ethynylbenzotriptycene (−)-**2** is an ideal compound for the CD exciton chirality method.

Similarly, the interchromophoric homoconjugation effect has no influence on the exciton circular dichroism of the bisanthracene **4** and bisnaphthalene **5** compounds. In the case of (+)-**4**, the pattern of the two Cotton effects of positive first and negative second signs around 40×10^3 cm^{-1} which are due to the ^1B_b transition of anthracene chromophores is little affected by variation of the ratio β_{hc}/β_{arom} (Figure 5). When the ratio is 23.7%, the calculated CD spectrum including the weak positive and negative Cotton effects in the ^1L_a transitional region is in good agreement with the observed one (Table III). Similarly, in the case of (+)-**5**, when the ratio β_{hc}/β_{arom} is 20%, good agreement was obtained as shown in Figure 6 and Table III.

From the present calculation results of compounds (+)-**1**, (−)-**2**, (+)-**4**, and (+)-**5**, the resonance integral β_{hc} of the interchromophoric homoconjugation in triptycene systems[16] was estimated to be 20–30% of the resonance integral of a regular aromatic C–C bond (Table III). This value (−0.478 to −0.717 eV) is reasonable in comparison with the previously reported value (−0.916 eV)[17] and the theoretical value (−0.567 eV) calculated by eq 11.

In conclusion, the SCF-CI-DV molecular orbital calculations including the interchromophoric homoconjugation effect satisfactorily reproduced the CD spectra of the chiral triptycenes and related compounds, establishing the absolute stereochemistries in a quantitative manner.

Acknowledgment. This work was supported in part by grants from the Ministry of Education, Science, and Culture, Japan (No. 447018), and the Japan Association of Chemistry.

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Conformation of Dimethyl Tartrate in Solution. Vibrational Circular Dichroism Results

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Abstract: Data on the temperature dependence of the O–H stretching VCD and the vicinal hydrogen NMR for dimethyl tartrate are interpreted as demonstrations of restricted conformational mobility of this molecule in dilute CCl_4 solution. New VCD for the C=O stretch is presented and is shown to be interpretable with the degenerate coupled oscillator model. Only one rotamer about the central C–C bond is found to be consistent with the observed VCD and NMR data.

Introduction

Vibrational circular dichroism (VCD) is a new technique with great potential for stereochemical analysis of chiral molecules in solution. VCD data have now been shown to be experimentally accessible in a wide variety of systems.[1] The major impediment to the utilization of this data for determination of molecular geometry is development of a reliable method of interpretation. To this end, theories dependent on vibrational analysis have been proposed[2] and applied with limited success.[3]

We have previously used a simple model for VCD, degenerate coupled oscillator (DCO) theory,[3b,4] to interpret the OH stretching VCD in dimethyl tartrate.[5] Our use of this theory follows Holzwarth and Chabay[4] in that we assume that the oscillators are achiral and become optically active only through their coupling. The resultant VCD is bisignate and dependent only on geometrical factors. This assumption ignores the intrinsic optical activity of each oscillator, which is expected to be quite small from evidence we shall give. This interpretation of the OH VCD was subsequently questioned and an alternative explanation proposed that assumed that the intrinsic VCD of the OH groups on two different conformers gave rise to the observed bisignate VCD.[6]

In this paper we present new data on the temperature dependence of the O—H stretching VCD, on the previously inaccessible C=O stretching VCD, and on the ^1H NMR of the vicinal CH groups of dimethyl tartrate. In addition, new VCD data for deuterated dimethyl tartrate and for dimethyl malate is discussed. Coupling of these three results leads us to propose that this molecule has two possible dominant conformers but only one rotamer about the central C-C bond in CCl_4 solution. This then becomes the first application of VCD for stereochemical analysis.

