	15×10^{-14} erg.
Trans-1,2 diol	2e	Yes	hydroxyl H's	2.3	13
	2p	No	C^3H	3.2	2
Cis-1,4 diol	1e,1P	No	C^3H	4.5	3
Trans-1,4 diol	2e	No	none	3.6	1.5
	2p	No	C^3H	4.5	3

Inter-molecular hydrogen bonding is possible for all these compounds.

In the following discussion the angles between the C-O bonds have been estimated from the models of the molecules. This is possible because the model of cyclohexane indicates that the chair form of the ring is a fairly rigid structure. If it were necessary to consider boat forms this angle would not be fixed because there is considerable freedom of rotation about the C-C bonds.

Considering the 1,2 diols, taking the cis isomer first, there are two possible configurations, each with one hydroxyl group polar and one equatorial. These are optical isomers so that they both have the same dipole moment. The steric hindrance encountered in this molecule probably need not be considered since the value of $m_1 m_2/d^3$ is so large, being about three times the value at which interaction may be expected to seriously reduce the freedom of rotation. Moreover, the model indicates the possibility of hydrogen bonding. This actually exists, as shown by the infra-red spectrum and is of the same type as catechol,[13] which is considered to exist in a cis-planar structure with almost complete intramolecular hydrogen bonding.

If the hydroxyl groups may be considered to be locked in the catechol configuration then the angle between the resultant vectors for the COH groups may be estimated from the model to be $60 \pm 5^{\circ}$. Arbitrarily assigning limits of $\pm 10^{\circ}$ to this angle, the resultant of these two vectors

may be calculated to lie in the range 2.73 to 3.06, if 1.7 is used for the COH moment. Further examination of the model shows that of the hydrogens attached to carbons, two polar up oppose two polar down while four equatorial hydrogens are opposed, leaving one equatorial and one polar hydrogen to be considered. The C-H bond angles in these cases are almost perpendicular. Using a moment of 0.4D for the C-H bond and an angle of 90°, the resultant is calculated to be 0.57 D units. The angle between this vector and the resultant of the COH groups appears to be roughly perpendicular, regardless of which of the two possible extreme positions of the COH groups is used, however, this angle is quite uncertain. If it were as large as 125° it would reduce the previously calculated moment by 0.2D unit, so that the lower limit of the range then becomes about 2.8. This value is still about 0.3 unit higher than the experimental value of 2.52. In view of the uncertainty of the calculation, reasonable agreement might be claimed, especially if the hydroxyls may be considered to execute gentle libration through small angles. This would have the effect of lowering the calculated moment somewhat. If a small percentage of the molecules exist in a configuration such that the vectors of the COH groups are generally opposed, or if there is a small amount of dimerization with all four hydroxyls bound in a symmetrical structure, the measured moment should be lower than that calculated.

The measured moment is about 0.1 D unit higher than that calculated on the basis of free rotation (2.21 - as mentioned in the theory, all these dihydroxy compounds should have a moment close to 2.21 if the angle between the axes of rotation is fixed, neglecting the small effects due to hydrogens attached to carbons.) Provided the effect of C-H bonds which must be considered is small, reasonable agreement might be obtained especially since interaction in this case should lead to a moment higher than that calculated for free rotation, however, free rotation is not possible in this case as is shown by the infra-red data and indicated by the high value of the interaction energy.

In the case of the trans-1,2 diol, two of the four possible configurations must be considered. One has both hydroxyls in polar positions, the other has both in equatorial positions. These are in tautomeric equilibrium. Examination of the model for the configuration with the equatorial hydroxyls shows the possibility of hydrogen bonding. In fact, the distances and angles concerned are practically the same as in the case of the cis-1,2 diol. The hydrogens to be considered for this configuration are the equatorial hydrogens on carbons corresponding to the hydroxyl carbons at the opposite end of the molecule. In this case, the hydrogens can be estimated with a fair degree of precision to have no more effect than a $\pm$ 0.1 D

