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## Circular Dichroism of *l*-Borneol

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**Abstract:** The circular dichroism and absorption spectra of *l*-borneol have been measured in the vapor phase and in solution. Four distinct bands are seen in the vapor phase circular dichroism which extends into the vacuum ultraviolet to 1350 Å. The two long wavelength bands were also measured in 1,1,1,3,3,3-hexafluoro-2-propanol solution. Theoretical rotation strengths were calculated in the independent systems approach using LeFevre, Denbigh, and Amos polarizabilities. The calculations can account for the observed circular dichroism if the first two transitions are assigned  $n\sigma_{OH}^*$  and  $n\sigma_{CO}^*$ , but they cannot account for the observed circular dichroism if either transition is assigned  $n3S_0$ . No matter which polarizability is used, *l*-borneol in the vapor phase is predicted to have the hydroxyl conformation which gives the least steric hindrance. The sign of the first band in solution is opposite to that found in the vapor phase. This is easily accounted for on the basis of the calculations if it is assumed that the hydrogen-bonded complex assumes a new hydroxyl conformation which would have the least steric hindrance. Circular dichroism and absorption spectra are also presented for (+)-2-butanol in solution.

Circular dichroism spectroscopy is a special kind of electronic absorption spectroscopy. For a molecule to have a circular dichroism spectrum, it must be asymmetric, and thus this spectroscopic property is sensitive to the conformation of the molecule. If the electronic properties of the molecule are known, then in principle at least, the circular dichroism spectrum gives information about conformation. On the other hand, if the conformation of the molecule is known, then the circular dichroism spectrum gives information about the electronic properties. However, complex quantum mechanical calculations are necessary to relate the spectrum to the electronic properties and the conformation.

For our quantum mechanical calculations we choose an independent systems theory, the Kirkwood-Tinoco approach.<sup>1,2</sup> The central assumption of independent systems theory is that we can divide a molecule into groups between which it is reasonable to assume that there is no exchange of electrons. The properties of the molecule are then calculated in terms of the properties of the groups. The properties of the groups are presumably easy to determine.

Small molecules consisting of one chromophore and a nonchromophoric backbone are well suited for comparison of approximate quantum mechanical calculations with experiment because of their theoretical tractability. To apply independent systems theory we choose the chromophore as one group and all the other bonds in the molecule as the other groups. This means that our group orbitals are localized on the chromophore, or else on and between the two atoms which form the other bonds. This contrasts with molecular orbital theory where the orbitals generally extend over the entire molecule. With the molecular orbital basis set, exchange terms are an important part of the calculation. With the independent

systems basis set, exchange terms within the chromophore or within the other bonds are considered, but exchange terms between the various groups are neglected. This model of a molecule goes along with the chemist's idea that each type of bond is an entity which has similar properties in different molecules. Indeed, many physical properties of molecules may be computed to a good approximation by summing the properties attributed to each bond.

Molecular orbital theory lends itself to ab initio calculations because of the ease with which the molecular orbital basis functions can be constructed. Although it is often not clear how to construct orthogonalized group functions for the independent systems approach, the theory has the advantage that it suggests approximations which suit our chemical intuition. Furthermore, the theory lends itself to the use of empirical parameters. When used in a semiempirical way, the actual construction of group functions can often be avoided.

It is hoped that the original approximation of neglecting exchange terms which occur between the groups and the further approximations which simplify the calculation will be good approximations, so that the method will relate circular dichroism accurately to conformation. Actual calculations on small molecules and comparisons of the calculations with measured circular dichroism spectra are necessary to determine the applicability of the method.

For our first work in this area, we measured the circular dichroism of five alkyl amino acids to 1600 Å. The spectra for alanine, valine, isoleucine, and leucine consisted of two circular dichroism bands. Our method, with its approximations and empirical parameters, was able to account for the correct sign and roughly the correct magnitude of the bands. Furthermore, the conformation predicted by our method agreed with the

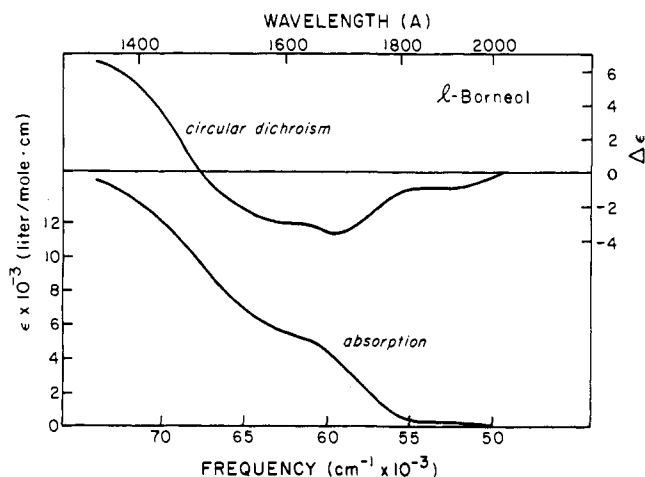


Figure 1. The absorption and circular dichroism spectra for *l*-borneol in the vapor phase.

conformation found in crystals and predicted by calculations involving various nonbonding interactions. These results increased our faith in the method. The spectrum of proline was more complicated and has not been interpreted satisfactorily.