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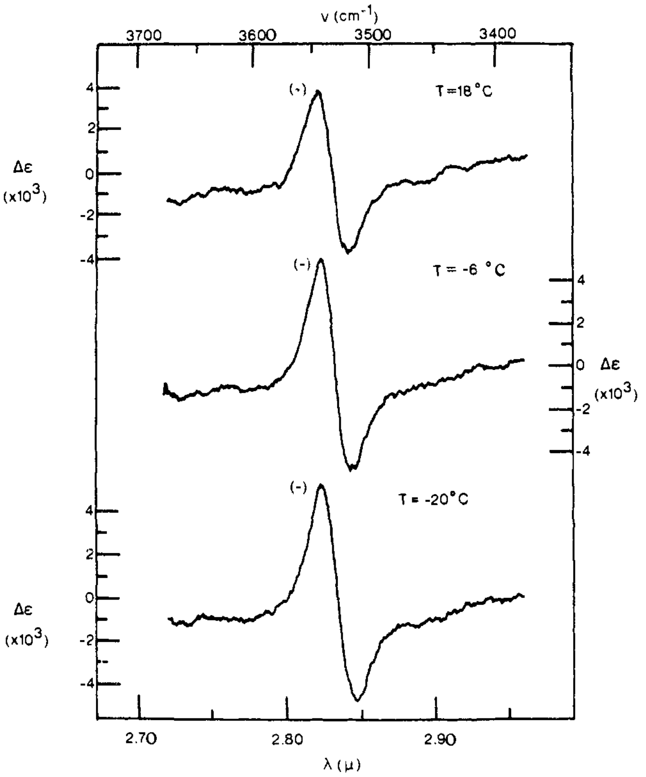

Figure 1. VCD of (−)-(2*S*,3*S*)-dimethyl tartrate 0.010 M in CCl_4 at various temperatures in the OH stretching region: sample path length 0.48 cm; time constant 10 s; resolution 16 cm^{-1}; temperatures as indicated. Spectra are single scans uncorrected for base-line fluctuations.

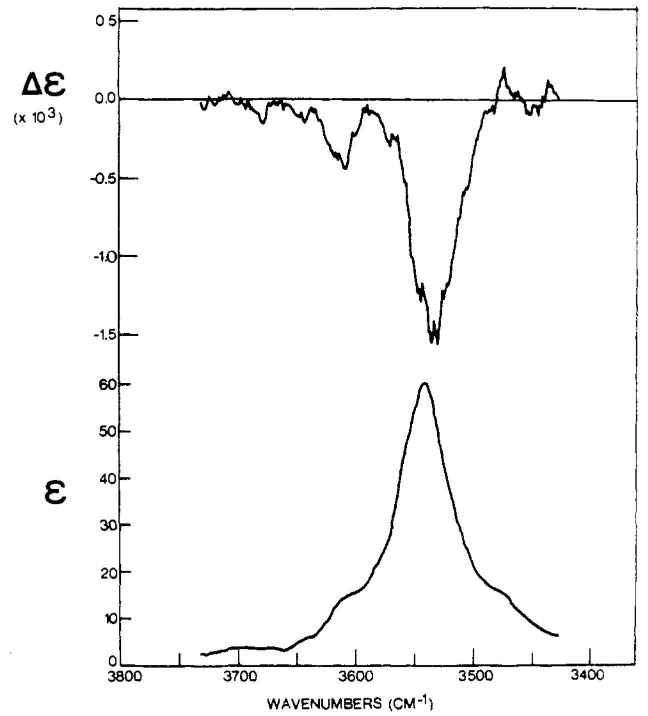

Figure 2. VCD and absorption spectra of the dimethyl ester of (−)-(2*S*)-malic acid 0.042 M in CCl_4 at room temperature in the O–H stretching region: sample path length 0.4 cm; time constant 10 s; resolution 16 cm^{-1}. Original transmission spectrum was digitally replotted in terms of ε and cm^{-1}. VCD was a single scan, digitized and replotted with a base line of the racemic compound, taken under identical conditions, substracted from it.

Experimental Section

The (+)-(2*R*,3*R*) and (−)-(2*S*,3*S*) isomers of dimethyl tartrate were obtained from Aldrich and Norse Chemical Co., respectively, and were studied without further purification as dilute solutions in spectroquality CCl_4. Dimethyl malate was synthesized by the reaction of (*S*)-(−)-malic acid and methanol in HCl-saturated solution and was purified by distillation. VCD spectra were measured on a newly constructed instrument at UICC of a design similar in concept to that previously described.[1c] Major modifications include substitution of an EIMAC 300-W Xe arc lamp for the tungsten lamp, a Cambridge Physical Sciences wire grid polarizer for the $LiIO_3$ polarizer, a Hinds CaF_2 modulator for the ZnSe one, and a CaF_2 focusing lens for the ellipsoidal mirror. A Spectronics HgCdTe detector consisting of two juxtaposed 2 × 2 mm diodes was used in the 6-μ (carbonyl) region and a Spectronics 2 × 10 mm InSb detector was used in the 3-μ (hydroxyl) region. No polarization scrambling was needed. This instrument will be described in detail separately.[7]