unit on the moment. Consequently, if this configuration can be said to be exactly analogous (i.e. rigidly bound hydroxyls) to the cis-1,2 diol, then the range for the calculated moment is about 2.7-3.2. Again, the lower limit is about 0.3 units above the experimental value (2.39). And the same qualitative arguments for the lowering of the moment would apply here as were applied in the cis-1,2 diol case. The tendency of this molecule towards dimerization is stronger than that of the cis-1,2 diol, as evidenced by the molecular weight data in camphor where even at the lowest concentration possible (0.01 to 0.02 mole fraction), the apparent molecular weight is in the range 180-200. Since the range of measurement of the solutions is not too much below this (0.007 to 0.001 mole fraction) dimerization would seem to be a definite possibility. The infra-red absorption spectrum may indicate hydrogen bonding between molecules in dilutions comparable to those used for the dipole moment measurements as mentioned previously. At any rate, if there is an equilibrium between monomer and dimer, the moment is practically impossible of estimation unless the distribution and configuration of the dimer is known with certainty. The absence of intramolecular bonding in this molecule as is indicated for the cis-1,2 diol is puzzling, since the models are so nearly alike and the measured moments are so nearly identical, unless the contribution of the 2b form

for the trans-1,2 is appreciable. However, in the infrared spectrum of the cis-1,2 diol, the two peaks are barely resolved by the instrument. Thus, only a very slightly weaker band as might exist in the trans-1,2 diol (2e) might fail to be resolved, but nevertheless be sufficiently strong to keep the hydroxyls in the catechol configuration.

For the 2p configuration, there is no possibility of intramolecular hydrogen bonding, free rotation is blocked by the polar hydrogens on the ring, and the interaction energy is about double that at which rotation may be expected to be hindered to a considerable degree. All of the hydrogens attached to carbons are opposed in this molecule and consequently need not be considered. The interaction of the groups in this configuration would not be expected to be such as to cause the resultant vectors of the OH groups to completely support or completely oppose one another, but probably the angles between them of greater than 90° would be favored because of the location of the groups. If this is actually the case, the moment should be less than 2.4. If Pitzer's general statement that tautomers having polar substituents have higher energies than those with equatorial substituents is applicable here, then the 2p configuration should be less favored than the 2e for this isomer. If this energy difference is of the same order of magnitude as exists in the dimethylcyclohexane derivatives or higher, then the 2e configuration

should be considerably favored.

If any conclusions may be drawn from this data and the theory involved, they are: first, free rotation is absent in the cis isomer and very improbable for either of the possible configurations of the trans; second, the existence of any appreciable amount of the 2p configuration of the trans isomer at these temperatures is unlikely; third, the most probable configuration for these isomers are those similar to catechol. The moments may be lowered due to libration of the hydroxyls through small angles about the rigidly bound positions, or by the formation of symmetrical dimers to a small extent.

It should be pointed out that the value calculated for catechol (2.71) was based on bond moments of 0.7 for C-O, 1.6 for O-H, and an angle for the COH group of 112, where the hydrogens add about 0.1 unit to the calculated value. These bond moments and this angle lead to a resultant moment for phenol of about 1.52 D, which is to be compared to a measured value of 1.7. If 0.1 is subtracted* from the phenol value for the para hydrogen, 1.6 is obtained for the COH group moment. Using this value, catechol may be calculated to have a moment of 2.76 for the cis-planar structure, where the hydrogens to be considered will raise this to 2.86. Since the measured value (2.58) is about 0.3 units lower, it is indicated that the method is

somewhat in error, or that there is some departure from the cis-planar structure, or that some symmetrical dimers are formed. If the former is the case, then the values calculated for the bonded structures of the cis-and trans-1,2 diols may be too high by about the same value. If this correction is applied, the lower range of the calculated values may be reduced to about 2.4, which is in good agreement with the measured values.

For the case of the trans-1,4 diol, two configurations must be considered: 2p and 2e. These are in tautomeric equilibrium. There is no possibility for intramolecular hydrogen bonding in either case. Free rotation is possible for the 2e configuration but is hindered by polar hydrogens for the 2p configuration. The molecular weight data indicates that association would be very small, even at much higher concentrations than the solubility in benzene would allow. The infra-red spectrum shows no hydrogen bonding. In each configuration all ring hydrogens are opposed so that they need not be considered.

For the 2p configuration angles between the resultant vectors of the OH groups of from about 40° to 180° would be allowed in the absence of interaction, however, the mutual potential energy value indicates that some interaction is to be expected. The disposition of the hydroxyls is again quite difficult to determine, although it may be concluded that they should be generally opposed, leading

to an appreciable reduction in the moment based on free rotation (2.21). Again, if Pitzer's general rule concerning polar configurations is applicable, the equatorial form should be favored.

