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Conformations of Tartaric Acid and Its Esters

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Abstract: Vibrational circular dichroism (VCD) spectra of optically active tartaric acid, dimethyl tartrate, diethyl tartrate, and diisopropyl tartrate were measured in the 1600–900-cm^{-1} region in different solvents and at different concentrations. It is found that VCD associated with the C*–O stretching vibrations is identical in all the molecules and reveals a configurational correlation. Ab initio calculations of the energies of several conformers of optically active tartaric acid indicated that the trans COOH conformation with hydrogen bonding between the OH and C=O groups attached to the same chiral carbon is of lowest energy. The experimental absorption and VCD intensities of the C*–O stretching vibrations could then be explained in terms of the trans COOR conformer by allowing for the charge flow along the C*–C* bond.

Vibrational circular dichroism (VCD) is a recently developed spectroscopic tool that has potential for revealing new stereochemical information in chiral molecules. Since each of the $(3N - 6)$ VCD bands of a chiral molecule is likely to provide configurational and conformational information, it is anticipated that VCD may ultimately be used to determine the three-dimensional structure of an entire molecule.

VCD in the C–H stretching region of optically active tartaric acid (**1**) in D_2O solution was reported by Moscowitz and coworkers.[1] They suggested that the observed VCD is readily attributable to the chirality of the individual halves of the molecule rather than to the coupling between them. The interpretation of VCD of optically active dimethyl tartrate (**2**), in the O–H and the C=O stretching regions, has been the subject of discussion for quite some time. Keiderling and Stephens found[2] bisignate VCD associated with the O–H stretching vibrations of (2*R*,3*R*)-**2**. Since bisignate VCD is a characteristic feature predicted by the coupled oscillator theory[3] and a coupled oscillator model calculation for an assumed conformation reproduced the experimental signs, they suggested that the coupled oscillator phenomenon is responsible for the observed O–H stretching VCD. However, Marcott et al. suggested[4] that the bisignate VCD in the O–H stretching modes of **2** is probably due to two different hydrogen-bonded conformers: one with internal hydrogen bonding between OH and C=O groups from the opposite halves of the molecule and another with internal hydrogen bonding between these groups attached to the same chiral carbon atom. Su and Keiderling carried out further VCD measurements[5,6] in the O–H stretching region by varying the temperature and also in the C=O stretching region. On the basis of these, VCD measurements on partially deuteriated dimethyl tartrate, VCD measurements on the dimethyl ester of malic acid, and additional coupled oscillator model calculations on **2**, they disagreed with the conclusions of Marcott et al.[4] and concluded that the observed VCD features in the O–H and C=O stretching regions of **2** can be explained by the coupled oscillator mechanism if **2** is assumed to have a conformation with the hydroxyl groups trans to each other. Two different possibilities were suggested for internal hydrogen bonding: one with hydrogen bonding between OH and OCH_3 groups from opposite halves of the molecule and another with hydrogen bonding between OH and C=O groups attached to the same chiral carbon. Sugeta and co-workers measured[7] VCD in the O–H stretching region of methyl 3-hydroxybutyrate and found bisignate VCD associated with the O–H stretching modes. Since there is no possibility for the coupled oscillator mechanism for the O–H stretching motion in this molecule, they suggested that the bisignate OH stretching VCD in **2** is due to two conformers, as suggested earlier by Marcott et al.[4] The ring current model interpretation[8] by Nafie and co-workers required the hydrogen bonding between the OH and C=O groups attached to the same chiral carbon. The choice between the trans OH and trans COOR conformations is probably unimportant for the ring current interpretation,[8] although the trans OH conformation was preferred.

Although the theoretical VCD models used in the interpretation of O–H and C=O stretching VCD in **2** predict the experimental VCD signs correctly, the conformations assumed in these approximate model calculations are not verified by other independent techniques. Most importantly, from ^{13}C NMR studies on **1** in aqueous solutions, Ascenso and Gil concluded[9] that the dominant conformation around the C*–C* bond is the one with the two COOH groups trans to each other. From the similarities in chemical shifts, Hasan suggested[10] that the two $COOCH_3$ groups in **2** are also trans to each other. Hargreaves and Richardson[11] concluded that the optical rotation of tartaric acid can be explained if rigid intramolecular hydrogen-bonded molecular conformations are assumed to be present in solution. A trans COOH orientation with hydrogen bonding between hydroxyl and C=O groups from opposite halves of the molecule was presumed to be favored. From Raman optical activity (ROA) studies, Barron had also suggested[12] the trans COOR conformation.