In subsequent work we measured the circular dichroism of (+)-2-butanol to 1350 Å. Although this is a particularly simple molecule, the uncertainty in its conformation made it necessary to consider the rotation of the ethyl group as well as the hydroxyl group. However, with a simple assignment of the transitions, the method was able to account for the observed circular dichroism of the molecule in the conformation expected from studying molecular models.

These successes lead us to evaluate the method more critically using molecules of fixed conformation. Here we choose *l*-borneol, a molecule with the same chromophore as (+)-2-butanol, but with its conformation largely fixed by the bicyclic backbone so that we need only consider the hydroxyl rotation.<sup>5</sup> This eliminates one variable and allows us to concentrate on the electronic properties which one must know in order to use independent systems theory to connect the circular dichroism spectrum with the conformation. In our formulation, it is necessary to know the polarizabilities of the various bonds which make up the molecule. There are a number of polarizabilities in the literature and these may well be the weakest parameters in the method. The calculation of the rotational strength for *l*-borneol allows investigation of the effect of the different polarizabilities on the results.

This report presents the circular dichroism of *l*-borneol in the vapor phase and in solution. In addition, we calculate the circular dichroism of *l*-borneol using three different polarizabilities in the independent systems approach. The effect of these polarizabilities on calculations of the circular dichroism of (+)-2-butanol is also presented. Independent systems theory can account for the circular dichroism spectra observed for these two alcohols.

### Experimental Section

*l*-Borneol was obtained from Aldrich Chemical Co. The vapor phase absorption spectrum was taken on a McPherson 225 vacuum ultraviolet spectrometer with a 1-m focus grating (600 L/mm). The vacuum ultraviolet circular dichroism spectrometer,<sup>6</sup> calibration,<sup>4</sup> and pressure measurement<sup>4</sup> have been described previously. The spectral slit width was 0.16 nm for absorption measurements and 1.6 nm for circular dichroism measurements. The vapor phase spectra were taken in a 50-cm cell with the optical density kept below 1.0 for all measurements. The solution spectra were taken in a 0.05-mm quartz cell using spectrograde 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) from Pierce Chemical Co.

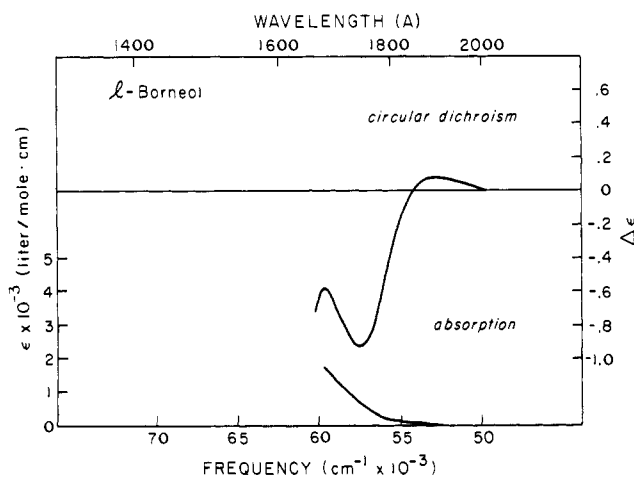


Figure 2. The absorption and circular dichroism spectra for *l*-borneol in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).

### Experimental Results

Figure 1 shows the gas phase absorption and circular dichroism spectra of *l*-borneol. The low-energy absorption band begins at the same energy as it did in the case of (+)-2-butanol,<sup>4</sup> but the higher energy bands are distinctly red shifted. The three low energy circular dichroism bands in *l*-borneol are negative. This is in contrast to (+)-2-butanol where the first two low energy bands were positive and only the third was negative. The second and third low energy bands are red shifted in analogy to the absorption bands. The fourth circular dichroism band is positive for both alcohols.

Figure 2 shows the circular dichroism spectrum of *l*-borneol dissolved in HFIP. Even with the absorption spectrum it is hard to tell if the two circular dichroism bands observed correspond to the first two bands in the vapor phase spectrum. It is possible that the hydrogen bonding solvent has blue shifted the first band uncovering a band not observed in the vapor phase. It is also possible that we are seeing the effects of two rotamers or two hydrogen bonded species in solution, or that we are seeing vibrational effects.

However, if we assume that the two circular dichroism bands do correspond to the first two bands observed in the vapor phase, then, the first band is now positive while the second band remains negative. In solution, both bands have a much smaller rotational strength than in the vapor phase. Since the first band occurs at about the same energy in both the vapor phase and solution, any hydrogen bond with HFIP would have to be with the COH hydrogen of *l*-borneol and not the nonbonding electrons. If the nonbonding electrons of *l*-borneol were involved in hydrogen bonding, one would expect the transition to occur at a higher energy. A shift to higher energy is observed for (+)-2-butanol dissolved in HFIP and water (Figure 3). An interesting point is the sign of the low energy band for both alcohols in the vapor phase and in solution. For *l*-borneol the low energy band is negative in the vapor phase but positive in solution, while for (+)-2-butanol it is positive in the vapor phase but negative in solution.