For the equatorial configuration the mutual potential energy is about one third the value for strong interaction, but about three times as large as the value at which interaction may be considered negligible. Consequently, the moment should be somewhat less than the free rotation value of 2.21, since interaction in this case would be definitely unfavorable to positions where the vectors would be generally supporting. The moment of this compound should be temperature sensitive and approach 2.21 as a limit. The measured value of 1.81 D is in support of these arguments. It does not rule out the existence of a polar configuration, although qualitatively the polar configuration should have a moment somewhat less than the equatorial because the interaction is stronger, and the presence of steric hindrance may cut down the availability of the smaller angles with which the larger moments are associated. Graphical integration over the range 40° to 180° assuming all angles equally probable, allows a maximum moment for the polar configuration of about 2.07 D. If the moment could be measured over a temperature range and were found to approach 2.21 as a limit, the existence of

any appreciable amount of the polar configuration could be ruled out. As yet, however, there is no justification for this other than the general rule of Pitzer's.

It may be concluded that the moment is in agreement with restricted rotation theory, even if both configurations of this molecule are present.

In the case of the cis-1,4 diol only one configuration is possible with one hydroxyl equatorial and one polar. The equatorial hydroxyl is free to rotate, but the polar hydroxyl encounters interference from polar hydrogens on other carbons. One polar and one equatorial C-H bond contribute a resultant of about 0.57D to the total moment but the relation between this resultant and the COH vectors is quite difficult to estimate. The mutual potential energy is large enough to account for considerable interaction, but the effect on the disposition of COH vectors is too difficult to determine, so that no attempt will be made to calculate a moment for this molecule. The free rotation value is about 2.8D, but the existence of free rotation is quite improbable.

The best value of the moment for this compound is 2.5 D, if the melting points may be used as a criterion. The relatively large value of this moment must indicate that the hydroxyl vectors are generally disposed in sup ort of one another, a possibility which is not eliminated by examination of the model. The model of the boat form of this molecule

shows the possibility of internal hydrogen bonding. If the energy contribution of such bonding were large, it might help to stabilize that configuration. In that case the value of the moment may be estimated to be as high as 3.4, since in the position of closest possible approach the C=H vectors would be in almost complete alignment. Unfortunately, solution studies by the infra-red method have not been run on this compound as yet.

Although the purity of the 1,2 cyclohexanedione is in question, if it may be assumed that it contains only small amounts (about 5%), the effect on the moment should be small even if the moment of the impurities were very large (4.0D), or very small, unless some unexplainable association effects might take place. If the measured moment can be assumed to be correct within 0.2D some conclusions may be drawn as to the structure of the compound in benzene, from a consideration of the molecular models and the available infra-red data.

This molecule is an α-diketone with a ring structure and according to theory should have a strong tendency toward enolization. Thus the molecule may be pictured to exist in an equilibrium state involving three forms as in Fig. 10.

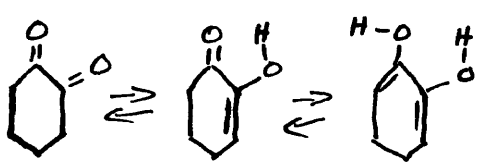


Fig. 10.

The model for the diketone structure indicates an angle of about 100° to exist between the carbonyl vectors.

The resultant based on this angle is 3.6. Two hydrogens with a resultant of about 0.57 add almost quantitatively to this to bring the moment to about 4.2. Even allowing room for an error in estimation of the angle of 10° would only bring the total moment down to 3.7. This is in very poor agreement with the experimental value of 2.75. Consequently, this form probably does not exist to any great extent in solution unless some sort of resonance phenomena due to conjugation of the carbonyl linkages as indicated in Fig. 11 would work toward reducing the moment. However, it is expected that any such effect would change the moment very little, because what is taken from one group would be added to the other.