The purpose of this paper is to report new VCD spectral data for optically active **1**, **2**, diethyl tartrate (**3**), and diisopropyl tartrate (**4**) and ab initio predictions of minimum-energy conformations for **1** with a view (1) to present a correlation between VCD and configuration and (2) to provide further understanding of the conformations in tartaric acid and its esters.

Configurational Correlation

The VCD spectra of **1**–**4** were measured as DMSO, CCl_4 (or $CDCl_3$), and CS_2 solutions in the region below 1600 cm^{-1} and some of these are shown in Figures 1–4. The VCD spectrum in this region of **1** in DMSO-**d$_6$** solvent and of **2** in CS_2 solvent have been reported before[6,13] in a different context. The spectra of all four molecules in DMSO solvent contain three VCD bands located at about 1200, 1140, and 1090 cm^{-1}. The position of the band at 1090 cm^{-1} is somewhat uncertain due to the overlapping absorption from the solvent. In CCl_4 and CS_2 solvents, this region is transparent and the corresponding band is located at ~1090 cm^{-1} for **2** and **3**. In the case of **4**, a band at 1105 cm^{-1}, presumed

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(1) Sugeta, H.; Marcott, C.; Faulkner, T. R.; Overend, J.; Moscowitz, A. *Chem. Phys. Lett.* **1976**, *40*, 397–398.

(2) Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1977**, *99*, 8061–8062.

(3) Holzwarth, G.; Chabay, I. *J. Chem. Phys.* **1972**, *57*, 1632–1635.

(4) Marcott, C.; Blackburn, C. C.; Faulkner, T. R.; Moscowitz, A.; Overend, J. *J. Am. Chem. Soc.* **1978**, *100*, 5262–5264.

(5) Su, C. N.; Keiderling, T. A. *J. Am. Chem. Soc.* **1980**, *102*, 511–515.

(6) Su, C. N. Ph.D. Thesis, University of Illinois at Chicago Circle, Chicago, 1980.

(7) Nakao, Y.; Sugeta, H.; Kyogoku, Y. *Chem. Lett.* **1984**, 623–626.

(8) Freedman, T. B.; Balukjian, G. A.; Nafie, L. A. *J. Am. Chem. Soc.* **1985**, *107*, 6213–6222.

(9) Ascenso, J.; Gil, V. M. S. *Can. J. Chem.* **1980**, *58*, 1376–1379.

(10) Hasan, M. *Org. Magn. Reson.* **1980**, *14*, 309–311.

(11) Hargreaves, M. K.; Richardson, P. J. *J. Chem. Soc.* **1957**, 2260–2271.

(12) Barron, L. D. *Tetrahedron* **1978**, *34*, 607–610.

(13) Polavarapu, P. L. In Fourier Transform Infrared Spectrosc. **1985**, *4*, 61–95.

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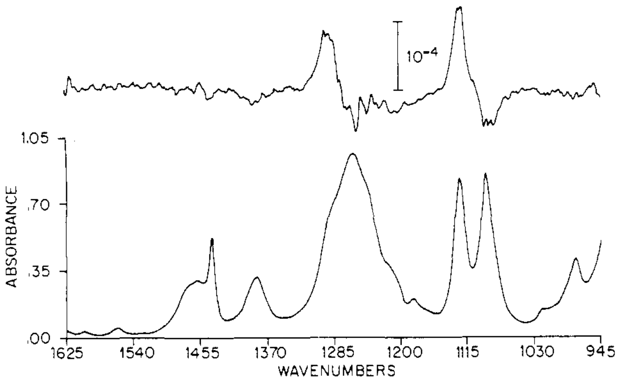

Figure 1. Vibrational absorption (bottom) and circular dichroism (top) for the (2*R*,3*R*) enantiomer of dimethyl tartrate in $CDCl_3$ (0.2 M). VCD was obtained as half of the difference between the raw VCD of enantiomers.

