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Infrared Circular Dichroism Associated with the OH-Stretching Vibration in the Methyl Ester of Mandelic Acid

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Abstract: The infrared circular dichroism (CD) spectrum associated with the OH-stretching vibration in methyl mandelate has been measured. The methyl mandelate CD results suggest a new interpretation of the CD spectrum of dimethyl tartrate.

Introduction

Experimental observation of circular dichroism (CD) associated with the CH-stretching vibrations in tartaric acid was recently reported by Sugeta et al.[1] Their results indicate that bisignate contributions to the spectra are not evident; hence, that the coupled-oscillator contribution arising from the coupling of the symmetric and antisymmetric stretching modes is negligible.[1,2] Keiderling and Stephens recently reported observing a bisignate spectrum in the OH-stretching region of *d*-dimethyl tartrate, [-CH(OH)COOCH$_3$]$_2$ (I), which they

I
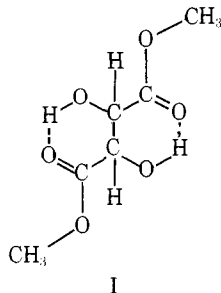
interpreted on the basis of a coupled-oscillator calculation that agreed qualitatively with the observed spectrum.[3]

In the present study measurements of vibrational CD associated with the single OH stretch in *d*-, *l*-, and *dl*-methyl mandelate, [PhCH(OH)COOCH$_3$] (II), have been made.

II
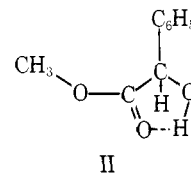
Methyl mandelate is structurally related to dimethyl tartrate but the interpretation of the vibrational CD spectrum should be more straightforward since it contains only one OH group and there is no possibility of a degenerate coupled-oscillator contribution to the rotational strength associated with the OH-stretching vibration. The results of the methyl mandelate study have important implications in the interpretation of the CD spectrum of dimethyl tartrate.

Experimental Section

The methyl mandelate samples used in this work were prepared by esterification of mandelic acid samples obtained from the Aldrich Chemical Co. The mandelic acid was dissolved in methanol and refluxed with ~5% concentrated sulfuric acid for 1 h. The product was mixed with H$_2$O and ether and enough Na$_2$CO$_3$ was added to bring the pH to about 3. The water layer was extracted several times and the ether evaporated. The product was dried over CaSO$_4$ and recrystallized from hot petroleum ether. [α]$_D$ values of +170.5 and -168.8° (*c* 1.000, CHCl$_3$) were observed for the *d* and *l* enantiomers, respectively.

Infrared CD measurements were made on the Holzwarth-Chabay

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Table I. Absolute Values of the Rotational Strengths (R) and Dipole Strengths (D) of the OH-Stretching Band at 3540 cm^{-1} in Methyl Mandelate[a]

concn, M	D, esu^2 cm^2	R, esu^2 cm^2
0.064	5.5×10^{-39}	1.9×10^{-43}
0.030	6.5×10^{-39}	2.4×10^{-43}
0.010	7.1×10^{-39}	2.1×10^{-43}

[a] The solvent is CCl$_4$.

spectrometer in our laboratory.[4] A time constant of 10 s and a resolution of about 10 cm^{-1} were used for all the spectra shown. Spectroquality CCl$_4$ was used as the solvent and its infrared absorption spectrum was checked to make sure that it was free of water. All spectra were obtained by subtracting absorption baselines[4] from the CD curves on a Tracor Northern Model NS-575 digital signal averager.

The CD and absorption spectra for d-S-, l-R-, and dl-methyl mandelate (0.010 M in CCl$_4$) are shown in Figure 1. In the absorption spectrum the absorption maximum of the OH-stretching band is at 3540 cm^{-1} and the CD spectra of the d and l enantiomers show single oppositely signed peaks at this same wavenumber. CD spectra recorded at concentrations of 0.064 and 0.030 M have the same shape and sign. In Table I we show the rotational strengths, R, and dipole strengths, D, obtained from the observed spectra of methyl mandelate at the three concentrations studied. Rotational strengths were obtained by graphical integration using the observed dl baselines. An average of the absolute values of the d and l rotational strengths was taken. We estimate an uncertainty of 25% in R. The infrared spectrum of methyl mandelate at varying concentrations shows at least three bands in the OH-stretching region. The large and very broad intermolecular hydrogen bonded component goes away on dilution and a much sharper band appears at 3540 cm^{-1}. A considerably smaller band is also evident at 3710 cm^{-1}. We attribute the band at 3710 cm^{-1} to the free OH's and the band at 3540 cm^{-1} to the intramolecularly hydrogen bonded molecules.[5]

