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DIELECTRIC RELAXATION IN LIQUIDS

II. ISOMERIC PENTANEDIOLS[1]

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ABSTRACT

For five pentanediols the infrared spectra, the dipole moments, and the static dielectric constants show an increasing degree of internal hydrogen bonding with increasing proximity of the OH groups. The dielectric dispersion loci at low temperatures are skewed arcs over most of the dispersion range. Values of the parameter β decrease from ca. 1 to 0.55 in the series 1,5-, 1,4-, 1,2-, 2,4-, and 2,3-pentanediol, which is also the order of increasing relaxation time τ_0 at low temperatures. Increased τ_0 is associated with increased irregularity of intermolecular hydrogen bonding, an effect which supports the view that relaxation proceeds by a co-operative mechanism which is facilitated by regularity in the liquid structure. At temperatures of "structural relaxation", values of log τ_0 are linear in $(T-T_\infty)^{-1}$; the proportionality constants, but not the T_∞'s, are the same for all five diols.

The experimental behavior at relatively high frequencies departs from both the skewed-arc and Glarum equations, although less from the latter. These departures are compared with the high frequency dispersion regions in *n*-propanol.

In a previous paper (1) the ability of the skewed-arc expression to represent the results of dielectric relaxation measurements of liquids has been discussed. Most monohydroxyl alcohols exhibit a principal dispersion region which is, within the experimental errors, of the classical Debye type ($\beta = 1$ in the skewed-arc representation). This is in contrast to the relaxation behavior of such polyhydroxyl alcohols as have been studied, for which values of β considerably smaller than unity must be invoked. It is natural to attempt to relate this qualitative difference in the relaxation behavior to the absence in the polyhydroxyl liquids of the same degree of regularity in *inter*molecular hydrogen bonding that exists in the simple alcohols. In order to examine the role played by *intra*molecular hydrogen bonding and steric factors in the extent and regularity of the hydrogen bonding between polyhydroxyl molecules, we have studied the relaxation behavior of five isomeric pentanediols. With one exception, the pentanediols may be cooled sufficiently to bring the dispersion regions within the frequency range required for bridge measurements.

Information about the extent of *intra*molecular hydrogen bonding was provided by an examination of the hydroxyl-group stretching bands in the infrared spectra of dilute solutions of the pentanediols in carbon tetrachloride and by measurement of the dipole moments of the pentanediols in dioxane solution.

EXPERIMENTAL METHODS

1,2-Pentanediol was prepared by bromohydrination of pentene-1 with N-bromosuccinimide, conversion to the epoxide (b.p. 76–78°), and hydrolysis to the diol with Dowex 50 resin.

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The infrared spectrum of a commercial sample of 2,3-pentanediol showed a strong spurious band at 1733 cm^{-1}, which disappeared after saponification with sodium hydroxide. An authentic sample of the 2,3-diol was prepared from pentene-2 (which gas-chromatographic analysis showed to consist of roughly equal proportions of the trans and cis forms) by performic acid oxidation and hydrolysis. The product (B) consisted of approximately equal amounts of *threo* and *erythro* isomers. Its infrared spectrum was almost identical with that of the saponified commercial product (A).

The other pentanediols were commercial products.

All the pentanediols were fractionated in a Todd still. The boiling ranges and refractive indices are given in Table I.

TABLE I

Pentanediol		Boiling range (p, mm)		n_D
1,2		83–84°	(3)	1.4387 (23°)
2,3	A	70–71°	(3.5)	1.4404 (20°)
	B			1.4405 (20°)
1,4		221–222°	(748)	
		103°	(4)	1.4451 (25°)
2,4	A	199–200°	(757)	1.4329 (25°)
	B	83°	(5)	1.4329 (25°)
1,5		239°	(759)	
		121°	(6)	1.4495 (25°)

1,4-Dioxane was refluxed for several hours over calcium hydride and distilled.

The dielectric constant and loss measurements at frequencies up to 500 kc/sec and the temperature measurement and control were essentially as outlined previously (2). Less accurate measurements at higher frequencies were made in the case of 1,5-pentanediol with (a) a Model 260A Boonton Q-Meter and a cell consisting of two parallel-plate platinum electrodes mounted in a glass vessel, and (b) a Model 250A Boonton RX-Meter and a cell constructed of two coaxial stainless steel electrodes with Teflon insulation.

Measurements of the dipole moments of the pentanediols in dioxane were made by the method previously described (3). Infrared spectra of the carbon tetrachloride solutions were obtained with a Perkin–Elmer Model 112 infrared spectrometer equipped with sodium chloride and calcium fluoride optics.

RESULTS AND DISCUSSION

Intramolecular Hydrogen Bonding

(a) OH Stretching Vibrations

The fundamental OH stretching vibration region of the infrared spectra of solutions of the pentanediols in carbon tetrachloride is shown in Fig. 1. Following Kuhn (4) and others, one may associate the presence in this region of two bands of concentration-independent relative intensity at low concentrations (less than 0.1% or 0.015 molar) with the presence of both free and *intra*molecularly hydrogen-bonded OH groups. The frequencies of free OH groups and of those taking part in *intra*molecular and, at higher concentrations, in *inter*molecular hydrogen bonds are given in Table II. The latter are somewhat concentration dependent; the values given are for concentrations in the range 0.2 to 0.6%.