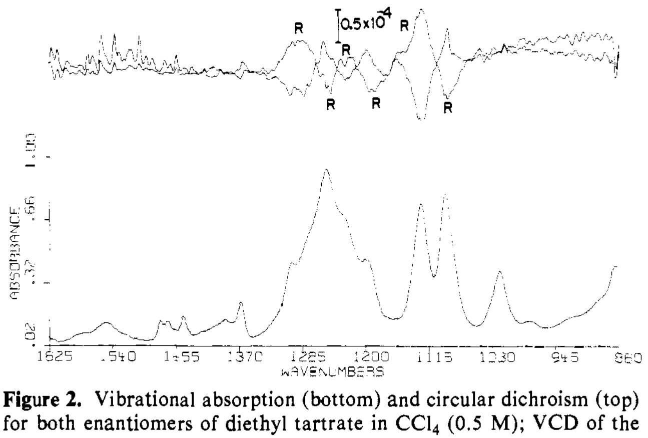

Figure 2. Vibrational absorption (bottom) and circular dichroism (top) for both enantiomers of diethyl tartrate in CCl_4 (0.5 M); VCD of the (2*R*,3*R*) enantiomer is labeled with R. The VCD spectra were obtained by subtracting the raw VCD of the racemic mixture from those of the individual enantiomers.

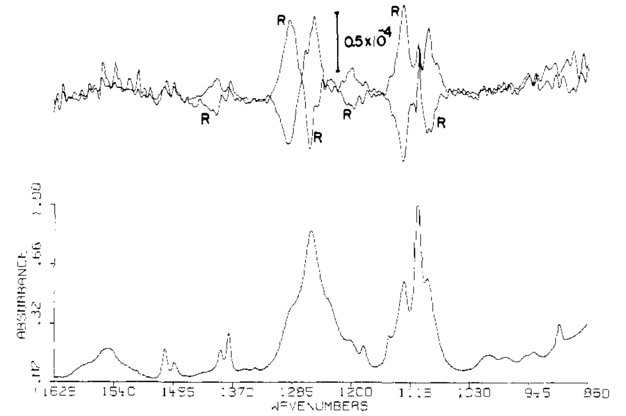

Figure 3. Vibrational absorption (bottom) and circular dichroism (top) for both enantiomers of diisopropyl tartrate in CCl_4 (0.2 M); VCD of the (2*R*,3*R*) enantiomer is labeled with R. The VCD spectra were obtained by subtracting the raw VCD of the racemic mixture from those of the individual enantiomers.

to be originating from the isopropyl groups, overlaps with the 1090-cm^{-1} band. The band at 1140 cm^{-1} in DMSO solvent is shifted to ~1125 cm^{-1} in CCl_4 and CS_2 solvents for **2**–**4**.

Of all the VCD bands seen for these molecules in the 1600–900-cm^{-1} region, those at about 1125 (or 1140 in DMSO solvent) and 1090 cm^{-1} are found to be consistent among all the molecules. The VCD signs associated with these bands also remain unaffected as the solvent is changed from DMSO to CCl_4 and CS_2. They are also unaffected as the concentration is varied over a wide range. VCD of **2** measured in CS_2 (0.01 M) on our instrument was found to be identical with the one measured by Su.[6] The insensitivity of both absorption and VCD of these two bands (which are assigned to C*–O stretching motions; see later) to the concentration and solvent, and hence intermolecular interactions, is taken to imply that either the conformational mobility around C*–C* is absent or alternately these two bands are insensitive to conformational mobility around the C*–C* bond. The absorption for **2**–**4** in CCl_4 and CS_2 solutions at ~1250 cm^{-1} is sensitive to the concentration. The absorption features around 1250 cm^{-1} are better resolved in dilute solutions but become broad in concentrated solutions. These band features are shifted to ~1200 cm^{-1} in DMSO for **2**–**4**. Based on the observation that Hollenstein et al.[14] identified the COH bending vibration in $CH_2OHCOOCH_3$ to occur at 1275 cm^{-1}, these concentration- and solvent-dependent variations reflect the intermolecular interaction effects, just as do the corresponding variations in the O–H stretching region. It should be noted that the C–O stretching vibration of the C–O–C group in **2**–**4** may also be present in the broad envelope at ~1250 cm^{-1}, since Hollenstein et al.[14] suggested that the corresponding vibration in $CH_2OHCOOCH_3$ appears at ~1235 cm^{-1}. Regardless of the predominant conformations around the C*–C* bond (see next section), in **1**–**4** the data presented here provide a useful relation between the absolute configuration and VCD signs. For the (*R*) configuration, VCD signs of the ~1125- and ~1090-cm^{-1} bands are positive and negative, respectively.