### Description of Calculation

**Theoretical Background.** The theory on which these calculations are based is the Kirkwood<sup>1</sup> theory as extended by Tinoco et al.<sup>2,7</sup> A more detailed description has been published elsewhere.<sup>2-4</sup> It is an independent systems approach in which the molecule is divided into groups. We divide the alcohols into optically inactive carbon-carbon bonds, carbon-hydrogen bonds, and a COH chromophore. The asymmetric location of the carbon-carbon and carbon-hydrogen bonds will give rise to optical activity in the COH chromophore.

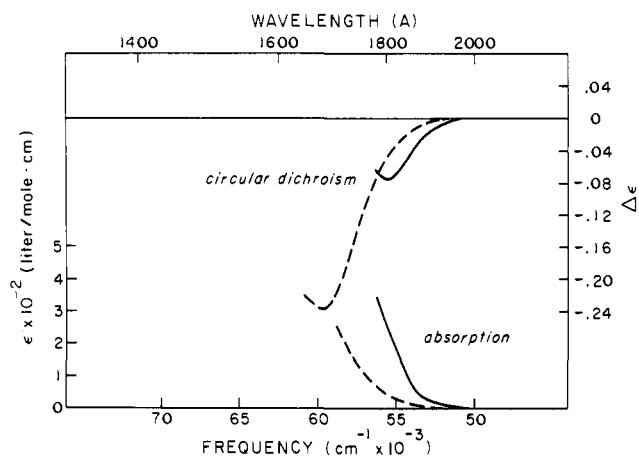


Figure 3. The absorption and circular dichroism spectra of (+)-2-butanol in water (—) and in 1,1,1,3,3,3-hexafluoro-2-propanol (---).

The notation used is as follows:<sup>2-4</sup>  $\alpha_j$  is the polarizability tensor of group  $j$ ;  $a, b$  label the unperturbed excited states of a group;  $c$  is the velocity of light;  $\mathbf{E}_{iOa}^j$  is the coulombic field at group  $j$  due to a transition charge density in group  $i$ ;  $h$  is Planck's constant;  $\text{Im}$  denotes the "imaginary" part;  $i$  denotes the COH chromophore;  $j$  denotes the carbon-carbon and carbon-hydrogen bonds (vicinal groups);  $\mu$  is the electric dipole moment with the group and transition indicated by subscripts;  $\mathbf{m}$  is the magnetic dipole moment labeled as above;  $\nu$  is the frequency of the transition labeled as above;  $\rho_s^{iOa}$  is the monopole of region  $s$  for transition  $Oa$  on group  $i$ ;  $r_{sj}$  is the vector distance from region  $s$  to group  $j$ ;  $r_{st}$  is the distance between regions  $s$  and  $t$ ;  $\mathbf{R}_{ij}$  is the vector distance from group  $i$  to  $j$ ;  $R_{OA}$  is the rotational strength of perturbed transition  $O \rightarrow A$  in the molecule (the area under a circular dichroism band measured in a special way); and  $V_{iab;j00}$  is coulombic potential energy of a transition charge density in group  $i$  with a permanent charge distribution in group  $j$ .

The dominant terms in the calculation of the rotational strength are, in the polarizability approximation:

$$R_{OA} = \sum_{j \neq i} \text{Im} \{ \mathbf{E}_{iOa}^j \cdot \alpha_j \cdot \mathbf{m}_{ia0} \} \quad (a)$$

$$- \sum_{j \neq i} \sum_{b \neq a} \text{Im} \{ V_{iab;j00} (\mu_{i0b} \cdot \mathbf{m}_{ia0} + \mu_{i0a} \cdot \mathbf{m}_{i0b}) / h (\nu_{i0b} - \nu_{i0a}) \} \quad (b)$$

$$+ (\pi \nu_{i0a} / c) \sum_{j \neq i} \mathbf{E}_{iOa}^j \cdot \alpha_j \times \mu_{i0a} \cdot \mathbf{R}_{ij} \quad (c)$$

where we choose to calculate the coulombic field and potential energy in the monopole approximation.

$$\mathbf{E}_{iOa}^j = \sum_s (\rho_s^{iOa} / r_{sj}^3) \mathbf{r}_{sj}$$

$$V_{i0a;j0b} = \sum_{s,t} \rho_s^{iOa} \rho_t^{j0b} / r_{st}$$

Term (b) is expected to be small as the dipole moment of a CH bond is only 0.4 D and therefore the static field is small. Term (a) has been left out of rotational strength calculations quite often. However, Hohn and Weigang<sup>8</sup> have suggested that term (a) and not term (b) may be responsible for the rotational strength of ketones. Also, Schellman<sup>9</sup> and Woody and Tinoco<sup>10</sup> have suggested that term (a) may in some cases be dominant. We calculated all three terms, but term (b) was small and will not be considered further.