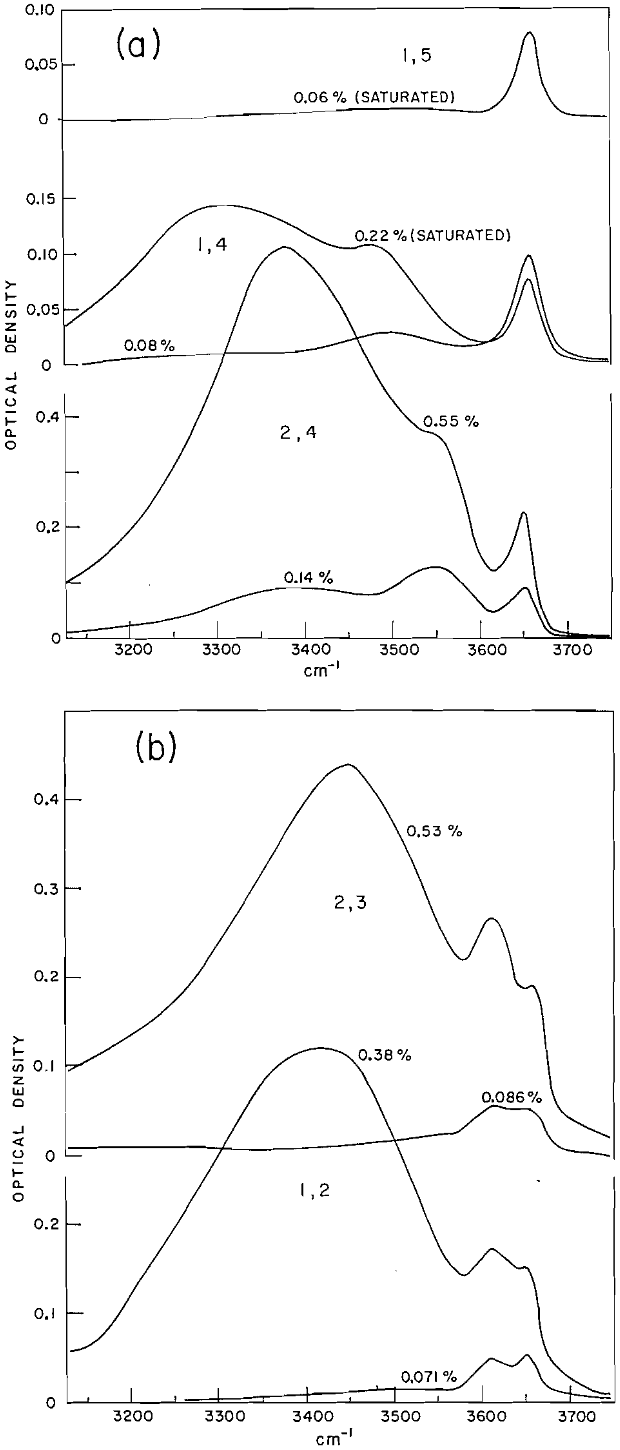

FIG. 1(*a*) and (*b*). OH stretching vibration region of the infrared spectra of the pentanediols in CCl_4.

TABLE II

OH stretching vibration bands of pentanediols in CCl_4

Diol	Frequencies (cm^{-1})			Approx. fraction of free OH groups*
	Free OH	*Intra*bonded OH	*Inter*bonded OH	
1,5	3639			1
1,4	3638	3464	3292	0.85
2,4	3639	3538	3369	0.65
1,2	3646	3604	3407	0.55
2,3	3646	3600	3437	0.50

*At low concentrations.

Like 1,6-hexanediol (4), 1,5-pentanediol shows no evidence of internal hydrogen bonding. A small degree of internal bonding takes place in 1,4-pentanediol, as shown by the presence of a weak band whose frequency shift from the free OH band ($\Delta\bar{\nu} = 174$ cm^{-1}) is similar to that shown by 1,4-butanediol (156 cm^{-1} (4); 170 cm^{-1} (5)). More extensive *intra*molecular hydrogen bonding takes place in 2,4-pentanediol; the frequency difference (101 cm^{-1}) is somewhat larger than for 1,3-propanediol (78 cm^{-1} (4)) or 1,3-butanediol (80 cm^{-1} (5)). The bands arising from internally bonded OH groups in the vicinal pentanediols are about as strong as those arising from the free OH groups. The frequency shifts are similar to those found in other *vic*-diols.

In view of the well-known correlation between $\Delta\bar{\nu}$ and hydrogen bond "strength", it is a fair inference that, although the number of molecules which are *intra*molecularly bonded *increases*, the strength of the bonds *decreases* in the sequence 1,4- to *vic*-diol. The frequencies associated with the broad bands due to *inter*molecular hydrogen bonding (Table II, column 4) likewise suggest that the bonds between molecules become somewhat weaker in the same sequence.

The estimates of the fraction of free OH groups given in the last column of Table II are based on the approximation that the extinction coefficient is the same for the free OH stretching band in all five pentanediols.

With increasing concentration the *intra*molecular hydrogen-bonding bands become obscured by the strong *inter*molecular ones. Solutions of the pentanediols in dioxane all show strong bands with peaks near 3480 cm^{-1} arising from association with the solvent.

(b) Dipole Moments

Because of the limited solubility of some of the pentanediols in CCl_4 and other inert solvents and the tendency of diol molecules in such solvents to associate even at low concentrations, the dipole moments were measured for solutions in dioxane. The results, based on measurements of 6 to 8 solutions in the weight fraction range between 0.005 and 0.08, are given in Table III. The dipole moments of some other diols are included for comparison.

Two primary solvent effects are to be expected: an enhanced moment for each OH group which is hydrogen bonded to the solvent, and a change (usually a reduction) in the molecular moment arising from the effect on the extent of *intra*molecular hydrogen bonding of the competition provided by bonding to dioxane. To get an indication of the magnitude of the first effect, the dipole moment of water in dioxane was measured with the same technique as was employed with the pentanediols. The resulting value of 1.91 debyes, like several earlier values (10), was only slightly greater than the vapor value of 1.85 debyes (11). The second effect is more difficult to gauge. The agreement

TABLE III
Dipole moments of diols (debyes) in dioxane

Diol	No. of C atoms between OH groups 2	3	4	>4	Reference
1,5-Pentane				2.37±0.03	This work
1,4-Pentane			2.51±0.03		
2,4-Pentane		2.71±0.03			
1,2-Pentane	2.24±0.02				
2,3-Pentane	2.13+0.05				
1,2-Ethane	2.27 (20°)				7
1,3-Propane		2.46 (20°)			7
1,2-Propane	2.25				8
1,4-Butane			2.47 (20°)		7
1,5-Pentane				2.39 (20°)	7
1,6-Hexane				2.48	8
2-Methyl-2,4-pentane		2.9			9
1,9-Nonane				2.45 (20°)	7
1,10-Decane				2.52	8

NOTE: Temperatures 25°, unless otherwise stated.

between the moment of 1,2-ethanediol in dioxane (2.29 debyes) and in the vapor (2.25 debyes) (12*a*) suggests that it is not great for the vicinal diols. The effect may well be greater for diols less completely internally hydrogen bonded than the vicinal ones.

The dipole moment of 1,5-pentanediol is very nearly $\sqrt{2}$ times as large as that typical of monohydroxyl alcohols (1.66 debyes). This suggests that there is, on the average, no net correlation between the directions of the two COH dipoles and that no appreciable internal hydrogen bonding exists. With increasing proximity of the OH groups in the pentanediols the moments increase, until, for the vicinal diols, they fall to their lowest values. As shown by the other moments in Table III, this trend is general for diols.