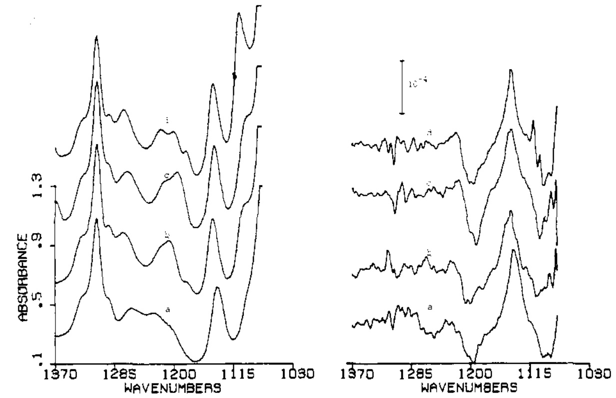

Figure 4. Vibrational absorption (left) and circular dichroism (right) of the (2*R*,3*R*) enantiomers of (a) tartaric acid, (b) dimethyl tartrate, (c) diethyl tartrate, and (d) diisopropyl tartrate in DMSO (0.5 M). VCD was obtained as half of the difference between the raw VCD of the enantiomers. The intense absorption at 1310 cm^{-1} and the two weak features around it, at 1331 and 1294 cm^{-1}, are due to the solvent.

Theoretical Analysis

On the basis of infrared investigation of **1** in KBr disks, Kozhevina and co-workers suggested[15] that the absorption bands at 1135 and 1090 cm^{-1} are assignable to the C*–O stretching motions. From the Raman spectra of metal tartrates in aqueous solutions Kaneko and co-workers also suggested[16] that the bands at 1123 and 1070 cm^{-1} are assignable to the C*–O stretching motions. Further, they concluded that since the 1123-cm^{-1} band is polarized and the 1070-cm^{-1} band is depolarized, these can be assigned respectively to the symmetric and antisymmetric combinations of C*–O stretching motions. These assignments compare favorably with the identification of the alcoholic C–O stretching vibration at 1090 cm^{-1} in $CH_2OHCOOH$ and at 1097 cm^{-1} in $CH_2OHCOOCH_3$ by Hollenstein et al.[14] On the basis of these previous studies[14-16] we presume that the bands of **1**–**4** at about 1140 and 1090 cm^{-1} in DMSO solvent (and at about 1125 and 1090 cm^{-1} in CCl_4 and CS_2 solvents) are assignable respectively to the symmetric and antisymmetric C*–O stretching motions. If these motions are assumed to be localized, then it is sufficient to consider the segment O–C*–C*–O with C_2 symmetry for VCD analysis. Further if it is assumed that the two C*–O groups are

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[14] Hollenstein, H.; Schar, R. W.; Schwizgebel, N.; Grassi, G.; Günthard, Hs. H. *Spectrochim. Acta, Part A* **1983**, *39A*, 193–213.

[15] Kozhevina, L. I.; Skryabina, L. G.; Tselinskii, Yu-K. *Zh. Prikl. Spektrosk.* **1980**, *33*, 1090–1096.

[16] Kaneko, N.; Kaneko, M.; Takahashi, H. *Spectrochim. Acta, Part A* **1984**, *40A*, 33–42.

independent (mechanically as well as electronically), then during these C*–O stretching vibrations there would not be any charge flow along the C*–C* bond, and the VCD intensity, represented by rotational strength, is given for symmetric and antisymmetric stretching motions (with frequencies ν_s and ν_a, respectively) of the C*–O groups in the O–C*–C*–O segment with a counterclockwise (CCW) dihedral angle (vide infra) as follows:[17]

$$R_s = \frac{h}{8\pi c}\left[eq_{C\text{-}O} + \frac{\partial eq_{C\text{-}O}}{\partial R_{C\text{-}O}} r^{\circ}{}_{C\text{-}O}\right]^2 \left(\frac{\partial R_{C\text{-}O}}{\partial Q_s}\right)^2 [4 \sin\theta \cos\theta (a \sin\phi - b \cos\phi)] \qquad (1)$$

$$R_a = \frac{-h}{8\pi c}\left[eq_{C\text{-}O} + \frac{\partial eq_{C\text{-}O}}{\partial R_{C\text{-}O}} r^{\circ}{}_{C\text{-}O}\right]^2 \left(\frac{\partial R_{C\text{-}O}}{\partial Q_a}\right)^2 [4 \sin\theta \cos\theta (a \sin\phi - b \cos\phi)] \qquad (2)$$

