J. Am. Chem. Soc. **1981**, *103*, 2395–2403

Vibrational Circular Dichroism of Optically Active Cyclopropanes. Experimental Results

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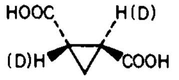
Abstract: The vibrational circular dichroism spectra of several trans-1,2-disubstituted cyclopropanes between 3200 and 1250 cm^{-1} are presented. Isotopic substitutions allowed assignments of many of the VCD bands to specific CH stretching or bending modes. A substituent group effect on the VCD ring modes is noted with the dimethyl ester species providing the best agreement to the theoretically predicted VCD in the CH stretching region. Possible explanations for deviations from theory are discussed. VCD for C=O stretching and ring CH$_2$ bending modes are predicted to be sensitive to substituent group conformation, and the observed spectra are discussed in these terms.

Vibrational circular dichroism (VCD) and its Raman analogue, circular intensity differential (CID), are measures of the optical activity of the vibrational modes of chiral molecules.[1,2] As such they have great potential for conformational analysis in that these vibrational transitions are fairly well resolved, are relatively straightforward to assign, and provide a variety of probes of the molecular structure. However, this potential has yet to be extensively exploited. Although both VCD and Raman CID are measurable in a wide variety of molecular systems and for various types of molecular vibrations, reliable theoretical interpretation of these data in terms of molecular structure has proven more difficult to achieve. Several theoretical models for VCD have been proposed; however application of all but the most simple of these is quite difficult. This situation is further complicated by the fact that, to date, most reported VCD has been measured for relatively large molecules with significant conformational mobility. To best test these theories, we need VCD data on a series of small, structurally related molecules of the same absolute configuration and of a known geometry. Comparison of the empirical trends with the theoretical predictions should then elucidate the strong and weak points of the theories as well as guide new theoretical development.

This paper is the first in a series that describes and interprets the vibrational optical activity of a series of substituted three-member ring compounds. These are particularly attractive due to their small size, rigid-ring conformation, and the wide variety of substitutions possible on the ring. Furthermore, extensive spectroscopic and calculational studies have been carried out on substituted cyclopropanes to determine their preferred conformations.[3] Substituents in the trans-1,2 positions of the cyclopropane give the molecule chirality. We have first studied symmetrically substituted cyclopropanes which can maintain a C_2 axis. Initial resolution was performed on the dicarboxylic acid,



and the other molecules studied were then prepared from it with retention of the absolute configuration of the diacid (1*S*, 2*S*). Additionally, the hydrogens on the 1,2 positions were exchanged with deuterium, enabling an analogous, isotopically substituted series to be studied. Here we report VCD in the range of 3200–1250 cm^{-1} for several of these trans-disubstituted cyclopropanes. These data include the C—H(D) stretching vibrations as well as the newly accessible CH deformations[4] and, where appropriate, the characteristic C≡N and C=O modes. Via comparison to deuteration results these bands have been assigned and their VCD qualitatively interpreted. Subsequent papers will discuss similar studies on chiral oxiranes (epoxides) and asymmetrically substituted cyclopropanes and will explore theoretical models of the VCD of these molecules.

Experimental Section

All VCD spectra were recorded on an infrared CD instrument constructed at UICC which has been described in detail elsewhere.[1c,4,5] In all cases VCD base lines were obtained by recording spectra of racemic samples on-line with a PDP 11/03 lab computer and then digitally subtracting them from the similarly recorded sample spectra before plotting. The absorption spectra were calculated from single-beam scans of sample and solvent. Both VCD and absorption spectra were corrected for pathlength and concentration and replotted in molar extinction (ϵ, $\Delta\epsilon$) units.

Most samples were dissolved in spectral-grade solvents used without further purification. For the acid chloride samples, residual water in the CCl$_4$ was removed by distilling the solvent from P$_2$O$_5$ to prevent hydrolysis. All of the compounds studied were prepared in our laboratory according to literature methods or standard synthetic procedures. Optical rotations were determined with a Perkin-Elmer 241 Polarimeter at room temperature.

(±)-Dimethyl *trans*-1,2-Cyclopropanedicarboxylate-*d*$_0$. The racemic dimethyl ester derivative was prepared by the reaction of methyl acrylate with methyl chloroacetate and sodium hydride in toluene according to method b of Doering and Sachdev.[6] The product obtained had physical and spectral properties in agreement with the literature: bp 81–83 °C (6 mm); NMR neat δ 1.2 (complex, 2 H), 1.9 (complex, 2 H), 3.5 (6H).[6,7]

(±)-*d*$_2$. The trans-1,2 hydrogens on the cyclopropane ring of the dimethyl ester species were exchanged with the deuterium atoms of CH$_3$OD in the presence of the base, NaOCH$_3$. Hydroxide-free sodium methoxide was first prepared by the reaction of dry methanol and sodium metal. In a typical reaction 2.7 g (0.05 mol) NaOCH$_3$ was dissolved in 33 g (1 mol) CH$_3$OD (Aldrich 99.5% D). After 15.8 g (0.1 mol) of the dimethyl ester species was added, the mixture was refluxed for several days. The exchange was monitored periodically by NMR, and the methanol was replaced with fresh CH$_3$OD as needed until a product ester which was >95% D at the trans-1,2 positions was obtained. The NMR of the vacuum-distilled neat liquid product showed the disappearance of

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(1) For reviews of VCD see: (a) L. A. Nafie and M. Diem, *Acc. Chem. Res.*, **12**, 296 (1979); (b) P. J. Stephens and R. Clark in "Optical Activity and Chiral Discrimination", S. F. Mason, Ed. Reidel, Dortrecht, 1979; (c) T. A. Keiderling, *Appl. Spectrosc. Rev.*, in press; (d) L. A. Nafie, *Vib. Spectra Struct.*, in press.