**Conformation.** The absolute configuration of *l*-borneol is shown in Figure 4.<sup>11</sup> The length of the carbon-carbon bonds was taken as 1.54 Å, the length of the carbon-hydrogen bonds

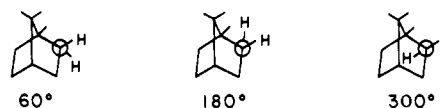


Figure 4. The conformation and absolute configuration of *l*-borneol with angles for various hydroxyl rotamers when looking down the carbon-oxygen bond.

Table I. Bond Polarizabilities in Å<sup>3</sup>

Bond	Uncorrected polarizabilities (0 kK)		Corrected polarizabilities (56 kK)		Polarizability from
	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\alpha_{\parallel}$	$\alpha_{\perp}$	
C-C	0.99	0.27	1.43	0.39	LeFevre
C-H	0.64	0.64	0.925	0.925	LeFevre
C-C	1.88	0.02	2.72	0.029	Denbigh
C-H	0.79	0.58	1.14	0.838	Denbigh
C-C	0.719	0.381	1.03	0.547	Amos
C-H	0.868	0.488	1.25	0.700	Amos

as 1.09 Å, and the length of the carbon-oxygen bond as 1.42 Å. The carbon-hydrogen bonds were taken as staggered for the three methyl groups. Rotation of these groups does not significantly affect the results since they are some distance away. The rotational strength is sensitive to rotation about the carbon-oxygen bond. The staggered conformations of the hydroxyl group with rotation about the carbon-oxygen bond are defined in Figure 4.

**Assignment of Transitions.** Both *l*-borneol and (+)-2-butanol have the same chromophore, the COH group, so the *l*-borneol transitions are assigned as in the case of (+)-2-butanol.<sup>4</sup> The first two transitions are assumed to be the  $\pi\sigma_{OH}^*$  and  $\pi\sigma_{CO}^*$  centered on the oxygen.

**Polarizability.** The polarizability approximation leads to several problems. First, only pairwise interactions are considered.

Second, the experimentally determined polarizabilities are for zero frequency and a polarizability at the frequency of interest should be used. The polarizability is corrected to the frequency of interest as in ref 3 and 4.

Third, there are many bond polarizabilities and anisotropies in the literature. We use the two most popular experimental values, those by LeFevre<sup>12</sup> and Denbigh,<sup>13</sup> plus a recently derived theoretical value by Amos.<sup>14</sup>

Experimentally the average molecular polarizability,  $\bar{\alpha}$ , and absolute value of the molecular anisotropy,  $\Gamma$ , can be determined. The average molecular polarizability is

$$\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3$$

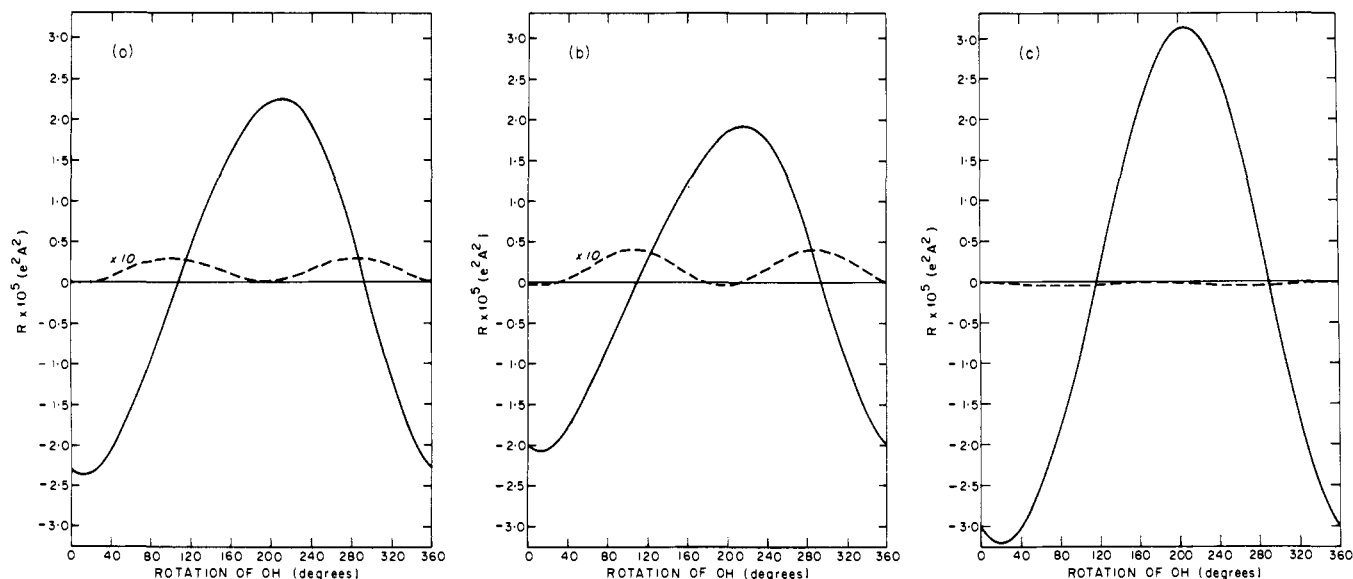
where  $\alpha_{\parallel}$  is the longitudinal bond polarizability and  $\alpha_{\perp}$  is the traverse bond polarizability. The molecular anisotropy is