We also repeated the measurements of Keiderling and Stephens on d-dimethyl tartrate and obtained a bisignate band shape in full agreement with their results.[3]

Discussion

Attempts to calculate the rotational strength associated with the OH-stretching mode in methyl mandelate using the harmonic-oscillator fixed partial charge (fpc) approximation resulted in values considerably less than what was observed experimentally. This result was independent of the H–C–O–H dihedral angle chosen. Such an underestimate of the observed rotational strength is typical of harmonic-oscillator fpc model calculations of CH- and OH-stretching bands.[6] If we take the feature at 3540 cm^{-1} in the IR spectrum of methyl mandelate as indicative of an intramolecular hydrogen-bonded structure, it seems that structure II is likely to predominate in a dilute CCl$_4$ solution of methyl mandelate.[7] Thus we believe that the OH stretch optical activity in methyl mandelate is associated with an intramolecularly hydrogen-bonded conformation such as structure II.

This interpretation of the single CD peak in the OH-stretching region of methyl mandelate has interesting implications concerning the interpretation of the bisignate shaped CD curve in the OH-stretching region of dimethyl tartrate. Comparing the results in Table I with the results of Keiderling and Stephens,[3] we see that the experimental R values for methyl mandelate are of the same magnitude as the $R_{\pm}$ value determined from the dimethyl tartrate CD spectrum, assuming a splitting of 3 cm^{-1} between the (+) and (−) band maxima. Since the optical activity in the mandelate may be thought in a crude sense to be equivalent to the intrinsic optical activity in one-half of the tartrate molecule with no possibility of a degenerate coupled oscillator, a degree of doubt is introduced as to whether the bisignate shape in the tartrate spectrum is actually due to coupled-oscillator behavior.
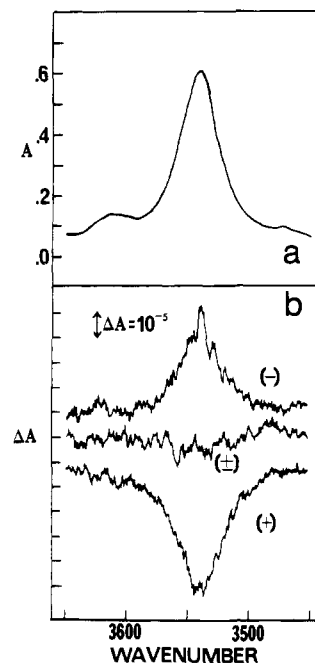

Figure 1. (a) Absorption spectrum of d-(S)-methyl mandelate in CCl$_4$ solution; (b) CD spectra of d-(S)-methyl mandelate, (+), l-(R)-methyl mandelate, (−), and dl-methyl mandelate, (±), in CCl$_4$ solution. In all cases the concentration of methyl mandelate is 0.010 M and the path length is 5.9 mm. The absorbance $A = \log(I_0/I)$. ΔA is the difference in absorbance for left minus right circularly polarized light; ΔA increases from the bottom to the top of Figure 1b. The CD zero has been displaced between the (+), (±), and (−) measurements.

This comparison is similar to what we have actually observed experimentally in the CH-stretching vibrations of tartaric acid and sodium mandelate. The CD peak at 2900 cm^{-1} for the single CH stretch in d-(S)-sodium mandelate was observed to have a rotational strength of 4×10^{-44} (esu cm)^2 for a 4 M solution using D$_2$O as the solvent. This is exactly half the rotational strength observed in a 2 M solution of l-(S,S)-tartaric acid, where both CD curves were positive in sign.[1] This is what one might expect if coupled-oscillator contributions to the CD spectrum are negligible, since tartaric acid has twice as many C*H bonds per molecule.

This can be seen more clearly if we consider the explicit expression for the coupled-oscillator rotational strength given by[1]

$$R^{\pm} = \tfrac{1}{2} \operatorname{Im}(\mu_1 \cdot \mathbf{m}_1 + \mu_2 \cdot \mathbf{m}_2) \pm \tfrac{1}{2}[\operatorname{Im}(\mu_1 \cdot \mathbf{m}_2 + \mu_2 \cdot \mathbf{m}_1) - (\omega/2c)(\mu_1 \times \mu_2 \cdot \mathbf{r}_{12})] \quad (1)$$