(2) Raman CID: L. D. Barron in "Optical Activity and Chiral Discrimination", S. F. Mason, Ed., Reidel, Dortrecht, 1979, and references therein.

(3) C. J. Wurrey and A. B. Nease, *Vib. Spectra Struct.*, **7**, 1 (1978) and references therein.

(4) C. N. Su, V. J. Heintz, and T. A. Keiderling, *Chem. Phys. Lett.*, **73**, 157 (1980).

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

(6) W. von E. Doering and K. Sachdev, *J. Am. Chem. Soc.*, **96**, 1168 (1974).

(7) T. Shono, T. Morikawa, A. Oku, and R. Oda, *Tetrahedron Lett.*, **14**, 791 (1964).

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the δ 1.9 band accompanied by the collapse of the complex band at δ 1.2 to a single peak.

(+)-d_0/d_2. The optically active dimethyl ester derivatives were prepared from the resolved (+) acid species (see below) by reaction with diazomethane in ether according to the standard method. The distilled products had similar boiling points and NMR identical with that of the corresponding racemates above. $[\alpha]_D = +236°$ (*c* 1.42, CCl_4).

(±)/(+)-d_6/d_8. All of the dimethyl ester derivatives in which the CH_3 groups are replaced with CD_3 groups were prepared from the corresponding acid chloride species by reaction with CD_3OD (Aldrich, 99.5% D) in CCl_4 containing pyridine as a catalyst. The NMR of the distilled products was consistent with that of the other esters but showed the disappearance of the δ 3.5 band corresponding to the 6 methyl H's.

(±)-*trans*-1,2-Cyclopropanedicarboxylic Acid-d_0. The racemic d_0 ester was hydrolyzed by refluxing with aqueous sodium hydroxide to yield the trans-diacid species. The product's melting point of 176 °C and NMR in D_2O (complex bands at δ 1.4 and 2.1) were in agreement with the literature.[6,7]

(±)-d_2. The d_2 ester was hydrolyzed by stirring for several days with 5% HCl solution at room temperature. No appreciable back-exchange of the trans deuteriums was noted under these conditions. The NMR was consistent with this formulation.

Brucine Resolution of *trans*-1,2-Cyclopropanedicarboxylic Acid (d_0 and d_2). Resolution of the enantiomers of the trans-diacid species was achieved by successive recrystallizations with (−)-brucine in a modification of the previous method.[6] A 1:1 mole ratio of brucine to the diacid was used instead of 2:1 with only hot water as the solvent. After several recrystallizations the recovered acid species had $[\alpha]_D = +228°$ (*c* 1.75, EtOH) with mp 172 °C. All optically active compounds discussed in this paper were derived from the resolved acids (d_0 and d_2) obtained by this method. (A small amount of the opposite isomer was also resolved by using *l*-ephedrine to $[\alpha]_D = -197°$ but was only used for the d_2 dicyano preparation.)

***trans*-1,2-Cyclopropanedicarbonyl Dichloride.** All of the acid chloride derivatives were prepared by the reaction of the corresponding diacid species with refluxing thionyl chloride. After excess $SOCl_2$ was pumped off, the product was vacuum distilled with bp 59 °C (4 mm). The NMR of the d_0 species in CCl_4 had two complex bands at δ 1.8 and 2.8 which is in agreement with the literature.[7] The d_2 acid chloride derivative gave a single NMR peak at the upfield position. The optically active species, $[\alpha]_D = +253°$ (*c* 2.18, CCl_4), was a solid at room temperature.

***trans*-1,2-Cyclopropanedicarboxamide.** The diamide derivatives were prepared from the diacid chloride species by reaction with cold 28% aqueous ammonia solution by the method of Shono et al.[8] The recrystallized (±) product had mp 284 °C (lit. 279 °C). The observed NMR chemical shifts of the d_0 diamide compound in D_2O (complex bands at δ 1.3 and 2.1) were somewhat smaller than those reported for the compound in CF_3COOH.[7] The NMR of the d_2 species was consistent with that observed for the other d_2 derivatives. The optically active form of the diamide had $[\alpha]_D = +265°$ (*c* 1.00, H_2O).