$$\Gamma = (\alpha_{\parallel} - \alpha_{\perp})(C-C) - 2(\alpha_{\parallel} - \alpha_{\perp})(C-H)$$

To obtain the needed tensor elements,  $\alpha_{\parallel}$  and  $\alpha_{\perp}$ , from the experimental data, the sign of  $\Gamma$  must be assumed. In early work around 1935, Sachsse assumed  $\Gamma$  was negative for ethane.<sup>15</sup> Between 1935 and 1965  $\Gamma$  was assumed to be positive by various workers.<sup>13,16,17</sup> Since 1965 some workers have suggested that  $\Gamma$  should be negative.<sup>18</sup> Very recent theoretical work by Amos<sup>14</sup> indicates that the ethane molecule is more polarizable perpendicular to the carbon-carbon bond than along it. This is equivalent to  $\Gamma$  being negative. He suggests that the reason Denbigh obtains a very high anisotropy for the carbon-carbon bond is his assumption of a positive  $\Gamma$ .

The polarizability values used are listed in Table I.

**Transition Moment Magnitudes.** The magnitudes of the electric and magnetic transition moments and of the corre-



**Figure 5.** The calculated rotational strength for an  $n\sigma_{\text{OH}}^*$  transition in *l*-borneol as a function of hydrogen rotation around the carbon-oxygen bond using various polarizabilities. Term (a) is (—) and term (c) is (---). (a) LeFevre polarizabilities, (b) Denbigh polarizabilities, and (c) Amos polarizabilities.

**Table II.** Transition Data

Transition	$m_{i0a},$ $e \text{ \AA} \times 10^3$	$\mu_{i0a},$ $e \text{ \AA}$	$E,$ kK	Exptl rotational strength $e^2 \text{ \AA}^2 \times 10^5$
$n\sigma_{\text{OH}}^*$	1.58	0.06	52.8	-0.86
$n\sigma_{\text{CO}}^*$	1.58	0.3	59	-2.7

sponding energies are listed in Table II. The electric transition moment magnitudes and the energies were evaluated from the absorption spectrum.

For the magnetically allowed transition  $2p_x$  to  $2p_y$ , the magnetic transition moment is equal to  $1.93 \times 10^{-3} e \text{ \AA}$  or  $1 \mu_B$ . In the case of *l*-borneol the  $n$  orbital was assumed to be pure  $p$  and the  $\sigma_{\text{OH}}^*$  and  $\sigma_{\text{CO}}^*$  orbitals were taken as  $sp^2$  hybridized. Since the  $\sigma_{\text{OH}}^*$  and  $\sigma_{\text{CO}}^*$  orbitals are not pure  $p$  the magnetic transition moment is multiplied by the appropriate molecular coefficients.<sup>4</sup>

### Theoretical Results

**$n\sigma_{\text{OH}}^*$  Rotational Strength.** Figure 5a shows the calculated rotational strength as a function of hydroxy hydrogen angle (Figure 4) for term (a) and term (c) using LeFevre polarizabilities. Clearly, term (a) must be included or the wrong sign would be obtained since term (c) is positive and the experimental rotational strength is negative. The hydroxyl must be between  $300^\circ$  ( $-60^\circ$ ) and  $90^\circ$  to give a negative rotational strength for this transition.

Essentially the same results are obtained for Denbigh polarizabilities (Figure 5b). Term (a) dominates the results with term (c) having the wrong sign for almost all conformations. The hydroxyl must be between  $300^\circ$  ( $-60^\circ$ ) and  $110^\circ$  for the rotational strength to be negative.

For Amos polarizabilities term (a) again dominates the results but in this case term (c), although very small, does have the correct sign for most conformations (Figure 5c). The hydroxyl must have a position between  $290^\circ$  ( $-70^\circ$ ) and  $110^\circ$  for the sign of the theoretical rotational strength to be negative.

For all three polarizabilities, LeFevre, Denbigh, and Amos, term (a) is much larger than term (c) and has a negative rotational strength as observed experimentally. All three polarizabilities predict the hydroxyl to be between  $300^\circ$  ( $-60^\circ$ )

and  $100^\circ$  for the  $n\sigma_{\text{OH}}^*$  transition. No matter which polarizability is used, it is necessary to calculate term (a).