Calculation of the resultant moment of the internally hydrogen-bonded molecules is in general prevented by a lack of knowledge of the geometry of the rings formed. The presence of a linear hydrogen bond between two OH groups generally results in a higher moment than that to be expected for unbonded configurations, but the constraints imposed by the comparably inflexible valence-bond angles are likely to lead to considerable bending of the O—H- -O bond in small rings. A certain amount of bending increases the moment beyond its value for a linear bond and values of about 3 debyes are to be expected for angles of the order of 135°. This is consistent with the observed moments of 1,4- and 2,4-pentanediol if the extent of *intra*molecular hydrogen bonding is not greatly less in dioxane than in carbon tetrachloride (compare Table II).

For much larger angles of bend of the hydrogen bond a fall in the resultant moment is predicted. This is the case for the *vic*-diols, which, as considered in more detail in the Appendix, appear to consist substantially of internally hydrogen-bonded forms in which the two CO bonds are not far from gauche in their relative orientation about the connecting C—C bond. Part, at least, of the reduction in "strength" of the hydrogen bonds with decreasing separation of the OH groups in the molecule may be attributed to their increasing departure from linearity.

There is some evidence that the extent of internal hydrogen bonding increases with alkyl-group substitution on the carbon atoms bearing the OH groups, as is to be expected from steric considerations. Thus there is a pronounced increase of moment in the series 1,3-propanediol, 2,4-pentanediol, 2-methyl-2,4-pentanediol (Table III). It appears possible for a highly substituted 1,5-pentanediol to be appreciably internally hydrogen bonded (13).

Static Dielectric Constants

Values of ϵ_0 for the pentanediols in the liquid state are plotted versus $1/T$ in Fig. 2.

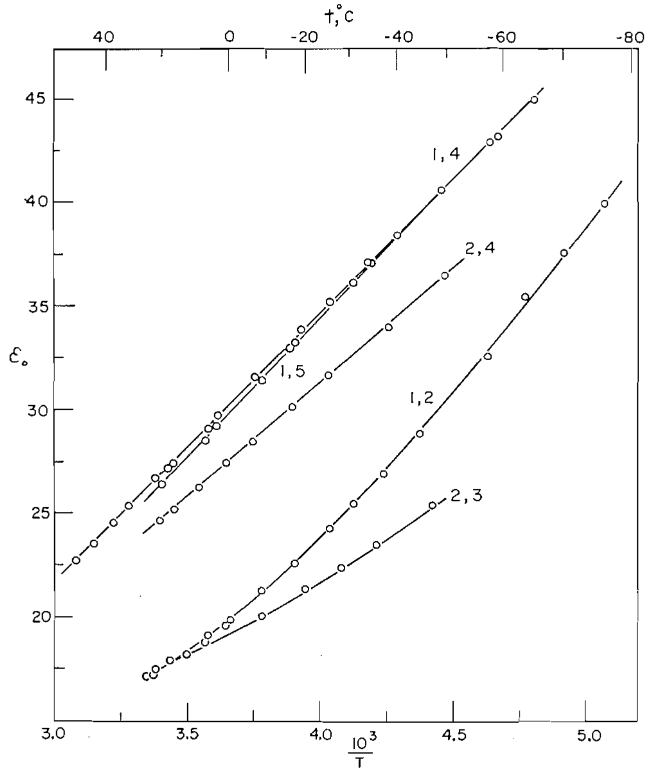

FIG. 2. Temperature dependence of the static dielectric constants of liquid pentanediols.

For three of the diols these values may be represented by a linear function of $1/T$ over the experimental temperature range. The static dielectric constants of the vicinal diols increase more rapidly at low temperatures and are given by

$$\epsilon_0 = a+b/(T-T_c)$$

for which the empirical constants have the values listed in Table IV.*

TABLE IV

Parameters for temperature dependence of ϵ_0

Pentanediol	Temp. range	a	$b\times10^{-3}$	T_c	Av. deviation (%)
1,5	−35 to 25°	−19.54	13.50	0	±0.2
1,4	−65 to 52°	-16.88_5	12.89	0	0.3
2,4	−50 to 25°	−12.51	10.96	0	0.2
1,2	−70 to 25°	− 1.13	3.244	120	0.6
2,3	−50 to 25°	+ 4.04	2.487	110	0.2

**Other reported dielectric constants of 1,5-pentanediol (with the values computed from the equation in parentheses) are: −20°, 33.5 (33.8); 0°, 30.0 (29.9); 25°, 26.3 (25.7) (14); and 20°, 26.2 (26.5) (7).*

The dielectric constants of 1,5- and 1,4-pentanediol suggest that the individual OH groups have almost as much freedom to associate with other molecules as has the single OH group in simple alcohols. Thus, each of these diols at 20° has a dielectric constant of which the part arising from the orientation of dipoles (ca. 27–3) is twice that of *n*-pentanol (15–3), a liquid with about half as many OH groups per unit volume. In the case of 1,4-pentanediol, it is likely that a reduced extent of *inter*molecular association is offset by the increased average moment resulting from some *intra*molecular hydrogen bonding. In 2,4-pentanediol the former effect predominates.

The lower dielectric constants of the vicinal diols reflect a high degree of internal hydrogen bonding. Formal calculation of the Kirkwood correlation factors from the observed dielectric constants give values somewhat greater than 2 at room temperature and progressively increasing values at lower temperatures. Although such values cannot be directly compared with those of simple alcohols, for which similar values are obtained (15), they are sufficiently high to suggest the presence of extensive hydrogen-bonded chains. The structure is complicated by the possibility of cross-linking of the chains of hydrogen bonds at some molecules which are not internally hydrogen bonded, a process which should result in higher dielectric constants and which may be responsible for the high values found, particularly for the 1,2-diol, at low temperatures.

Most of the pentanediols remained liquid at temperatures lower than those at which the dielectric dispersion – absorption effects (next section) occurred at audio frequencies.* However, the 1,5-diol froze rapidly when cooled below −30°, even when as much as 5% water was added. Examination of its dielectric constant in the solid revealed no anomalies at temperatures down to −190°. The dielectric constant remained almost invariant at about 2.7 as the sample was heated from this temperature until it started to rise a few degrees below the melting point (−16°).

Dielectric Relaxation

A typical absorption–dispersion locus for each pentanediol is illustrated in Fig. 3.