Studies of the temperature dependence of the VCD at 2.8 μ (O–H stretch) were done in a jacketed brass cell with Infrasil quartz windows fixed at a 0.48-cm separation. Precooled N_2 gas flowing through the outer jacket provided temperature variation. The difference between sample and the monitoring thermocouple temperature was judged negligible from measurement of sample melting points. NMR spectra of CCl_4 and $CDCl_3$ solutions of dimethyl tartrate were measured as a function of concentration and temperature on a Bruker WP-80 Fourier-transform instrument.

Results and Discussion

The results of the temperature-variation study on the OH stretch VCD for (−)-dimethyl tartrate are shown in Figure 1. It is clear from the figure that, over this range, there is no qualitative change in the bisignate line shape. An increase in the magnitude of both lobes of the VCD signal, correlated with a concurrent increase in the absorption strength, was noted at lower temperatures. Spectra shown are single scans that evidence some degradation in base-line quality and signal-to-noise ratio due to the low-temperature cell. Hence the base line is not flat and the spectra are only of use for comparison with each other. Freezing of the solution prohibited study at lower temperatures. This experiment was also attempted in $CDCl_3$, but both the absorption and VCD spectra obtained were broader and the VCD signals weaker than with CCl_4. A bisignate shape of the same sign was also found for the OH stretch in $CDCl_3$ and was preserved from 20 to −50 °C, but quantitative evaluation was not possible owing to the low signal-to-noise ratio obtained.

This lack of temperature dependence over at least a 40 °C change in temperature for the OH stretch VCD is consistent with the earlier interpretation using the DCO model.[5] In other words, one or more conformations each gives rise to a sigmoidal VCD due to coupling of two OH stretching modes on a single molecule. If the bisignate nature of the VCD were due to the overlap of two oppositely signed signals from two different conformations in solution,[6] the relative heights of the two peaks would change as the conformer populations changed with temperature. This latter interpretation can remain valid only if the conformers are of approximately equal energy.

Exploring this alternate interpretation further, we note that the two conformers proposed by Marcott et al.[6] are composed of either two five-membered or two six-membered hydrogen-bonded rings. These same structural moieties can also exist in dimethyl malate, but only one ring can be formed; hence, a coupled oscillator signal cannot result. (Malic acid is identical with tartaric acid except for the substitution of a hydrogen for one of the hydroxyl groups.) The VCD of the dimethyl ester of (*S*)-(−)-malic acid is shown in Figure 2. Two points are clear from the results: the VCD is single signed and is quite weak. The rotational strength of this band is only -1.9×10^{-43} (esu cm)^2, approximately equal to that found for dimethyl mandelate.[6] (The appropriateness of comparing malate and tartrate structures is reinforced by their near-identical OH stretching frequencies, which are both red shifted from the expected free OH value.)

The VCD of dimethyl malate is inconsistent with the interpretation of ref 6 and further supports a DCO interpretation of the tartrate. In other words, if tartrate forms two different internally hydrogen-bonded rings, then malate would be expected to do likewise. If these rings give rise to oppositely signed VCD, then the dimethyl ester of malic acid must have a bisignate and not single-signed spectrum. The observed narrow OH absorption band and single-signed VCD argue against such an interpretation. (The two different hydrogen-bonding mechanisms would give rise to different OH stretching frequencies.)

Further, if two signals of opposite sign and similar magnitude to that found in the malate were to give rise to a bisignate signal as large as that found in the tartrate molecule, they would have to be separated by at least half their line width. Such a separation is not consistent with the observed tartrate OH absorption line width and VCD line shape. The latter indicates substantial overlap of two oppositely signed effects and implies that the source of the tartrate VCD is of greater rotational strength than that of the malate VCD. This is consistent with the DCO model but inconsistent with the alternative two-conformer interpretation.