where μ_1 and $\mathbf{m}_1$ are respectively the electric and magnetic dipole transition moments of the first local oscillator and μ_2 and $\mathbf{m}_2$ those of the second local oscillator; $\mathbf{r}_{12}$ is the vector between the origins of the multipole expansions of the two oscillators. The first term in eq 1 represents the contribution from intrinsic rotational strengths of the two local oscillators, the second the coupled-oscillator contribution. R^+ is the rotational strength of the transition to the (+) state corresponding to the in-phase combination of the two oscillators and R^- is the rotational strength of the transition to the (−) state corresponding to the out-of-phase combination. If the first term is completely dominant and if the energies of the (+) and (−) states are close, we expect to see a monosignate feature in the CD spectrum, since R^+ and R^- are approximately equal and have the same sign. If the second term is completely dominant, we expect to see a bisignate feature since R^+ and R^- are approximately equal in magnitude and oppositely signed. But there will be some cancellation if the energies of the (+) and (−) states are close relative to the bandwidths and the can-

cellation will be complete if the (+) and (−) states are exactly degenerate. The observation of a monosignate feature in the CD spectrum of the C*H stretching modes of tartaric acid was taken as evidence that, in that particular case, the first term in eq 1 is dominant and the second either negligible or effectively canceled because of the closeness of the (+) and (−) states. The observation on sodium mandelate which has only a single C*H oscillator and for which the rotational strength is given simply by

$$R = \text{Im}(\boldsymbol{\mu} \cdot \mathbf{m}) \qquad (2)$$

supports this conclusion, and further suggests that $\boldsymbol{\mu} \cdot \mathbf{m} = \mu_1 \cdot \mathbf{m}_1 = \mu_2 \cdot \mathbf{m}_2$, i.e., that the intrinsic rotational strength of each C*H local oscillator in tartaric acid is about the same as the intrinsic rotational strength of the C*H oscillator in sodium mandelate.

The bisignate feature at 3536 cm^{-1} in the CD spectrum of dimethyl tartrate is, admittedly, strongly suggestive of coupled-oscillator behavior, i.e., that the second term in eq 1 is completely dominant over the first. Clearly, there are two oppositely signed peaks of roughly the same intensity;[3] there may be some cancellation due to overlapping of the bands, in which case the apparent magnitude of the observed CD spectrum is not only dependent on the rotational strengths of the individual bands, but also intimately related to the energy splitting between them.[8] Unfortunately, it is difficult to establish by an independent method what the splitting is between the (+) and (−) states. We have been unable to distinguish two bands in the infrared absorption spectrum and we were unable to obtain useful Raman polarization data, such as were used in the interpretation of the CH-stretching CD of tartaric acid.[1] Keiderling and Stephens[3] deduced a vibrational splitting of 3 cm^{-1} from the observed CD spectrum and the rotational strengths calculated on the basis of a coupled-oscillator model. They compared this with values calculated on the assumption that the splitting was due to dipole–dipole interaction; the calculated splitting is, of course, geometry dependent and the maximum value obtained was 1.2 cm^{-1}.[3]

However, if we assume that the intrinsic rotational strength of each OH local oscillator in dimethyl tartrate has a value close to that which we find for methyl mandelate, $R \cong 2 \times 10^{-43}$ esu^2 cm^2, we should expect the first term in eq 1 to make a substantial contribution to the OH rotational strength of dimethyl tartrate and would expect to see either a monosignate CD spectrum as in the CH region of tartaric acid, or, at least, a strongly distorted bisignate feature. Clearly, this expectation is at variance with the observations,[3] and this causes us to question the coupled-oscillator explanation of the dimethyl tartrate spectrum.[3]

One could explain the bisignate feature in the dimethyl tartrate spectrum in terms of two molecular species, e.g., structures I and III, present in roughly equal concentrations,

III
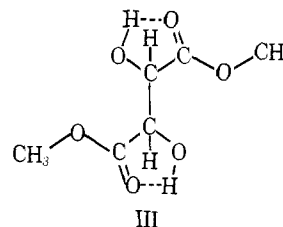
if the rotational strengths associated with structure I were opposite in sign but similar in magnitude to that associated with structure III. Indeed, Barron, by the independent method of Raman optical activity spectroscopy, concludes that dimethyl tartrate has "two or more conformers . . . present in significant proportions".[9] Also, one would expect these two structures to have slightly different OH-stretching frequencies which would account for the apparent splitting. Note that the angle of the OH bond relative to the asymmetric center differs by approximately 120° between the dimethyl tartrate conformations I and III, leading to roughly mirror image geometries for the HC*−OH entities in the two cases. It is possible then that the two conformations could contribute to the OH stretch CD with opposite sign. The fact that the hydrogen bonding in I is in a six-membered ring while that in III is in a five-membered ring could account for a large enough splitting in the OH frequencies such that the oppositely signed CD intensities from the two conformations would not completely null each other.

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