Since 1,5-pentanediol could not be sufficiently supercooled to bring the dispersion effects into the frequency range of bridge measurements, Q-meter and RX-meter measurements were made at higher frequencies. As shown in the plot of Fig. 3 for the 1,5-diol at −30°, the Q-meter results show considerable scatter, a large part of which may be attributed to changes in lead capacitance brought about by connecting and disconnecting the low potential lead to the cell. In the hope that these effects would show a random scatter, a large number of measurements were made. The RX-meter measurements, for which the height of the liquid between the coaxial electrodes was varied to eliminate fixed capacitance, were more reproducible, but were complicated by inductance effects at high frequencies. The data were not sufficiently accurate to distinguish between a semicircular locus with additional high-frequency dispersion regions, as in the simple alcohols, and a slightly skewed locus (with β of the order of 0.9). From measurements over a very extensive frequency range, Mme. Moriamez-Boullet reported (14) the presence of at least two distinct dispersion regions, of which the principal (low-frequency) one was semicircular. In view of the evidence already given for the ability of each OH group in 1,5-pentanediol to freely associate with other molecules, relaxation behavior similar to that of the simple monohydroxyl alcohols might well be expected.

For the other four pentanediols studied, as is evident from the extent of the agreement between the experimental and calculated points (Fig. 3), the skewed-arc locus provides

One sample of 2,4-diol slowly froze after being maintained for several days at −45°.

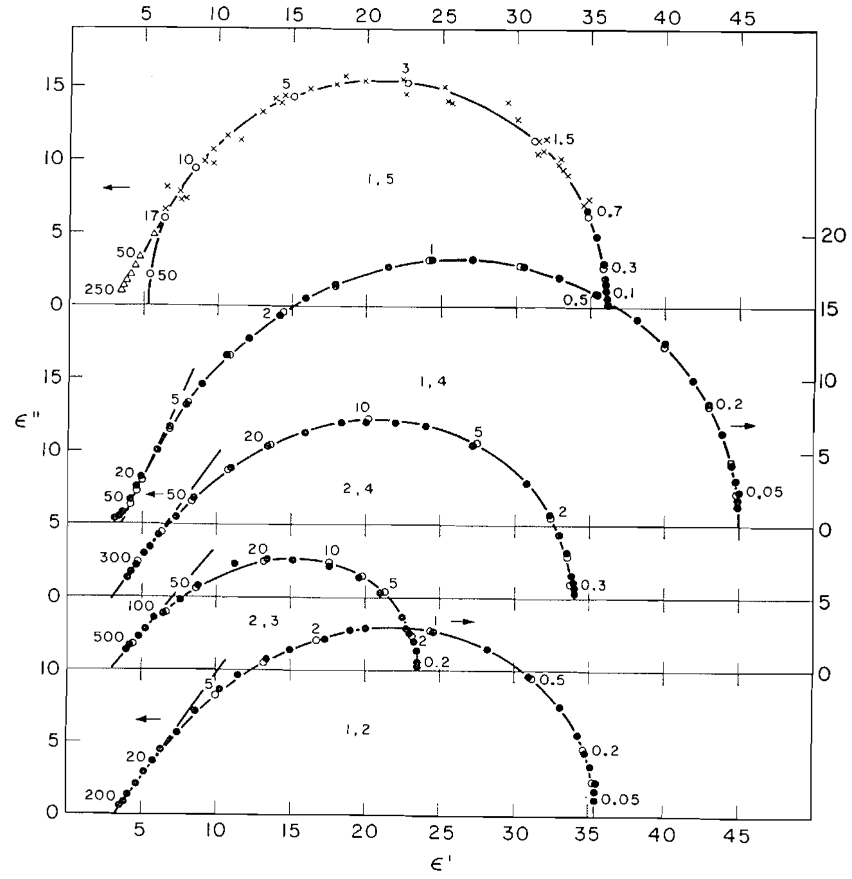

FIG. 3. Complex dielectric constant loci of the pentanediols: ● bridge, × Q-meter, and △ RX-meter measurements; ○ values calculated from the parameters starred in Table V. Numbers on loci are frequencies in Mc/sec for 1,5-pentanediol, in kc/sec for the others.

an accurate description of the dispersion effects (except at relatively high frequencies). Values of β tend to become smaller with the approach of the two OH groups to one another.

Values of the parameters used in the calculation of the absorption–dispersion loci of Fig. 3 are given in Table V, together with the corresponding skewed-arc parameters at several other temperatures.

Relaxation Times

The variation of the relaxation times with temperature is shown in Fig. 4.

The τ_0 values for 1,5-pentanediol are based on three types of measurement, as indicated in the caption of the figure. Debye behavior has been assumed. Bridge measurements of ϵ'' were made at frequencies on the low-frequency side of the absorption region and the relaxation times were calculated from the slope of a plot of ϵ'' vs. frequency, according to

$$[1] \qquad \epsilon'' = 2\pi(\epsilon_0 - \epsilon_1)\beta\tau_0 f,$$

with, in this case, $\beta = 1$. The experimental ϵ'' values were corrected for the contributions

TABLE V

Typical dispersion parameters of the pentanediols

Pentanediol	T (°K)	ϵ_0	ϵ_1	β	τ_0 (sec)
1,5	293.5	26.49		(1)	1.53×10^{-9}
	257.2	33.08		(1)	1.33×10^{-8}
	243.2	36.10*	(5.25)†	(1)	4.60×10^{-8}*
1,4	317.8	23.55			
	295.7	26.74			
	266.5	31.59	(3.48)	(0.77)	3.44×10^{-8}
	233.1	38.53	3.50	0.75	1.87×10^{-6}
	207.8	44.95*	3.64*	0.760*	2.23×10^{-4}*
	193.2	49.7	3.71	0.71	2.0×10^{-2}
1,2	296.8	17.31			
	264.5	21.32	(3.20)	(0.65)	1.70×10^{-8}
	228.5	28.86	3.25	0.64	2.27×10^{-6}
	209.5	35.51*	3.26*	0.629*	1.84×10^{-4}*
	197.2	40.0	3.30	0.63_5	1.07×10^{-2}
2,4	294.5	24.69			
	267.1	28.50	(3.00)	(0.68)	3.9×10^{-8}
	234.9	33.86*	3.08*	0.620*	2.49×10^{-5}*
	223.7	36.5	3.17	0.59	7.58×10^{-4}
2,3	296.9	17.37	(2.61)	(0.60)	4.0×10^{-9}
	253.8	21.39	(2.81)	(0.56)	5.0×10^{-7}
	237.8	23.52*	2.83*	0.545*	1.77×10^{-5}*

*Denotes values used for the computed loci of Fig. 3.
†Values in parentheses are values assumed in order to calculate τ_0.

from d-c. conductance. Relaxation times by this method were considered less accurate than those derived from the frequencies of maximum loss given by the Q-meter and RX-meter measurements, and were assigned half the weight in fitting the temperature dependence of the relaxation times by least squares.