An attempt was also made to test the DCO interpretation by deuteration of OH groups. Dimethyl tartrate-d_2 shows a bisignate VCD in the OD stretching region of the same sign as found in the OH for the d_0 molecule. Further, a sample of the same concentration that was ~50% deuterated shows bisignate VCD of the same sign but with ΔA ~¼ the magnitude of the unmixed species in both the OH and OD regions. This is precisely the result expected for a DCO-dominated spectrum where only the d_0 and d_2 molecules give rise to significant VCD. But, if two different conformers caused the bisignate shape, only a halving in ΔA would be expected.

It might be noted that the two lobes of the tartrate OH VCD are not identical.[5] This may be evidence of the intrinsic VCD neglected in our DCO treatment, but may also result from the absorption band shape being asymmetrical and the VCD band shape approximating a derivative of the absorption in direct analogy to the rigid shift theory of MCD.[8] This interpretation is further suggested by the VCD and absorption line shapes at slightly higher concentration. Broadening to higher energy in absorption is accompanied by a broadening and a lowering in intensity of the high-energy lobe of the VCD as would occur in a derivative line shape consistent with a DCO model.

These conclusions are further supported by our measurement of the splitting of the ^{13}C satellites on the ^1H NMR of the vicinal CH's. The hydrogen coupling constant, $^3J_{HH}$, is <2 Hz in dilute CCl_4 or $CDCl_3$ solution over a range of 50-7 °C. At lower temperatures, line broadening prevents determination of $^3J_{HH}$. By comparison to applications of the Karplus relationship to similar systems,[9] we conclude that the vicinal CH's in the dominant conformer are in a gauche orientation. At high concentrations $^3J_{HH}$ increased to >5 Hz. This is as expected due to the mixture of conformers that would accompany the intermolecular hydrogen bonding evident in these solutions. These NMR results restrict the rotameric conformation about the central C-C bond to two possibilities: CH bonds gauche but with the C-O bonds to the hydroxyl groups either trans or gauche. The VCD results further limit this choice.

In the carbonyl stretching region we find a single absorption peak and a bisignate VCD opposite in sign to the OH VCD (Figure 3). This is one of the first reports of VCD at energies below 2000 cm^{-1}.[10] The poor signal-to-noise ratio in these spectra is due to low efficiencies of both the light source and the HgCdTe detector at 6 μ. The VCD are completely reproducible qualitatively, but the quantitative value of $\Delta\epsilon$ may be in error by more than ±50%.

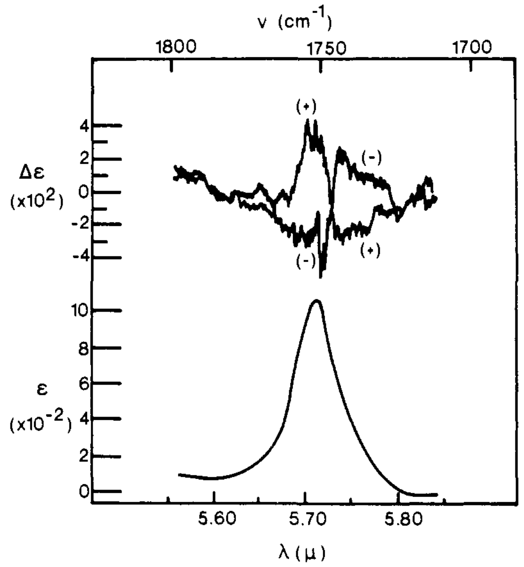

Figure 3. VCD and absorption spectra of (+)-(2*R*,3*R*)- and (−)-(2*S*,3*S*)-dimethyl tartrate 0.013 M in CCl_4 at room temperature in the C=O stretching region: sample path length 0.05 cm; time constant 30 s; resolution 10 cm^{-1}. Original transmission spectrum was replotted in terms of ϵ. VCD spectra are single, sequential scans uncorrected for base-line fluctuation. The base line can be taken as the sum of (+) and (−) spectra.

To interpret the VCD, we have calculated the DCO effects expected in the O—H and C=O bands for various dimethyl tartrate conformations using

$$R_{\pm} = \mp \frac{\pi\nu}{2c}(\mathbf{T}_{ab}\cdot\boldsymbol{\mu}_a \times \boldsymbol{\mu}_b)$$

where the upper signs give the rotational strength, R_+, of the symmetric combination of stretches.[4] Here, $\mathbf{T}_{ab}$ is the vector from $\boldsymbol{\mu}_a$ to $\boldsymbol{\mu}_b$, the two dipole oscillators, and π, ν, and c have their usual meanings.