In these equations[17] $eq_{C\text{-}O}$ represents the equilibrium bond charge of the C*–O bond (taken to be equal to the partial charge on the oxygen atom), $R_{C\text{-}O}$ represents the internal coordinate for stretching of the C*–O bond with equilibrium bond length $r^{\circ}{}_{C\text{-}O}$, Q_s and Q_a are normal coordinates for symmetric and antisymmetric motions, and θ and ϕ are angles for projecting the C–O group (corresponding to A_1–B_1 in ref 17) onto the C_2 axis and a principal axis perpendicular to it. The corresponding absorption intensities are given[17] as

$$A_s = \frac{N\pi}{3c}\left[eq_{C\text{-}O} + \frac{\partial eq_{C\text{-}O}}{\partial R_{C\text{-}O}} r^{\circ}{}_{C\text{-}O}\right]^2 \left(\frac{\partial R_{C\text{-}O}}{\partial Q_s}\right)^2 (4 \cos^2\theta) \qquad (3)$$

$$A_a = \frac{N\pi}{3c}\left[eq_{C\text{-}O} + \frac{\partial eq_{C\text{-}O}}{\partial R_{C\text{-}O}} r^{\circ}{}_{C\text{-}O}\right]^2 \left(\frac{\partial R_{C\text{-}O}}{\partial Q_a}\right)^2 (4 \sin^2\theta) \qquad (4)$$

By solving the secular equation for the two stretching modes, noting that there is no kinetic energy coupling between the two C*–O stretching internal coordinates, it can be shown that $\nu_s = (1/2\pi c)[(f_{C\text{-}O} + f_{12})/\mu]^{1/2}$ and $\nu_a = (1/2\pi c)[(f_{C\text{-}O} - f_{12})/\mu]^{1/2}$, where $f_{C\text{-}O}$ is the force constant of the C*–O bond and f_{12} is the interaction force constant for the C*–O stretching internal coordinates. Then the relation for the frequency separation, $\Delta = \nu_s - \nu_a$, in cm^{-1}, and the interaction force constant, f_{12}, in mdyn/Å, becomes

$$\nu_0 \Delta = (f_{12}/\mu) \times 0.17 \times 10^7 \qquad (5)$$

where μ is the reduced mass (in atomic mass units) of C*–O and $\nu_0 = (\nu_s + \nu_a)/2$.

The O–C*–C*–O segment with a 60° CCW dihedral angle corresponds to the trans COOR conformer while that with a 60° clockwise (CW) dihedral angle corresponds to the trans H conformer for (2*R*,3*R*) enantiomers of **1–4**. VCD and absorption intensities predicted by eq 1–4 for these two dihedral angles are shown in Figure 5. The observed VCD pattern, with positive VCD for the symmetric C*–O stretching and negative VCD for the antisymmetric C*–O stretching motions in the (2*R*,3*R*) enantiomers of **1–4**, matches with that predicted by eq 1 and 2 for these enantiomers assuming a trans COOR conformation. The predicted VCD sign pattern for the trans H conformer is opposite to that observed. Thus it is reasonable to assume that for **1–4** in solution the trans COOR conformer is dominant. If the C*–O stretching frequencies are insensitive to the conformation around the C*–C* bond, the presence of some trans H conformer cannot be ruled out. Similarly the presence or total absence of trans OH conformer cannot be deduced from the VCD associated with C*–O stretching modes because, for a O–C*–C*–O segment with trans C*–O groups, zero VCD would be predicted due to the presence of a plane of symmetry.