**$n\sigma_{\text{CO}}^*$  Rotational Strength.** Figure 6a shows the  $n\sigma_{\text{CO}}^*$  rotational strength using LeFevre polarizabilities for term (a) and term (c) as a function of hydroxyl position. Term (a) has a much greater magnitude than term (c) and term (c) has a positive rotational strength while the experimental value is negative. Term (a) has a negative rotational strength between  $30^\circ$  and  $130^\circ$  and between  $210^\circ$  and  $310^\circ$ .

The rotational strength vs. hydroxyl position for Denbigh polarizabilities is shown in Figure 6b. Term (c) has a significant magnitude but the wrong sign for almost all conformations. Term (a) has a larger magnitude and the sum of terms (a) and (c) will give a negative rotational strength between  $30^\circ$  and  $110^\circ$  and between  $210^\circ$  and  $290^\circ$ .

Figure 6c shows the results for terms (a) and (c) using Amos polarizabilities. In this case term (a) is somewhat larger than term (c) but this time it has the wrong sign for all conformations and we must rely on term (c) to give the correct sign. A negative rotational strength will be obtained between  $30^\circ$  and  $100^\circ$  and between  $210^\circ$  and  $280^\circ$  when both terms (a) and (c) are considered.

The predicted position of the hydroxyl is essentially the same for LeFevre, Denbigh, and Amos polarizabilities. However, in the case of the Amos polarizability it is term (c) that allows the correct sign of the rotational strength to be obtained whereas for LeFevre and Denbigh polarizabilities it is term (a). However, no matter what polarizability is used it is clear that both terms (a) and (c) must be calculated for alcohols.

**$n3S_0$  Rotational Strength.** Since some workers<sup>19,20</sup> consider the first transition for alcohols to be  $n3S_0$  in character, it is of interest to calculate the rotational strength for this transition. The  $n3S_0$  transition has the same electric transition moment direction as the  $n\sigma_{\text{OH}}^*$  and  $n\sigma_{\text{CO}}^*$  transitions and therefore it has the same conformational dependence as term (c) for these transitions. The magnitude of the rotational strength, however, depends on the magnitude of the  $n3S_0$  electric transition moment and its energy. Since a  $n3S_0$  transition is magnetically forbidden, term (a) will not contribute. If the first transition were  $n3S_0$ , both LeFevre and Denbigh polarizabilities would predict a positive rotational strength for the  $n3S_0$  transition while Amos polarizabilities predict a negative rotational strength for this transition. The experimentally observed rotational strength is negative, therefore, using

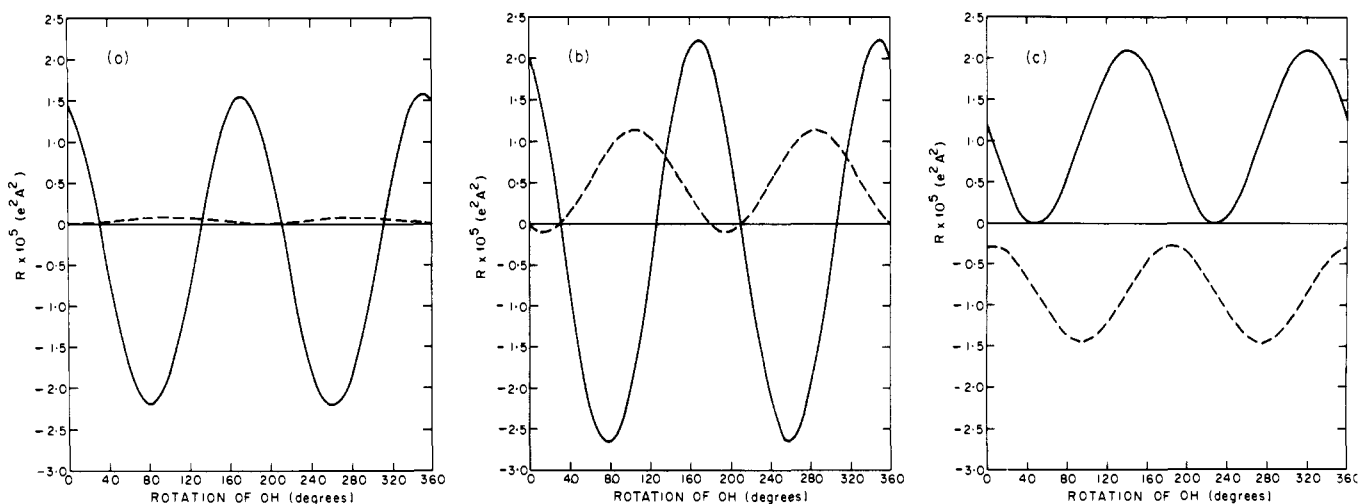


Figure 6. The calculated rotational strength for a  $n_{CO}^*$  transition in *l*-borneol as a function of hydrogen rotation around the carbon-oxygen bond using various polarizabilities. Term (a) is (—) and term (c) is (- - -). (a) LeFevre polarizabilities, (b) Denbigh polarizabilities, and (c) Amos polarizabilities.