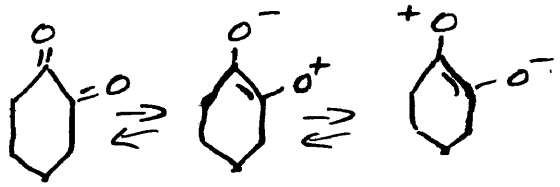


Fig. 11

The infra-red absorption spectrum indicates that this substance in the liquid state exists with about one half the carbonyls enolized and with the hydroxyl hydrogens bonded. No distinction is made here between intra- and intermolecular bonding, but the data could be explained by single molecules, singly enolized, and having the hydroxyl hydrogen bridged to the carbonyl oxygen within the molecule. If such a picture would apply in dilute benzene solution and if the bonding keeps the ring and

hydroxyl position rigid, then the angle between the carbonyl vector and the resultant vector for the C-OH group may be estimated from the model to be 134°. The calculated moment on this basis would be 2.02. However, resonance of the type previously discussed for crotonaldehyde and 3,5 dimethylcyclohexenone would be expected unless the hydroxyl group has an inhibiting effect. If resonance is uninhibited, the system is clearly analogous to the 3,5 dimethylcyclohexenone molecule where resonance adds about 0.90 unit to the moment of the molecule. If this is considered to act along the C=O axis, the moment for our compound may be re-calculated to be 2.80. Three hydrogens may act to add an uncertain amount to this value. If the effect is small then the calculated moment gives a very good check with the experimental.

Free rotation of the hydroxyl group would allow a calculated value of 3.27 or 3.98 for the moment depending on whether or not resonance is considered. The agreement is very poor, but free rotation is not to be expected on the theoretical grounds previously considered for the 1,2 diols. In this case the mutual potential energy would be even greater due to the larger value for the C=O bond moment.

If the doubly enolized form is considered, an angle of close to 60° (actually estimated to be 57°) should exist between intramolecularly hydrogen bonded OH groups

and the moment should be close to that of catechol (2.58). If a value of 1.7 is used for the OH vector the moment is calculated to be 2.94 and two hydrogens act to add a small amount to this as in the case of the trans-1,2 diol. This value may be considered to be in fair agreement with the experimental value. Resonance possibilities of the type indicated in Fig. 12 would be expected to have a neutral effect since the molecule is symmetrical and the two extreme electronic configurations should cancel.

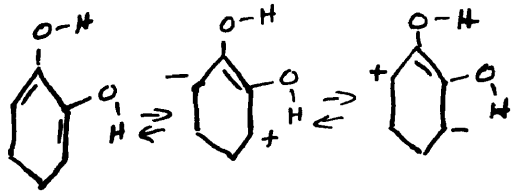


Fig. 12.

Dimers might possibly be formed as considered for the case of the 1,2 diols for either of the enol forms considered here. If all groups are bound in a symmetrical structure the result should be to decrease the moment. If they are not symmetrical, then the effect on the moment cannot be determined. It is suggested that, because the oxygen of the carbonyl is strongly electronegative and probably made considerably more so by the resonance effect, an unusually strong intra-molecular hydrogen bond could be formed in this case and association might therefore be resisted.

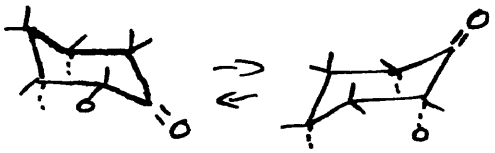
The strong hydrogen bond and the resonance effect

should contribute in a large measure toward stabilizing the singly enolized form of the molecule. Because this form may be indicated for the liquid by the infra-red absorption spectrum, it is considered that this compound exists to a large extent in benzene solution in the singly enolized form, even though the moment calculated for the doubly enolized structure gives a reasonable check.

In connection with the cyclic diones, the moment for 1,4 cyclohexanedione has been measured to be 1.4. Since the moment should be zero if the chair form exists primarily, the value obtained was explained[43] on the basis of a mixture of chair and boat forms. The model indicates that the chair form is a fairly rigid structure and if Pitzer's work applies here the boat form probably exists to only a very small extent. However, if one carbonyl should be enolized and the hydroxyl group free to rotate, (even though the interaction here may be appreciable due to the magnitude of the C=O bond moment, the range of possible angles is not very great), the free rotation equation would predict a value of 3.3. A doubly enolized structure should give a free rotation value of 2.21, but this might be expected to be lower and similar to the equatorial configuration for the trans-1,4 diol. All these values are still quite high. The doubly enolized structure probably would not exist to any appreciable extent because

there is no stabilizing influence such as resonance or hydrogen bonding. So that the moment is more probably due to an equilibrium mixture of the diketone and the singly enolized form. Measurement of the infra-red absorption spectrum should help considerably to elucidate the structure of this molecule.