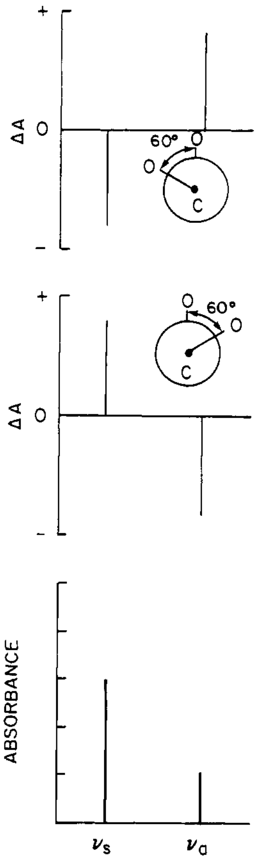

Figure 5. Theoretical vibrational absorption (bottom) and circular dichroism (top) for the symmetric and antisymmetric stretching vibrations of the O–C*–C*–O segment with C_2 symmetry. Absorption and circular dichroism intensities for these two modes are shown on an arbitrary scale.

At this point in the interpretation the experimental observations and theoretical predictions from eq 1–4 are in poor qualitative agreement. The absorption intensities for the 1125- and 1090-cm^{-1} bands in CCl$_4$ and CS$_2$ solvents are nearly equal, whereas eq 3 and 4 predict the ratio of the intensity of the symmetric to the antisymmetric C*–O stretching motion to be $\cot^2\theta$, which for a O–C*–C*–O segment with a 60° dihedral angle would be ~3.

For the trans OH conformer, the antisymmetric C*–O stretching mode will have a nonzero absorption intensity while the symmetric C*–O stretching mode will have zero intensity. If both trans COOR and trans OH conformers are present and their C*–O stretching bands appear at about the same position, then the antisymmetric C*–O stretching mode would have more intensity than that predicted for a single conformer, thereby making the ratio of symmetric to antisymmetric C*–O stretching absorption intensity much less than 3. Since the two absorption bands under consideration have nearly equal intensities (Figures 1–3), the experimental data do not rule out the existence of a trans OH conformer in solution.

In deriving eq 1–4, it is assumed[17] that the two C*–O groups are mechanically and electronically independent and, therefore, that there is no charge flow along the C*–C* bond. If we include the charge flow along the C*–C* bond, we predict nearly equal absorption intensities for the two C*–O stretching vibrations (vide infra). Then the uncertainty at this point rests in determining if the equal intensities observed for C*–O stretches are due to one or more of the following possibilities: (a) the presence of trans OH conformer, (b) the charge flow along the C*–C* bond, and (c) the coupling of C*–O motions with some other atomic motions.

Ab Initio Calculations

In order to overcome the ambiguities mentioned above we have carried out ab initio studies of equilibrium conformations of

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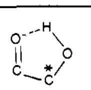
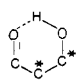
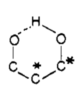
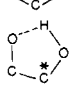
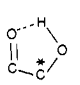
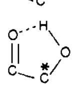
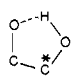
(17) Polavarapu, P. L. *J. Chem. Phys.* **1986**, *85*, 6245.

Table I. Ab Initio Predictions of the Relative Energies of Various Conformers of Optically Active Tartaric Acid

conformation about the C*–C* bond	type of intramolecular H bonding	relative energy, kcal/mol STO-3G/ STO-3G	3-21G/ STO-3G	6-31G/ STO-3G	6-31G/ 6-31G
trans COOH		0[a]	0[b]	0[c]	0[d]
		0.5	7.6	8.5	7.7
		0.6	6.9	7.8	
		1.9	4.6	4.2	
trans OH		3.2	5.3	5.4	5.4
trans H		2.9	8.6	8.5	
		2.9	9.4	8.6	

[a] The SCF energy of this conformer is −596.13244 hartrees. [b] The SCF energy of this conformer is −600.77528 hartrees. [c] The SCF energy of this conformer is −603.85550 hartrees. [d] The SCF energy of this conformer is −603.87922 hartrees.

tartaric acid. First we computed the molecular structure that minimizes the total SCF energy for each of the conformations given in Table I employing the minimal STO-3G basis. This basis has correctly predicted[18] the equilibrium structure of ascorbic acid as measured by X-ray diffraction. Similarly, computations[19] on glycolic acid with STO-3G basis were found to give qualitatively the same results as those obtained with larger basis sets. The relative energies of all conformers investigated are presented in the column of Table I designated STO-3G/STO-3G. To gauge the effect of employing larger basis sets we have then recomputed the energy of each conformer in two larger and presumably more accurate split-valence basis sets, 3-21G and 6-31G, maintaining the STO-3G optimized structures. These values are given in Table I with labels 3-21G/STO-3G and 6-31G/STO-3G. It can be seen from Table I that the same conformation is predicted to be the most stable one and in fact its stability relative to the others is greatly increased. The relative energies among the higher energy forms bear little resemblance to the STO-3G/STO-3G results. The 3-21G/STO-3G and 6-31G/STO-3G values are, however, in quite good agreement with each other.