Values of τ_0 of the other pentanediols were obtained from bridge measurements alone. Relaxation times of less than 3×10^{-7} second made use of values of β estimated by extrapolation from lower temperatures, and at the high end of the temperature range equation [1] was employed.

From Fig. 4 it is apparent that, with the possible exception of the 1,5-diol, the relaxation times do not follow an equation of the form

$$\log_{10}\tau_0 = A'+B'/T. \tag{2}$$

They may, however, be represented over most of the temperature range of the measurements by

$$\log_{10}\tau_0 = A+B/(T-T_\infty), \tag{3}$$

as in the case of a number of other alcohols (15, 16, 17) and alkyl halides (18). It was found that the values of B, as determined by least-squares best fit of equation [3] to the data, were very nearly the same for the four pentanediols. In fact, for the values of A and T_∞ of Table VI, a plot of the product $(\log_{10}\tau_0-A)(T-T_\infty) = B$ yields values of B which are, within experimental error, equal to 985 over most of the temperature range. (See inset of Fig. 5.) Moreover, the less accurate and extensive data for 1,5-pentanediol can be represented by the same B, with A and T_∞ given in Table VI, slightly better (average deviation between experimental and computed relaxation times of 6.7%) than by equation [2] with A' and B' evaluated by least squares (average deviation 7.7%). It is to be noted (Fig. 5) that, although the data for the 1,5- and 1,4-diols show no departures from equation [3] with $B = 985$ up to room temperature, those for the

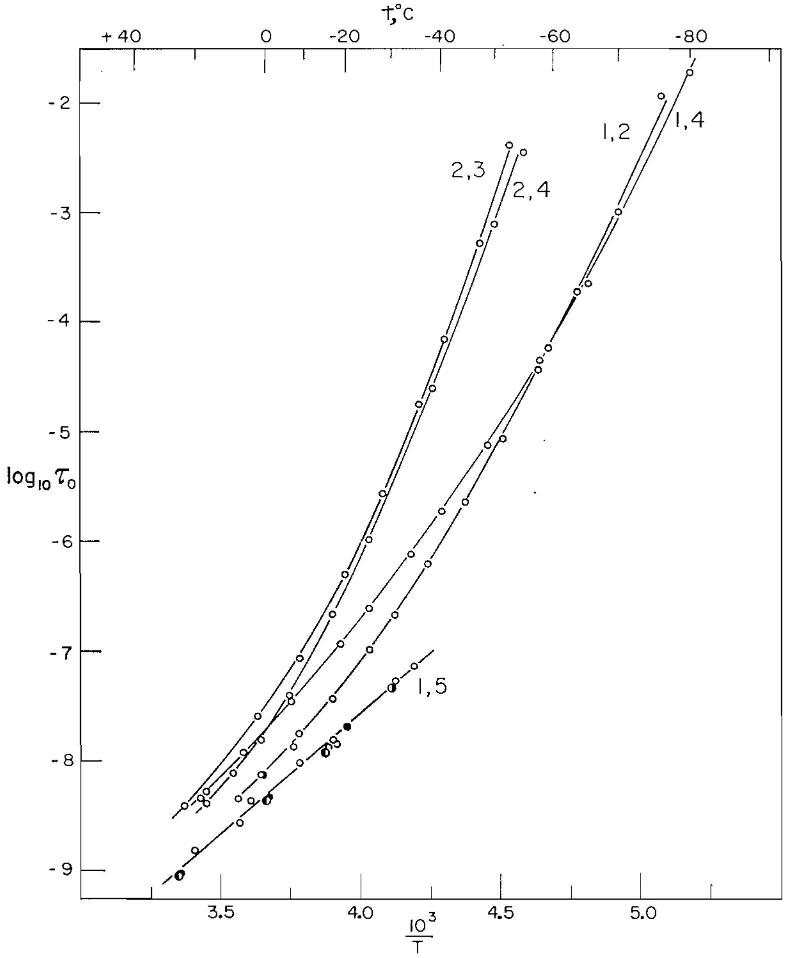

FIG. 4. Arrhenius plots of the relaxation times of the pentanediols: ○ bridge, ◑ Q-meter, ◐ RX-meter measurements; ● from reference 14.

TABLE VI

Parameters of equation [3] for the pentanediols. $B = 985$

Diol	T_∞ (°K)	A	Temp. range (°C)	No. of points	Av. deviation (%)
1,5	92	−13.814	−35, +25	13	6.7
1,4	111	−13.804	−80, +20	13	2.4
2,4	143	−15.327	−55, +3*	7	3.5
1,2	118.5	−14.595	−75, −15*	10	2.5
2,3	144	−15.279	−73, −10*	7	4.0

*Departures from equation [3] occur at higher temperatures.

2,4- and particularly for the vicinal diols show consistent departures at the high temperature end (Fig. 4) in the sense of greater relaxation times than predicted by equation [3]. It may be significant that the greater the degree of *inter*molecular hydrogen bonding the higher the upper temperature limit of validity of the equation.

Published values of the constant B of equation [3] as it has been applied to other

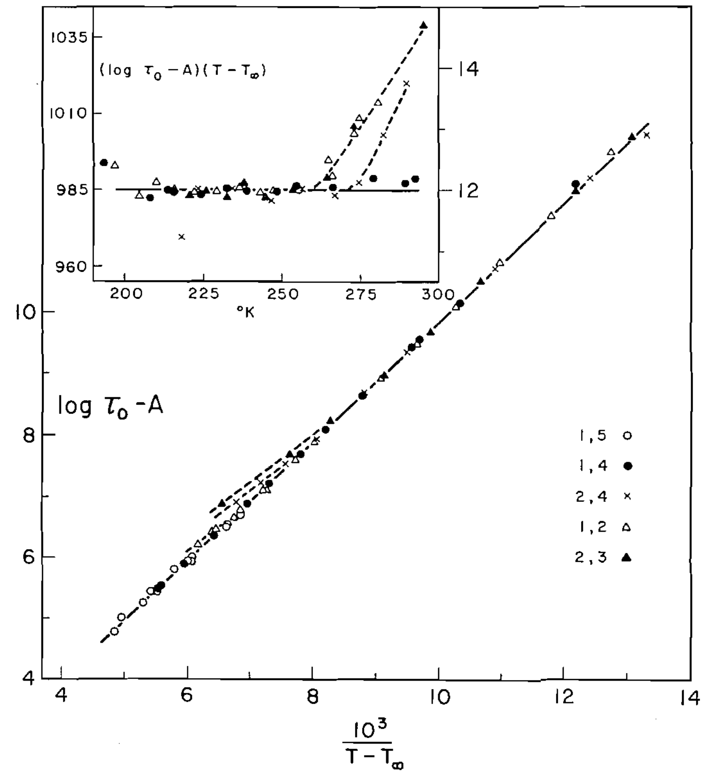

FIG. 5. Dependence of log $\tau_0 - A$ on $1/(T - T_\infty)$ for the values of A and T_∞ listed in Table VI. Inset: temperature variation of $(\log \tau_0 - A)(T - T_\infty)$.