If the structure of α-hydroxycyclohexanone is written as the name suggest, tautomers of the same kind as considered for the diols become possible. These are indicated in Fig. 13. In one case, the hydroxyl group is polar and in the other equatorial. Each of these has a mirror image, however, the optical considerations are not important here. For the equatorial form, intramolecular hydrogen bonding is possible and should be quite strong. If the hydrogen of the hydroxyl is rigidly held as near the carbonyl oxygen as possible, the angle between the carbonyl vector and the resultant vector of the C-H group is 145° as estimated from the model. The moment is calculated to be 1.7D. The resultant of three carbon-hydrogen bonds ($\sim$0.6) adds almost completely to the carbonyl vector and when this is considered the moment is raised to about 2.2D. Again, allowing a $\pm$ 10 range for error in the estimated angle, the range of the



(e) (p)

Fig. 13.

calculated moment is found to be 1.99 to 2.48. This is not consistent with the average experimental value of 2.8.

The polar form leads to a calculated moment of about the same range, provided the interaction is strong enough to keep the two vectors in a position of maximum opposition, since the estimated angle for this configuration is 148°. Interaction should be quite strong in this case due to the proximity of the groups and their large magnitudes. It should be greater than the value for the trans-1,2 diol (2.5). For both these configurations any libration of the hydroxyl about the C-O bond must give rise to a higher moment, since the positions calculated are those of maximum opposition of the two vectors. It is suggested that the stabilizing influence of the hydrogen bond should favor predominance of the equatorial configuration.

Free rotation in either instance would predict a moment of about 3.3. Again, it is not expected because of the large value of the mutual potential energy.

The fact that this compound is capable of enolization is shown by the infra-red spectrum of the solid which shows only a very weak carbonyl absorption peak. The enol form would be expected to have a moment someplace between that of catechol (2.58) and the cis-1,2 diol (2.33), since intra molecular hydrogen bonding is possible in this form. The estimated angle between the resultants of the hydroxyl groups is 60° if they are locked in the

catechol configuration. Some rotation about C-C bonds is possible and the maximum possible angle between the resultants is about 60°. This would lead to a weakening of the hydrogen bond however, so that the angle would be more probably in the range: $60^{\circ} \pm 10$, and the moment calculated to be 2.8 -3.0. The two hydrogens to be considered would have only a very small effect as in the case of the trans-1,2 diol. Free rotation leads to a moment of about 2.21, but is not likely to exist.

Dimerization in solution is quite possible in view of the molecular weight data. Again, if it results in symmetrical configurations, the moment should be lowered, while if the dimers were not symmetrical no effect could be estimated. In view of the linear relation obtained for the polarization vs. N_2 data, dimerization is probably small in extent.

The hydroxy-ketone should be stabilized in solution by the stronger intramolecular bond. The measured value of the moment is consistent with this picture if some libration of the hydroxyl occurs, although it doesn't rule out the possibility of quite large amounts of the enol form which should be favored by the low dielectric constant of the benzene solvent.

It has been mentioned that the melting points obtained for this compound and its action in benzene solution are peculiar. For example, the white solid which crystallized

from the vacuum distilled product melts over a range 112 to 130° C. This is an unusually large range even for an impure substance and might result from the keto-enol equilibrium and dimerization between several forms in the solid. The vacuum distilled liquid is probably the ketone form, while the white solid melting over a one degree range at 139° C. is probably dimerized. The solubility data is probably consistent with this picture. By relatively long refluxing the solid can be brought into benzene solution in quite large concentrations. Once in solution the substance resists recrystallization, coming out only after long periods of time, and then with quite large losses. This might indicate that the long refluxing time is necessary to break down enolic dimers and also allow a shift in the equilibrium toward the ketonic form to take place, allowing more of the enol form to go into solution. On the other hand the enolic form should be favored by the low dielectric constant but if the shift toward this form is slow at low temperatures the recrystallization would be accompanied by time delay and large losses. The infra-red absorption spectrum ties in these arguments nicely since it shows the presence of only very small amounts of carbonyl in the solid, but appreciable amounts in the liquid.

It may be concluded that this compound exists in

benzene solution as a mixutre of isomers with a tendency toward the enolic form. The dipole moment data does not allow a choice between polar and equatorial forms of the hydroxy ketone because they should give about the same moment, although the equatorial form is probably stabilized by hydrogen bonding.