We have also computed the optimized structures of three conformers of particular interest employing 6-31G basis. These relative energies (listed in Table I with label 6-31G/6-31G) are clearly very close to those given by the 3-21G and 6-31G calculations at STO-3G structures.

From these extensive calculations it appears that the lowest energy conformation of tartaric acid is stabilized by intramolecular interactions at the level of split-valence basis sets. This stabilization is not particularly sensitive to the starting structures employed as is evident from the last three columns of Table I. All four series of calculations concur that the trans COOH conformation is energetically favored. With regard to the intramolecular hydrogen-bonding effects, STO-3G/STO-3G predictions are *contradicted* by 3-21G/STO-3G as well as 6-31G/STO-3G predictions. The latter two predictions indicate that for the trans COOH conformer the intramolecular hydrogen bonding between the OH and C=O groups attached to the same chiral carbon is preferred over the other intramolecular hydrogen-bonding schemes by 4–8 kcal/mol.

Interpretation of Observed Intensities

From the above observations it appears best to consider that for **1** the trans COOH conformation is the most stable one and that the trans OH and trans H conformers are unlikely to exist. Since VCD features for the same configuration of **1**–**4** are identical, it is reasonable to suggest that the same trans COOR conformation is preferred for **2**–**4**. Then the discrepancy in the observed absorption intensities noted earlier might be due to the charge flow along the C*–C* bond or the coupling of C*–O stretching motions with some other motions. The influence of charge flow along the C*–C* bond on absorption and VCD intensities is analyzed here. The procedure for the following formulation is similar to the one used earlier,[17] except that the two C*–O groups are no longer considered to be electronically independent.

To eliminate the complexity in presenting the equations, we assume that the fixed partial charge (FPC) contributions to intensities are smaller than the charge flow contributions. Then ignoring the FPC terms, the ratio of absorption intensities is found to be

$$\frac{A_a}{A_s} = \left[\left(2\frac{\partial eq_{C-O}}{\partial Q_a}r^\circ{}_{C-O}\sin\theta\right)^2 + \left(\frac{\partial eq_{C-C}}{\partial Q_a}r^\circ{}_{C-C}\right)^2 + \frac{\partial eq_{C-O}}{\partial Q_a}\,\frac{\partial eq_{C-C}}{\partial Q_a}r^\circ{}_{C-O}a'\sin\theta\right] \Bigg/ \left(2\frac{\partial eq_{C-O}}{\partial Q_s}r^\circ{}_{C-O}\cos\theta\right)^2 \tag{6}$$

where $a' = 8(R^\circ{}_{C_1{}^*y}\cos\phi + R^\circ{}_{C_1{}^*z}\sin\phi)$, with $\mathbf{R}^\circ{}_{C_1{}^*}$ representing equilibrium coordinates of $C_1{}^*$ in the principal coordinate system.[17] The gradients of q_{C-O} correspond to those of $q_{A_1-B_1}$ in the notation of ref 17.

This equation (which gives the same result as eq 3 and 4, when $\partial q_{C-C}/\partial Q_a = 0$) can be put in a better perspective if we assume that $\partial q_{C-O}/\partial Q_a \simeq \partial q_{C-C}/\partial Q_a \simeq \partial q_{C-O}/\partial Q_s$. Then we find that $A_a/A_s \simeq {}^4/_3$, which is in better agreement with the observed intensities than the 1:3 ratio predicted by eq 3 and 4.

We also find that $\partial q_{C^*-C^*}/\partial Q_a$ does not contribute to the VCD intensities, since the directional components accompanying this term cancel. Therefore we obtain $R_a/R_s \simeq -1$, even when charge flow along the C*–C* bond is explicitly considered.

From this analysis it appears that if we allow for the charge flow along the C*–C* bond and if charge flow contributions are considered to be more important than FPC terms, then the observed VCD and absorption intensities can be explained satisfactorily. It should be emphasized that we have not considered the possible coupling of these C*–O motions with other motions in the molecule, and such considerations would be needed to explain the observed intensities more accurately.