These conformations were constrained to have the vicinal CH's be gauche. The hydroxyl and ester group orientations were determined by forming the shortest possible intramolecular hydrogen bonds to either the ether or the carbonyl oxygens of the ester.[5,6,11] In most cases, the $C_4'O_5$-$C_3O_1O_2$ (Figure 4) atoms on each half of the molecule were approximately coplanar.[12] In the DCO model, only two of these conformers can reproduce the observed VCD sign patterns for both the O—H and C=O stretches. Both conformers are variations of only one rotamer about the C-C bond which has trans hydroxyl groups and gauche ester groups (Figure 4a). One conformer (Figure 4b) has hydrogen bonding to the ester oxygen of the opposite half of the molecule forming fused six-membered rings[5] while the other (Figure 4c) has hydrogen bonding to the carbonyl oxygen on the same half of the molecule forming linked five-membered rings.[6]

The results of DCO calculations with these two conformers are in Table I.[13] The coordinates of the O—H and C=O dipoles were generated from molecular internal coordinates. Then the relative angles[14] were varied ±10° to estimate the sensitivity to geometry. The magnitude of μ was determined from the integrated absorption spectrum and T_{ab} taken between the centers of mass of the two dipoles. The calculated dipolar splitting between the symmetric and antisymmetric bands, $2V$, is strongly dependent on the relative orientation of the dipoles but, over the range of angles tested, often varies in a sense opposite to that of the rotational strength, $R_{\pm}$. The net result is that the line shape corrected calculation, $\Delta\epsilon$, is less sensitive to orientation than is either $R_{\pm}$ or $2V$. Considering the approximate geometries used and the approximate nature of the DCO model and dipolar splitting assumptions, the

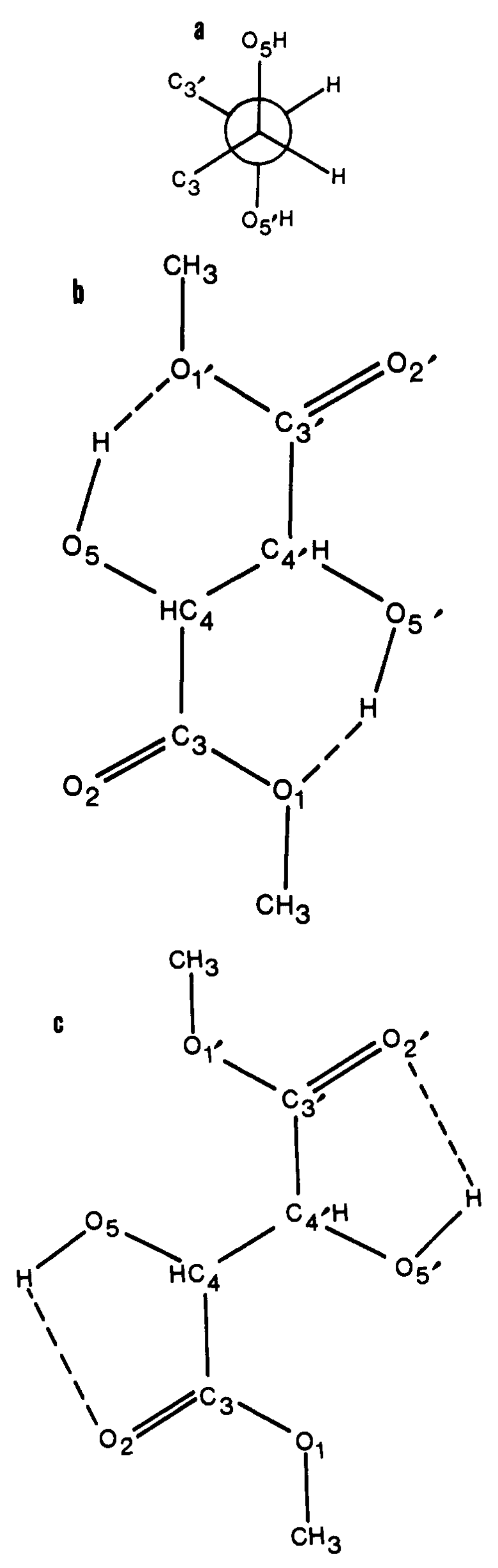

Figure 4. Conformations of dimethyl tartrate consistent with VCD and NMR results: (a) Newman projection showing the C_4-$C_{4'}$ conformation of (2*R*,3*R*); (b) projection on the *x*-*y* plane of the six-membered ring structure; (c) projection on the *x*-*y* plane of the five-membered ring structure. Assumed hydrogen bonding is indicated by dashed line.