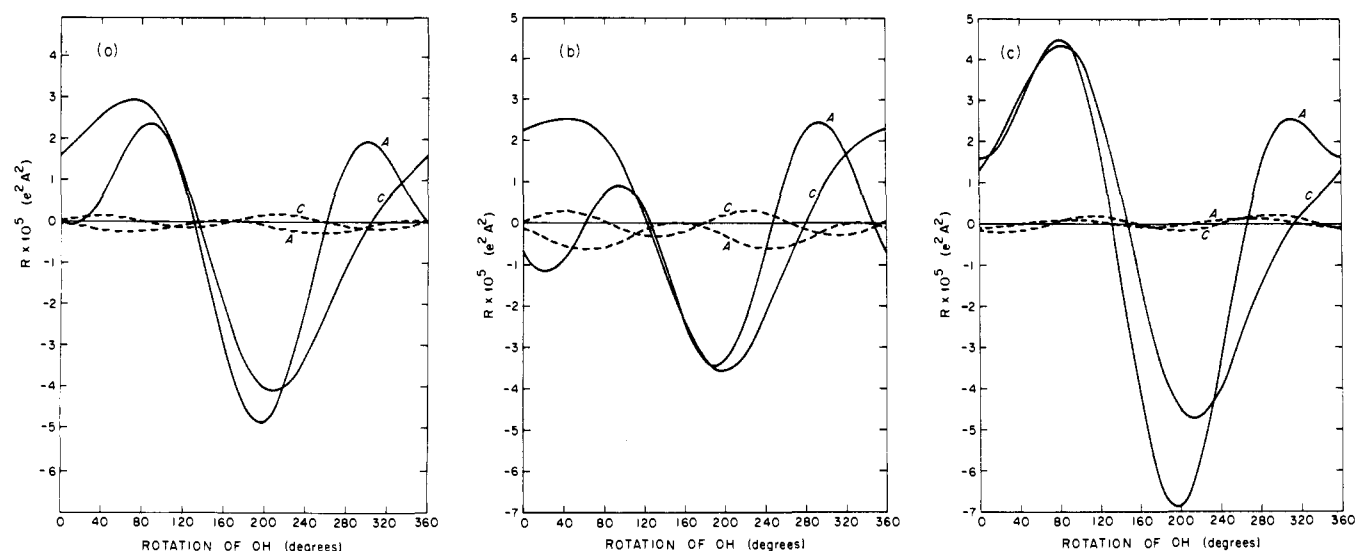


Figure 7. The calculated rotational strength for an  $n_{OH}^*$  transition in (+)-2-butanol for conformation A and conformation C. Term (a) is (—) and term (c) is (- - -). (a) LeFevre polarizabilities, (b) Denbigh polarizabilities, and (c) Amos polarizabilities.

LeFevre or Denbigh polarizabilities the first transition could not be  $n_{3SO}$ . Amos polarizabilities give the correction sign but very low magnitude when compared to the experimental value ( $-0.1$  vs.  $-0.87$ ).

**(+)-2-Butanol Rotational Strength.** Since all three polarizabilities gave the same conformational prediction for *l*-borneol, it is of interest to see how the various polarizabilities will affect the (+)-2-butanol results. Figures 7 and 8 show the theoretical rotational strength for (+)-2-butanol using LeFevre, Denbigh, and Amos polarizabilities. They are presented for the two conformations of the ethyl group in (+)-2-butanol considered previously.<sup>4</sup> The conformation with the methyl group anti to the  $CH_3$  group of the ethyl is denoted by "A" while the conformation with the hydroxyl group anti to the  $CH_3$  group of the ethyl is denoted by "C".

Amos polarizabilities give similar conformational predictions to the LeFevre polarizabilities discussed in ref 4. Denbigh polarizabilities give different predictions as to the conformation of (+)-2-butanol which we feel are incorrect. However, the uncertainty of the conformation of (+)-2-butanol due to the rotation of the ethyl group does not allow one to rule out Denbigh polarizabilities. The important point to notice is the necessity of including term (a) to get the correct sign for the