The dipole moment of cerin (2.39) had been measured previously[29] and was considered to be inconsistent with the α-hydroxy ketone structure based on a calculated moment of 3.3D. The moment previously calculated is quite wrong however, and if cerin has the α-hydroxy ketone structure it should have about the same moment as calculated here for adipoin. In cerin, of course, the tautomers become stable isomers because the configuration of the ring and a mixture of isomers was probably measured. However, as has been shown, the isomers probably should have about the same moment and, if the compound doesn't enolize to any appreciable extent in benzene solution, separation and measurement of the isomers of cerin or a similar compound should enable confirmation or otherwise, of this analysis.

Finally, it may be stated that the dipole moments measured for these compounds are not capable of any simple or quantitative interpretation, even in conjunction with the infra-red and molecular weight data which has been presented. Suggestions are made below for work which might

further clarify the structures and configurations of these molecules.

It may be possible to obtain more definite information about the configurations of the disubstituted cyclohexanes by measuring the moments of the dichloro derivatives. Since only one cis-1,2 configuration is possible, the moment should enable a calculation of the angle between the C-Cl bonds. This angle could then be employed in a recalculation of the moment for the cis-1,2 diol. Measurement of the moment for the trans-1,2 dichloro compound might give a definite indication of the presence or absence of the 2p configuration, because the angle between the C-Cl bonds in the 2p case would be close to 180°. The presence of appreciable amounts of this configuration should result therefore in a considerable reduction of the measured moment from a value based on an approximate angle of 60°. (μ for the 2e configuration). If the 2p configuration were absent in this case the measured moment should be quite similar to that of the cis-1,2 dichloro derivative.

The moment for the cis-1,4 dichloro compound should enable a more exact estimation of the angle between C-Cl bonds, which again could be applied in other cases. The moment for the trans-1,4 dichloro compound should be very close to zero, regardless of the presence or absence of the 2e configuration, and hence should not enable any decision to be made about the polar configuration in this case.

The effect of association in solution might be determined by running all these substances in dioxane solution, where considerably greater concentrations are possible. For example, the formation of symmetrical dimers should result in a marked decrease in the slope of the polarization curves with higher concentrations.

Similar derivatives of decalin where the fused rings should result in rigid structures, with no possibility of chair $\rightleftarrows$ chair tautomerism, should produce isomers capable of separation. The moments of these should be more easily interpreted in terms of the existing theory and might help considerably in the interpretation of the structures of the compounds concerned here. This might be particularly interesting in the case of the α-hydroxy ketone compound. However, the isomerism of decalin itself would make the task of preparation, separation, and identification of isomers one of considerable complexity.

CONCLUSION

If the amount of boat tautomer of certain di-substituted derivatives of cyclohexane may be considered to be very small at low temperatures, then limited conclusions as to the form and/or configuration of these compounds in benzene solution can be drawn on the basis of general theory and the experimental work which has been presented.

Free rotation of hydroxyl groups about the C-O bond in any dihydroxy compound where the angle between the C-O bond is fixed would be expected to lead to a measured moment of 2.2, where small variations are possible due to the disposition of C-H bonds in the molecule. Such free rotation is not expected in any of the compounds concerned here because estimations of the mutual potential energies between groups show that in every case the value is high enough to result in group interaction. Furthermore, except in the case of the trans-1,2 diol, wherever the molecular models indicate the possibility of hydrogen bonding, such has been found to be the case. While the infra-red data do not always indicate which type of bonding exists, molecular weight determinations in camphor and linear polarization curves indicate that in general, association does not persist to any great extent in such high dilutions as are employed here. Moreover, comparison of calculated moments based on intramolecular bonding

give reasonable qualitative checks with the experimental moments.

Where keto-enol tautomerism is possible, the infrared absorption spectra shows that it does exist, although the dipole moment data does not allow a choice between forms nor an estimation of their distribution.

Considering each compound separately, the conclusions as to structure follow below.

Cis-1,2 dihydroxycyclohexane has only one configuration which contributes to the moment. In dilute solutions the hydrogen of one hydroxyl is bonded intramolecularly to the oxygen of the other, although the value of the dipole moment indicates the possibility of libration of the hydroxyls (or at least the unbonded hydroxyl) about the C-O bond, or some association into symmetrical dimers.