hydroxyl-containing liquids (16) are considerably smaller than 985, but this value is approached in the case of highly associated glycerol, for which $B = 957$ has been reported. It is now believed that the available data indicate a common value of B (≈ 985) for liquids at low temperatures. The lower values of B that have been reported probably arise from the inclusion in the data treated of relaxation times obtained at temperatures beyond the range of the common low-temperature behavior.

The case of *n*-propanol may be particularly mentioned. By a combination of bridge and transient techniques, relaxation times between 10^{-8} and 10^{3} seconds have been measured for this liquid. Published (19) parameters for equation [3] (including $B = 477$) describe the experimental relaxation times between 210 and 130° K (that is, up to ca. 10^{-4} second) but not those obtained at lower temperatures. With $B = 985$, together with $A = -14.354$ and $T_\infty = 44°$, on the other hand, the relaxation times in the range 10^{-5} to 10^{3} seconds may be accurately described. Deviations similar to those shown by the vicinal pentanediols become evident at temperatures above 150° K.

The similarity between the temperature dependence of dielectric relaxation times, viscosities, and d-c. conductivities at low temperatures is a matter of common observation, as is also their tendency to depart from such common behavior as the temperature is raised (16, 20, 2). In the case of the pentanediols the conductivities (Fig. 6) vary with temperature very much as do the relaxation times. It was not possible to follow the temperature dependence of conductivity with the same accuracy as for the relaxation

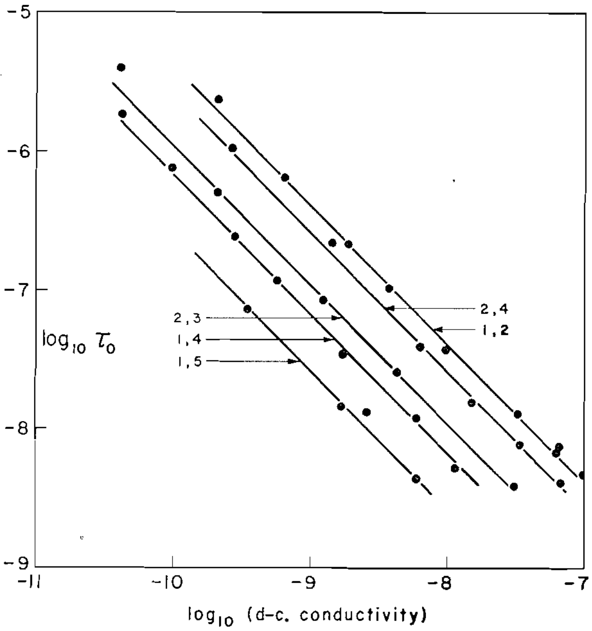

FIG. 6. Plot showing the proportionality between the relaxation times and d-c. conductivities of the pentanediols.

times, since it changed not only from sample to sample, but also slowly with time after the cell had been filled.

The evidence suggests that physical rate processes of many liquids at low temperatures may be represented by equation [3] with a common value of B and a value of T_∞ characteristic of the liquid. For a given liquid only A changes with the rate process being measured. It is planned to examine elsewhere the question of the general validity of equation [3] as a characteristic feature of what may be called "structural relaxation" of liquids.

It is apparent that the present representation of structural relaxation has much in common with Ferry's method of expressing mechanical relaxation times of polymers in terms of their values at an arbitrary standard temperature (21). When put into the form of equation [3], his expression corresponds to a value of B some 10% lower than the one employed here.

Dispersion at High Frequencies

If the principal dispersion region in 1,5-pentanediol is taken to be of the simple Debye type, our data (cf. Fig. 3) show the presence of an additional dispersion region at relatively high frequencies. They are consistent with the results of Mme Moriamez-Boullet (14), who reports at $-20°$ a second dispersion region which is a circular arc defined by $\epsilon_1 = 5.4 \pm 0.2$, $\epsilon_2 = 2.9 \pm 0.2$, $\alpha = 0.11 \pm 0.02$, and a most probable relaxation time some 80 times smaller than the single relaxation time of the primary dispersion.

The other pentanediols, like other liquids exhibiting skewed-arc behavior (1), show additional dispersion–absorption effects at frequencies of the order of several hundred times as great as that which corresponds to τ_0. The nature of these departures from the limiting straight line predicted by the skewed-arc locus for high frequencies is illustrated in the ϵ'' vs. ϵ' plots of Fig. 7.