agreement with experiment is very good and acts as further support of our interpretation.

Conclusion

Table I. Calculated VCD of (+)-(2*R*,3*R*)-Dimethyl Tartrate in the DCO Model

mode	conformer[a] Figure 4b	conformer[a] Figure 4c	expt[b]
$R_{\pm}$[c]	$\pm 1.9 \times 10^{-42}$	$\mp 1.3 \times 10^{-42}$	
OH $2V$[d]	-1.8	$+2.6$	
$\Delta\epsilon_{obsd}$[e]	$-3.5\ (\pm 0.4) \times 10^{-3}$	$-3.5\ (\pm 0.8) \times 10^{-3}$	-4×10^{-3}
$R_{\pm}$[c]	$+4.5 \times 10^{-42}$	$+4.5 \times 10^{-42}$	
CO[f] $2V$[d]	$+7.0$	$+7.0$	
$\Delta\epsilon_{obsd}$[e]	$+8\ (\pm 4) \times 10^{-2}$	$+8\ (\pm 4) \times 10^{-2}$	3×10^{-2}

[a] Calculated using dipole coordinates generated from molecular internal coordinates corresponding to Figure 4 and assuming the CO-COO group to be planar. Units: $R_{\pm}$ (esu cm)^2; $2V$ (cm^{-1}); $\Delta\epsilon$ (L mol^{-1} cm^{-1}). [b] Estimated from Figures 1 and 3. Error is potentially substantial for CO. Both are uncorrected for slit width effects. [c] Rotational strength: calculated as defined in ref 4, eq 8. [d] Dipolar splitting: calculated as defined in ref 14, eq 7 and 8. [e] Value of $\Delta\epsilon$ for the higher energy component. The number in parentheses is the range of values calculated for change of ±10°. [f] The geometry of the C=O group is the same in both conformations.

In summary, we have presented new data on the dimethyl tartrate OH VCD temperature and deuteration effects, the NMR coupling constants, and the C=O VCD that are consistent with the DCO interpretation. Although it may be maintained that the DCO mechanism is not proven in an absolute sense, we feel that the alternate explanation[6] is inconsistent with the above data and with the dimethyl malate OH VCD for the reasons discussed previously and hence has become highly unlikely.

More importantly, with this establishment of the DCO model for interpretation of at least some VCD comes the possibility of stereochemical analysis with a simple model. We have used VCD to predict the dominant conformers of dimethyl tartrate in solution. Our data does not distinguish between the hydrogen-bonding mechanisms 4b or 4c. The apparent restricted motion about the central C-C bond and shorter hydrogen-oxygen bond distance possible with the six-membered rings would favor 4b, but no conclusions are warranted at this time. Our preliminary fixed partial charge calculations with a consistent force field[3c] for these conformers qualitatively agree with the DCO predictions for the C=O bond but are currently unable to adequately mimic hydrogen bonding to reliably calculate the OH VCD.

This system has also been studied by Barron using Raman CID.[15] Unfortunately, owing to the high concentrations used in that work (nearly neat), no comparison can be made. Consistent with our NMR results, he concludes that more than one conformation exists at high concentration.

Acknowledgment. This research was supported by the National Science Foundation (CHE 77-14615), the UICC Research Board, and an HEW Biomedical Research Support Grant (RR07158-02) to UICC. Acknowledgment for partial support is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. The National Science Foundation supported purchase of the NMR. We wish to thank Dr. A. M. Wyrwicz for help with the NMR and Professor P. J. Stephens for early support of this work.