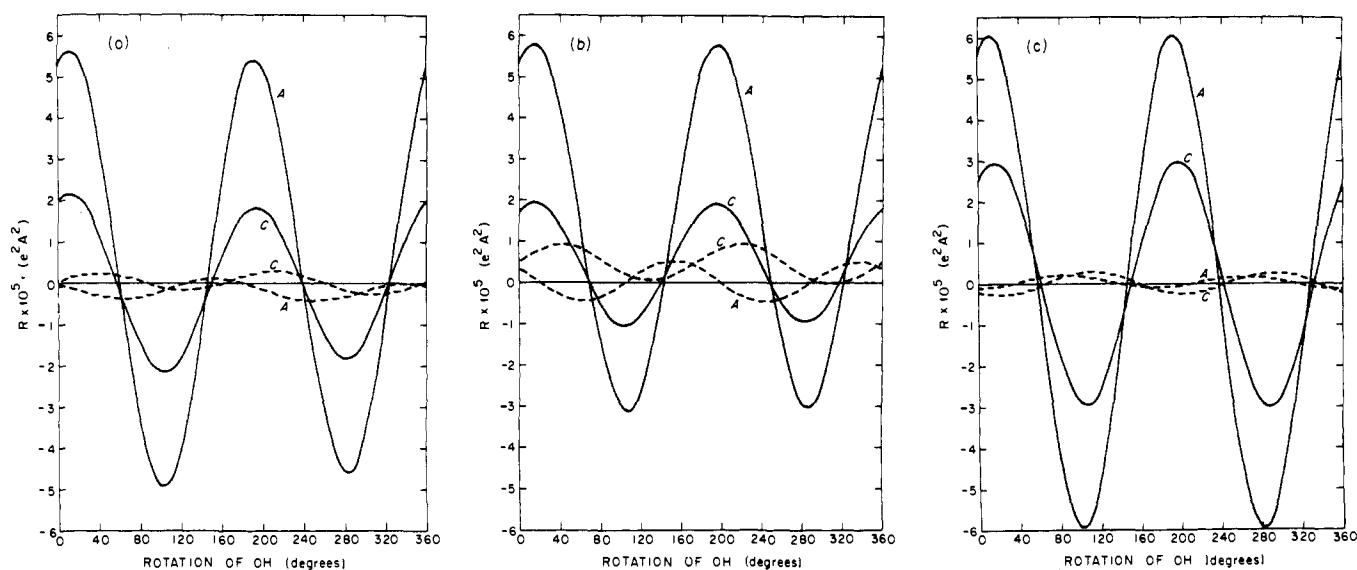
Amos and Denbigh polarizabilities as well as for the LeFevre polarizabilities used previously.

## Discussion

The conformation predicted for *l*-borneol by comparison of experimental and theoretical rotational strength is exactly that expected from examining a space filling model of *l*-borneol. For the calculated rotational strengths of both transitions to be negative the average position of the hydroxyl must be between  $30^\circ$  and  $100^\circ$  or else about  $290^\circ$ . Consideration of a space-filling model indicates that the most favorable position for the hydroxyl is  $60^\circ$ .

The theoretical results for *l*-borneol are insensitive to the polarizability chosen. LeFevre, Denbigh, and Amos polarizabilities and anisotropies all predict essentially the same sign dependence of the theoretical rotational strength on conformation. Therefore, to recommend one polarizability over the others one would have to rely on intensity arguments. This is a questionable procedure since the theoretical rotational strength for each conformation should be weighted by the unknown probability of finding the molecule in that conformation.

For (+)-2-butanol the Amos polarizability gives the same



**Figure 8.** The calculated rotational strength for an  $n\sigma_{CO}^*$  transition in (+)-2-butanol for conformation A and conformation C. Term (a) is (—) and term (c) is (- - -). (a) LeFevre polarizabilities, (b) Denbigh polarizabilities, and (c) Amos polarizabilities.

conformation dependence as LeFevre polarizabilities. Denbigh polarizabilities give results which have a different conformational dependence, but it is unclear whether or not this argues against Denbigh polarizabilities because of the large conformational uncertainty for (+)-2-butanol.

These calculations are consistent with the assignment of the first two transitions in *l*-borneol as  $n\sigma_{OH}^*$  and  $n\sigma_{CO}^*$ . Definite assignment of the order of transitions is not possible here since both transitions are negative for *l*-borneol. Any ordering would have to rely on intensity arguments, which as already mentioned is a questionable procedure. However, these assignments are also consistent with the (+)-2-butanol calculations<sup>4</sup> where the lowest energy transition was assigned  $n\sigma_{OH}^*$  and the next transition was assigned  $n\sigma_{CO}^*$ .

The first transition in alcohols is often assigned as  $n3S_0$ . This assignment cannot be used with independent systems theory to account for the circular dichroism observed for either of the two alcohols.

The circular dichroism spectra of these alcohols in solution shows the danger in extending results in the vapor phase to solution work. The sign of the first CD band changes in solution from the sign observed in the vapor phase for both *l*-borneol and (+)-2-butanol. Apparently, hydrogen bonding with the solvent changes the preferred orientation of the alcohol hydroxyl group. In the case of *l*-borneol the lowest circular dichroism band is not shifted in energy indicating that the HFIP is hydrogen bonded via the nonbonding electrons of HFIP and the hydroxy hydrogen of *l*-borneol. The conformation which appears most likely on studying a model is that with the borneol hydroxyl rotated to an angle of about  $102^\circ$  since the HFIP is

sterically hindered in the  $60^\circ$  region. Starting at about  $110^\circ$  the  $n\sigma_{OH}^*$  transition would be slightly positive for all polarizabilities. The  $n\sigma_{OH}^*$  transition would be negative for LeFevre and Denbigh polarizabilities at about  $110^\circ$ .

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