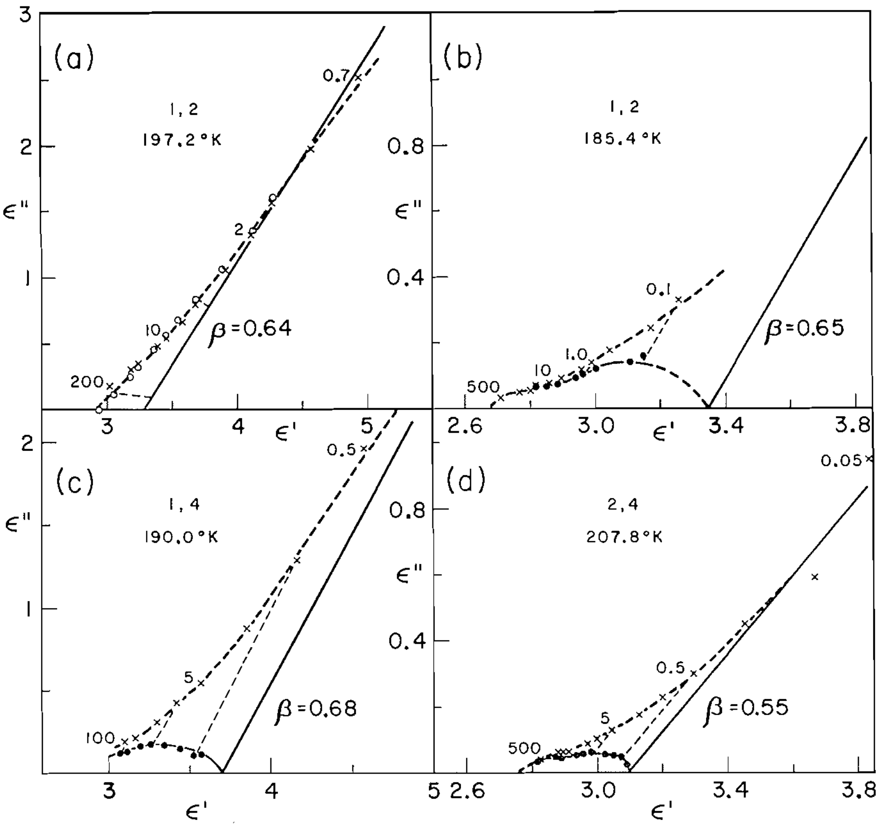

FIG. 7. Departures at relatively high frequencies of pentanediols from skewed-arc behavior: × experimental points; ○ Glarum locus with $a_0 = 4$, $\tau_0 = 1.07\times10^{-2}$ sec; ● points obtained by subtraction from experimental points of skewed-arc loci with values of τ_0 of (*b*) 6.4, (*c*) 3.2×10^{-2}, (*d*) 1.6 sec.

In order to explore the possibility that these effects may arise from the superposition of the skewed-arc locus and some physically distinct relaxation mechanism occurring at relatively high frequencies, attempts have been made to subtract the contribution of the skewed-arc locus to the experimental results. This procedure is more approximate than was the case of, for example, *n*-propanol (16, 19) since the skewed-arc locus makes much larger contributions at high frequencies and requires one more parameter (β) for its representation than does the Debye semicircle. As shown in Fig. 6(*b*, *c*, *d*), it is possible to obtain, by this somewhat laborious procedure, a residual absorption which resembles two overlapping circular arcs, much like those reported for *n*-propanol. It should be pointed out that the only justification for this arbitrary method of treating the data lies in the similarity between the resulting residues and those obtained for simple alcohols. Moreover, slight changes in the skewed-arc parameters lead to either overlap of the residual locus with the high-frequency end of the skewed-arc locus or to negative residual absorption at some frequencies. To get residues of the type shown, it is necessary to assign values of τ_0 which are somewhat larger than predicted by the linear relationship (see above) between $\log \tau_0$ and $1/(T-T_\infty)$.

The Glarum model (22) of relaxation leads to an expression which differs appreciably from that of the skewed arc only at high frequencies. The Glarum equation is capable of representing the experimental results for the pentanediols to considerably higher frequencies than is the skewed-arc equation. This is illustrated for 1,2-pentanediol in Fig. 6(*a*). At still higher frequencies (or lower temperatures, Fig. 6(*b*)) the experimental absorption exceeds that of the Glarum locus which, in the limit of high frequencies, becomes a straight line which approaches the ϵ' axis at 45°. It is interesting to note that subtraction of the Glarum locus from the experimental one now leaves a single arc, which approximately corresponds to the higher-frequency arc of the pair that resulted from subtraction of the skewed arc.

In all events, there is an extremely broad loss spectrum at very high frequencies, which, if not completely accounted for by the diffusion-controlled relaxation process of Glarum, does appear to arise from a mechanism different from the co-operative orientation of locally ordered molecules responsible (1) for the behavior at lower frequencies.

The values of ϵ_1, whether determined by the high-frequency intercept of the skewed-arc or of the Glarum locus, decrease in the order 1,5-, 1,4-, 1,2-, 2,4-, and 2,3-pentanediol (see Table VII). This is roughly the order in which the relative number of weak and broken hydrogen bonds increases, so that the magnitude of ϵ_1 cannot be directly related to the orientation of free or weakly hydrogen-bonded OH groups. At very high frequencies the absorption approaches zero at values of ϵ' of the order of 2.6 to 2.7, somewhat in excess of likely values of the square of the refractive indices, but similar to the dielectric constant observed for solid 1,5-pentanediol at comparable temperatures.

TABLE VII

Variation of ϵ_1 and β with temperature (based on data between ca. −80 and −20° C)

Pentanediol	Skewed arc				Glarum, $\epsilon_1(-60°\text{ C})$
	$\epsilon_1(-60°\text{ C})$	$d\epsilon_1/d(10^3/T)$	$\beta(-60°\text{ C})$	$d\beta/d(10^3/T)$	
1,5	(5.2_5) (−30° C)		(1)		(5.2_5) (−30° C)
1,4	3.61	+0.020	0.73	−0.10	3.2_1
1,2	3.29	0.014	0.64	−0.03	2.9_8
2,4	3.17	0.012	0.55_5	−0.15	2.8_4
2,3	2.92	0.004	0.52_5	−0.03	2.6_9

Temperature Dependence of the Dispersion

As may be seen from Table VII, the value of β in the skewed-arc representation tends to decrease with decreasing temperature. Although the values of $d\beta/d(1/T)$ tabulated are only approximate, they seem to show no systematic dependence on β. Moreover, the variation of β with temperature cannot be related to a model which assumes that the distribution of relaxation times arises from the presence of a temperature-independent distribution of barrier heights to rotation, such as may approximately account for the broadening of the dispersion exhibited by some solids with decreasing temperature (23).

In the Glarum representation (22), the shape of the dispersion–absorption locus depends on a_0 alone. As the temperature gets lower, the value of a_0 decreases, that is, the contribution of the diffusion-controlled relaxation becomes greater. Since $a_0 = l^2/D\tau_0$, this may be naively accounted for if the average defect diffusion relaxation time (l^2/D) increases less with decreasing temperature than does relaxation time for co-operative molecular rotation (τ_0) and the values of the two "relaxation times" therefore approach one another.

No extensive results are yet available for liquids at temperatures corresponding to β

less than 0.5 ($a_0 < 1$) where the Glarum theory makes the interesting prediction of behavior intermediate between that of the skewed arc and circular arc.

CONCLUSIONS

It may be concluded that departures of this type of asymmetric locus from the Debye semicircle arise from the presence of disordered regions in the liquid.