If the 2p configuration for trans-1,2 dihydroxycyclohexane should have a higher energy value than the 2e configuration by several kilocalories per mole, then the latter should be present in greater abundance. Molecular models of the 2e configuration show that hydrogen bonding similar to that occuring in the cis-1,2 diol can occur. Group interaction in the trans-1,2 diol can be quite strong and should lead to a configuration similar to the cis, and because the measured moments are almost identical, it is concluded that the configurations are similar.

No definite conclusion can be reached regarding the configuration of the hydroxyl groups in the cis-1,4 diol, although the high value of the moment indicates that their resultant vectors are generally supporting rather than otherwise.

The 2p configuration for trans-1,4 dihydroxycyclohexane is not eliminated from consideration by the dipole moment data, but if it can be ruled out on energy grounds, the measured moment of 1.81 D is qualitatively in agreement with restricted rotation theory for the 2e configuration.

Comparison of the measured moment for 1,2 cyclohexanedione with those calculated on the basis of all possible forms indicates that a singly enolized form with the hydroxyl hydrogen bound quite rigidly to the carbonyl oxygen probably exists to a large extent in benzene solution. Resonance of the resulting conjugated double bonds may contribute about 0.8D unit to the value of the total moment. The infrared absorption spectrum of the liquid is not in disagreement with this interpretation.

Keto-enol tautomerism is possible in the α-hydroxycyclohexane molecule. The solid form is shown by infra-red data to be the enol form, while in very dilute carbontetrachloride solution some ketonic form exists. The hydroxyls are indicated to be bonded internally in both cases. Hydrogen bonding should stabilize the equatorial configuration of the ketone form. The measured moment is most consistent with the enol form, but may correspond to an

equilibrium mixture of the two.

SUMMARY

The dipole moments of certain disubstituted derivatives of cyclohexane have been measured. Ranges of moments have been estimated for various forms and configurations from the Fisher-Herzfeld models of the molecules, or from the free rotation equation. The results are tabulated below.

TABLE II

Compound	Meas'd Moment	Config. and Calc'd Moment	
Cis-1,2 dihydroxy-cyclohexane.	2.32 ± 0.02D	bonded-	2.6-3.3
		free rotation	2.2
Trans-1,2 dihydroxy-cyclohexane	2.39 ± 0.03	2e, bonded-	2.7-3.2
		2e, free rotation-	2.2
		2p, free rotation-	2.1
Cis-1,4 dihydroxy-cyclohexane	~2.50	free rotation-----	2.2
		boat form-bonded--	3.4
Trans-1,4 dihydroxy-cyclohexane	1.80 ± 0.03	2e, restricted rotation------	< 2.2
		2p, restricted rotation------	< 2.1
		free rotation-----	2.2
1,2 Cyclohexane-dione	~2.75	dione----------	3.7-4.2
		singly enolized, bonded----------	2.8
		singly enolized, free rotation of hydroxyl---------	4.0
		doubly enolized, bonded----------	2.9-3.0
		doubly enolized, free rotation of both hydroxyls----	2.2
α-Hydroxycyclo-hexanone	~2.8	ketone, equatorial hydroxyl--	2.0-2.5
		ketone, polar hydroxyl--	"
		ketone, free rotation of hydroxyl	3.3
		enol, bonded------	2.8-3.0
		enol, free rotation	2.2

The infra-red absorption spectra of these compounds under certain conditions have been recorded in the hydroxyl and carbonyl ranges and the results interpreted in terms of configurations and molecular structure.

Molecular weights for all compounds except 1,2 cyclohexanedione have been measured by the Rast method. Strong association at the higher concentrations is generally indicated.

The measured value obtained previously for eerin (2.39) does not check the value obtained for α-hydroxycyclohexanone ($\sim$2.8). The value for eerin is consistent with the calculated value for the α-hydroxyketone structure assuming intramolecular hydrogen bonding.

A qualitative explanation for the moment of 1,4 cyclohexanedione is offered.