Conclusions

The observed VCD associated with the C*–O stretching vibrations, in conjunction with approximate theoretical models, can be interpreted in favor of the trans COOR conformation. The trans OH conformation, however, could not be ruled out. The ab initio calculations at the 6-31G level strongly suggested the predominance of the trans COOR conformer. These calculations also suggest that only the internal hydrogen bonding between the C=O and OH groups attached to the same chiral carbon is energetically favored. With this conformational information, the observed VCD and absorption intensities can be satisfactorily understood if the charge flow contribution is assumed to be dominant and the charge flow along the C*–C* bond is nearly equal to that along the C*–O bond.

The interpretation is based on the assumption that the C*–O stretching band assignments are valid. From the experimental separation of the two bands (≃35 cm^{-1}) and their band positions, eq 5 predicts the interaction force constant f_{12} to be ≃+0.16 mdyn/Å. This value is well within the range expected for

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stretching motions of C*–O groups (in the directly connected O–C*–C*–O segment). This gives further confidence, although is not a proof, that the C*–O stretching band assignments are reasonable.

In DMSO solvent, the C═O stretching region shows two absorption bands (not shown here) as opposed to one in dilute CCl_4 solutions. Despite this strong indication for intermolecular hydrogen bonding in DMSO solvent, VCD associated with the assumed C*–O stretching bands remains unaffected by the solvent. Then it may be assumed that VCD associated with the C*–O stretching bands is insensitive to intermolecular interactions.

The trans COOR conformation can also explain the VCD associated with the O–H (and C═O) stretching bands,[5,6] if it is recognized that the absorption bands associated with the two O–H (and C═O) stretching bands were not resolved, and therefore the identification of symmetric and antisymmetric components is quite uncertain. In fact eq 5 predicts that if the separation of the O–H stretching bands is of the order of 1 cm^{-1}, then f_{12} would be of the order of 0.002 mdyn/Å, and for such small interaction force constant the sign (which determines whether the symmetric or antisymmetric band is the higher frequency component) is difficult to determine. Viewing in another way, if the trans COOR conformation, as predicted by the present 6-31G calculations, is taken to be predominant, then eq 1, 2, and 5 and Figure 5 determine the f_{12} for O–H stretches to be $\simeq +0.002$ mdyn/Å and that for C═O stretches to be $\simeq +0.007$ mdyn/Å. This approach then makes VCD useful for deducing the signs of interaction force constants experimentally.

It appears that tartaric acid and its esters are unusual molecules for VCD analysis since VCD bands associated with the O–H, C═O, and C*–O stretching motions have bisignate features that arise from the symmetric and antisymmetric motions. There are also bisignate features at ~1250 cm^{-1} where, as mentioned earlier, the C*–O–H bending vibrations and C–O–C stretching vibrations are likely to appear. More experimental studies to identify these bands and to interpret the corresponding VCD are in progress.

Experimental and Computational Details

All samples were obtained commercially and the optical rotations specified by the supplier were verified. VCD and absorption spectra were recorded at 4-cm^{-1} resolution on a FTIR spectrometer as described elsewhere.[13] VCD measurements were made, in most of the cases, for both enantiomers as well as for the racemic mixture (which was prepared by mixing equal amounts of the enantiomers). The raw VCD of the racemic mixture was then subtracted from those of the enantiomers. In the figures which contained the VCD for both enantiomers, showing the mirror image quality, spectra were obtained in this manner and usually contain more noise. VCD spectra with a better signal-to-noise ratio are obtained by taking half of the difference between the raw VCD of the enantiomers. In the figures which contained VCD for only one enantiomer, the spectra were obtained in this manner.

Ab initio calculations were carried out by using the GAUSSIAN-80 and GAUSSIAN-82 programs[20,21] and the default analytical-gradient procedure[22] for optimizing molecular structures that they contain. Standard STO-3G,[23] 3-21G,[24] and 6-31G[25] basis sets were employed. In computing the minimum-energy structure of each conformer, all structural parameters were optimized independently, but constraining the molecule to be of C_2 symmetry and the carboxyl groups to be planar. Test calculations showed these two constraints to have virtually no effect on the final results for the conformers studied.

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Registry No. Tartaric acid, 87-69-4; dimethyl tartrate, 608-68-4; diethyl tartrate, 87-91-2; diisopropyl tartrate, 2217-15-4.

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