The increased asymmetry of the loss spectrum which results from increased interference with *inter*molecular hydrogen bonding as the OH groups move in from the ends of the pentane chain, in the sequence 1,5-, 1,4-, 1,2-, 2,4-, and 2,3-pentanediol, is accompanied at low temperatures by a large increase in the most probable relaxation time τ_0.* This type of relaxation is therefore not made easier by structural irregularity, within the present limits, but rather takes place most readily for liquids with the highest degree of local order. It is apparent that regularity of structure is somehow important in the activation process. This co-operative relaxation process may involve the sharing among many molecules of an accumulation of energy obtained at the expense of the vibrational energy of the quasi-crystalline lattice. The common nature of the variation of τ_0 with temperature is consistent with this picture.

REFERENCES

1. D. W. Davidson. Can. J. Chem. **39**, 571 (1961).
2. D. W. Davidson. Can. J. Chem. **35**, 458 (1957).
3. R. Walker and D. W. Davidson. Can. J. Chem. **37**, 492 (1959).
4. L. P. Kuhn. J. Am. Chem. Soc. **74**, 2492 (1952).
5. V. I. Malyshev and V. N. Murzin. Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **22**, 1107 (1958).
6. L. P. Kuhn. J. Am. Chem. Soc. **80**, 5950 (1958).
7. J. A. A. Ketelaar and N. van Neurs. Rec. trav. chim. **76**, 437 (1957).
8. C. P. Smyth and W. S. Walls. J. Am. Chem. Soc. **53**, 2115 (1931).
9. A. H. White and S. O. Morgan. Physics, **2**, 313 (1932).
10. L. G. Wesson. Tables of electric dipole moments. The Technology Press, Cambridge, Mass. 1948.
11. A. A. Maryott and F. Buckley. Tables of dielectric constants and electric dipole moments of substances in the gaseous state. Natl. Bur. Standards (U.S.) Circ. No. 537. 1953.
12. C. P. Smyth. Dielectric behavior and structure. McGraw-Hill Book Co., Inc., New York. 1955. (*a*) p. 370; (*b*) p. 244.
13. K. Kulka, J. A. Rogers, Jr., O. Hansen, and R. J. Eiserle. J. Org. Chem. In press.
14. C. Moriamez-Boullet. Compt. rend. **246**, 2364 (1958).
15. W. Dannhauser and R. H. Cole. J. Chem. Phys. **23**, 1762 (1955).
16. D. W. Davidson and R. H. Cole. J. Chem. Phys. **19**, 1484 (1951).
17. F. X. Hassion and R. H. Cole. J. Chem. Phys. **23**, 1756 (1955).
18. R. H. Cole. Izvest. Akad. Nauk S.S.S.R. Ser. Fiz. **24**, 4 (1960).
19. D. W. Davidson and J. Wheeler. J. Chem. Phys. **30**, 1357 (1959).
20. D. J. Denney. J. Chem. Phys. **30**, 159 (1959).
21. M. L. Williams, R. F. Landel, and J. D. Ferry. J. Am. Chem. Soc. **77**, 3701 (1955).
22. S. H. Glarum. J. Chem. Phys. **33**, 639 (1960).
23. D. W. Davidson. Can. J. Chem. **39**, 1321 (1961).
24. R. G. Bennett. Compte rendu du 9^e Colloque Ampere, Geneva, 1960. p. 62.

APPENDIX

Calculation of the Dipole Moment of Vicinal Diols

In Table VIII are listed values of dipole moments for assumed models of vicinal diols. The OH and OC bond moments have been taken to be 1.51 (12*b*) and 1.10 debyes, respectively, with all angles assumed, for simplicity, to be tetrahedral. Since the small CH moments have not been taken explicitly into account, their effects are approximately included in the value taken for the OC moment.

Forms (*c*) to (*g*) are internally hydrogen bonded. In (*d*) the free OH group is rotated

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**A similar steric effect is noticed in the recent results of Bennett (24), who finds that 1-phenyl-propanol ($\beta = 0.7$) exhibits much higher relaxation times at low temperatures than do 3-phenyl-propanol and 2-phenyl-ethanol ($\beta = 1$).*

TABLE VIII

Calculated dipole moments of vicinal diols

Model	Dipole moment (debyes)
(*a*) Free rot. about all bonds	2.07
(*b*) Free rot. about trans CO bonds	2.01
(*c*) CO bonds cis, all atoms coplanar	2.91
(*d*) CO bonds cis, e.o. in plane	2.52
(*e*) CO bonds gauche, $r_{\mathrm{O---H}}$ min, $r_{\mathrm{H---H}}$ max	2.64
(*f*) CO bonds gauche, first e.o. in plane of CO, O---H	2.48
(*g*) CO bonds gauche, second e.o. in plane of CO, O---H	2.10

about its CO bond through 120° from the planar case (*c*) so as to bring the direction of maximum electron density of either of the lone pair electron orbitals (e.o.) into the plane of the rest of the molecule.

In the three gauche forms, (*e*) to (*g*), the length of the hydrogen bond is made a minimum by rotation of the bonded OH group about its CO bond. Form (*e*) results from rotation of the free OH group about the CO bond until its H atom is as far as possible from the H atom in the bond. In (*f*) and (*g*) one or the other of the e.o.'s on the O atom is brought by this rotation as near as possible to the H atom in the bond.

The O---H and O---O distances are 1.84 and 2.49 Å, respectively, for the cis forms, and 2.33 and 2.82 Å for the gauche forms, with the following bond lengths assumed: OH 0.97, OC 1.42, C—C 1.54 Å. The O—H---O angles, measured within the ring, are 122° (cis) and 111° (gauche).

Most of the calculated dipole moments of the internally hydrogen-bonded forms are higher than the experimental moments of Table III. Form (*g*) fits the data best, but, since there is no good reason for preferring it to (*f*), the r.m.s. value of the moments of these two forms should be taken. This value (2.31 debyes) is sufficiently close to the experimental moments to suggest that the predominant hydrogen-bonded species are approximately gauche forms in which the orbitals of the lone pair electrons of the O atom in the hydrogen bond tend to be oriented toward the H atom. It is likely that the energy of the hydrogen bond is too small to produce much of a rotation from the normal gauche toward the cis configuration. Although there is no evidence for an appreciable population of trans forms in CCl_4 (compare Table II), it is possible that such forms may be promoted in dioxane by hydrogen bonding to the solvent.

The approximate nature of the calculations should be borne in mind. Thus, the values of the OH and OC bond moments (1.55 and 1.30 debyes) required to give agreement with the experimental moment of 1.66 debyes for monohydroxyl alcohols are considerably larger than the ones assumed here, and result in calculated moments which are larger by some 0.2 debyes than those given in Table VIII. If the O angle is taken to be 105° instead of tetrahedral, the bond moments and the resultant moments are somewhat reduced.