BIBLIOGRAPHY

1. Polar Molecules, P. Debye, Chemical Catalogue Co. Inc. (1929).
2. Dielectric Constant and Molecular Structure, C. P. Smyth, American Chemical Society Monograph. (1931).
3. Dipole Moments, R.J.W. Le Fevre, Methuen and Co. Ltd. (1938).
4. Dipole Moments, A General Discussion held by the Faraday Society, Sept. 1934. Published under separate cover as an appendix of the Transactions of the Faraday Society. (1934).
5. a) Weigle, Helv. Phys. Acta. 6, 681 (1933).
   b) Muller, Trans. Far. Soc. 30, 731 (1934).
   c) Goss, ibid. pg. 751 et sequo.
   d) Guggenheim, Nature 137, 450 (1936).
6. a) Onsager, J.A.C.S. 58, 1486 (1936).
   b) Kirkwood, J. Chem. Phys. 7, 911 (1939).
7. Williams, Z. Physikal Chem. 138A, 75 (1928).
8. Eucken and Meyer, Physik. Z. 30, 397 (1929).
9. de Bruyne, et. al., J.A.C.S. 55, 3936 (1933).
10. Fuchs and Wolf, "Hand-und Jahrbuch der Chemischen Physik." Vol. 6, I, Akad. Verlags. m.b.h., Leipzig (1935). p. 398.
11. Weissberger and Sangewald, Physik. Z. 30, 792 (1929).
12. Lander and Svirbely, J.A.C.S. 67, 322 (1945).

13. Nature of the Chemical Bond, L. Pauling, Cornell Univ. Press, 2nd Ed. (1940), pg. 305.

14. Kumler and Fohlen, J.A.C.S. 67, 437 (1945).

15. Meyer, Z. physik. Chem. 8B, 27 (1930).

16. a) Hassel, Tids. Kjemi Bergvesen 3, 32 (1943).

b) Hassel and Ottar, Arch. Math. Naturvidenskab 45, No. 10, 1 (1942) and earlier papers there cited.

17. Rasmussen, J. Chem. Phys. 11, 249 (1943).

18. Footnote (10), Pitzer, et. al., J.A.C.S. 69, 2488 (1947).

19. a) Aston, et. al., J.A.C.S. 63, 2029 (1941).

b) Aston, et. al., Ibid. 65, 341 (1943).

c) Pitzer, Sci. 101, 672 (1945) and earlier papers.

20. Kumler, J.A.C.S. 67, 1904 (1945).

21. a) The Theory of Resonance - G. Wheland, John Wiley & Sons, Inc., London (1944). pg. 50.

b) Ref. 13, Chapt. IX.

22. a) Ref. 13, pg. 290 et sequo.

b) Modern Theories of Organic Chemistry, H.B. Watson, Oxford Univ. Press (London), 1941. pg. 168.

23. Ref. 13, pg. 325.

24. Ref. 21a., pg. 208.

25. a) Ref. 21a., pg. 211.

b) Ref. 22b., pg. 163.

26. a) Ref. 21a., pg. 208.

b) Ref. 13, pg. 217 et sequo.

27. a) Smyth, J.A.C.S. 63, 57 (1941).

b) Smyth and Lewis, ibid. 62, 721 (1940), and earlier papers.

28. Molar Polarization in Dilute Solutions, R. Davis, M.S. Thesis, University of Maryland. (1940).

29. The Dipole Moments of Some Organic Compounds by the Solution Method, J. Lander, M.S. Thesis, University of Maryland. (1942).

30. The Systematic Identification of Organic Compounds. Shriner and Fuson, John Wiley and Sons, Inc. New York, 1935. pg. 67.

31. a) Molecular Spectra and Molecular Structure, Herzberg, Prentice-Hall. (1939).

b) Infrared Spectroscopy; Barnes, Gore, Liddel, and Williams, Reinhold Pub. Co. (1944).

c) L. Daasch, Anal. Chem. 19, 799 (1947), and references there quoted.

32. Rothestein, Ann. Chim. 14, 461 (1930).

33. Wilson and Read, J.C.S. 147, 1270 (1935).

34. Oldberg, et. al., J.A.C.S. 66, 1096 (1944).

35. Coops, et. al., Rec. trav. chim. 57, 303 (1938).

36. Perrine and White, J.A.C.S., 69, 1542 (1947).

37. Rauh, et. al., J. Org. Chem. 10, 199 (1945).

150294

38. Buehman and Richardson, J.A.C.S. 67, 397 (1945).

39. Kotz and Grethe, J. prakt. Chem. 2, 80, 488 (1909).

40. Charlton, et. al., J.C.S. 144, 30 (1932).

41. Bergmann and Gierth, Ann. 448, 48 (1936).

42. Ref. 13, pg. 167.

43. Le Fevre and Le Fevre, J.C.S. 147, 1696 (1935).