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A Local Mode Description of the CH-Stretching Overtone Spectra of the Cycloalkanes and Cycloalkenes

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Abstract: The overtone spectra of the cycloalkanes, cyclopentane to cyclooctane, and three cycloalkenes (cyclopentene, cyclohexene, and cycloheptene) are measured in the liquid phase up to $\Delta v_{CH} = 7$ for the cycloalkanes and up to $\Delta v_{CH} = 6$ for the cycloalkenes. The principal bands in the cyclopentane and cyclohexane spectra correspond to axial and equatorial CH bonds. We demonstrate that these bands correspond to the properties of the CH bonds in the static limit, and for cyclopentane introduce a possible definition for axial and equatorial bonds. Single bands are observed in cycloheptane and cyclooctane and their structures explained. The overtone bands of the cycloalkenes are principally composed of two peaks, one corresponding to the olefin hydrogens and one corresponding to the methylene hydrogens. The methylene peak shows some doublet structure in cyclopentene and cyclohexene which can be understood on the same basis as in the corresponding saturated molecules. The local mode frequencies and diagonal local mode anharmonicity constants are obtained from an analysis of the spectral data.

I. Introduction

The local mode model has been successfully applied to explain the CH-stretching vibrational overtone spectra of many molecules.[2-5] In this model, the principal features of the spectrum are associated with modes of vibration with all the quanta for the transition localized in a single CH oscillator. These local modes are sensitive to differences among the nonequivalent CH bonds in the molecules. For example, transitions involving aryl and alkyl hydrogens in toluene and the xylenes have been resolved,[2b] as have transitions for the CH_3, CH_2, and CH hydrogens in the alkanes.[5] In fact, characteristic local mode frequencies and local mode anharmonicities have been found for CH_3 and CH_2 oscillators for a whole series of alkane molecules.[5]

For a pure local mode overtone where all v_i quanta are absorbed in a single chemical bond, the transition energy, ΔE, has been found to be given by[3,6,7]

$$\Delta E = v_i \omega_i + v_i^2 X_{ii} \qquad (1)$$

A plot of $\Delta E / v_i$ vs. v_i will yield ω_i, the local mode frequency, as the intercept and X_{ii}, the local mode diagonal anharmonicity constant, as the slope. This simple two-parameter model fits the observed overtones with $\Delta v_{CH} \geq 3$.[3-7]

The cycloalkanes and cycloalkenes have CH bonds which interchange among chemically inequivalent sites. The various interchanges occur with a wide range of different rates. We expect that the overtone spectra may vary—some of the spectra may show the static splittings of the inequivalent sites and some may be motionally averaged. The degree of motionally averaging is characterized by the quantity $2\pi\tau\Delta\nu$, where τ is the interchange limited lifetime of the molecule at one site and $\Delta\nu$ is the static splitting of the spectral feature. If this quantity is much greater than 1, the spectral feature displays the static splitting $\Delta\nu$.[8]

We report on the splittings of the CH overtone bands. The splittings provide a measure of the changing properties of CH bonds as a function of conformation.

II. Experimental Section

The spectra corresponding to $\Delta v_{CH} = 3$ and 4 were measured on a Cary 14 spectrophotometer operated in the infrared mode. The 0-1 absorbance scale slidewire was used and the spectra were measured in 1- ($\Delta v_{CH} = 3$) and 10-cm ($\Delta v_{CH} = 4$) cells. The spectra for $\Delta v_{CH} = 5$, 6, and 7 were determined either with the Cary 14 and a 0.1 absorbance scale slidewire or with the Cary 118, Cary 218, or Perkin-Elmer 555 using 0.1, 0.02, and 0.01 absorbance scales. For $\Delta v_{CH} = 5$, 6, and 7 the spectra were measured in 10-cm cells. All samples were run vs. air as a reference. Frequencies for $\Delta v_{CH} = 5$, 6, and 7 were measured to ±0.5 nm, which results in errors of ~±8 cm^{-1} for $\Delta v_{CH} = 5$ and of ~±15 cm^{-1} for $\Delta v_{CH} = 7$.

The samples used were all of commercial spectral grade or comparable quality. The spectra show sloping base lines which are intrinsic features of the overtone spectra. The spectra of contaminated samples show much more strongly sloping base lines. Furthermore, we found that the various spectrometers had a variety of not quite straight instrumental (i.e., no sample) base lines which could lead to bizarre

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