***trans*-1,2-Cyclopropanedicarbonitrile.** The dinitrile derivatives were prepared by the reaction of P_2O_5 with the diamide species in a modification of the method of Shono et al.[8] The reaction was carried out in a modified sublimation apparatus in which the solid product collected on the cold finger. It was found that the addition of a small amount of powdered Zn metal both aided in the mixing of the reactants and had a possible catalytic effect, thus improving the yield. The physical and spectral properties agreed with the literature: mp 72 °C[8] and NMR in $CHCl_3$ (complex bands at δ 1.6 and 2.1).[7] The NMR of the d_2 species was consistent with the other trans-d_2 derivatives. The optically active form had $[\alpha]_D = +381°$ (*c* 1.01, $CDCl_3$).

Diphenyl *trans*-1,2-Cyclopropanedicarboxylate. The diphenyl ester was prepared in the same manner as the d_6 and d_8 dimethyl esters from the reaction of phenol with the diacid chloride derivative. The white solid product had a melting point of 86 °C and the NMR showed three complex bands (10 H at δ 7.2, 2 H at δ 2.4, 2 H at δ 1.6). For the optically active form, $[\alpha]_D = +300°$ (*c* 1.51, CCl_4).

Results

C–H Stretching Region. Because of the partially aromatic nature of the cyclopropane ring, the stretching modes of C–H bonds on the ring are characteristically at higher frequencies than for other types of C–H bonds, e.g., methyl groups. This is illustrated in Figure 1 which shows the complete C–H stretching region for the d_0 and d_2 dimethyl ester compounds. The four C–H bonds associated with the cyclopropane ring have vibrations which are all found at frequencies above 3000 cm^{-1}. The highest methyl ester mode is around 3000 cm^{-1} and overlaps slightly with one of the ring C–H modes. Although the VCD for these two groups of C–H stretching modes is comparable in magnitude, $\Delta\epsilon < 1 \times 10^{-3}$, the absorption intensities for the ring C–H stretching modes are about 1 order of magnitude weaker than those of the methyl groups. This is an illustration of the usefulness of VCD in gaining spectral information in cases where ordinary absorbance data is difficult to obtain.

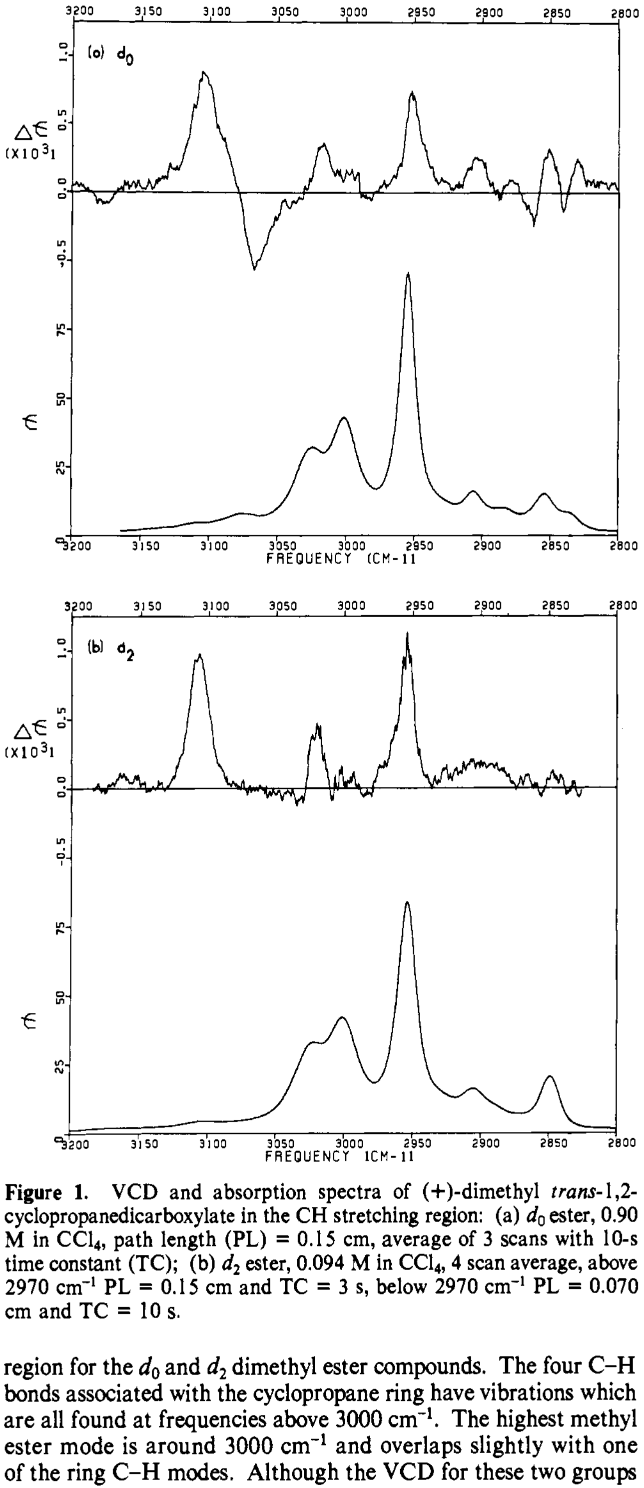

Figure 1. VCD and absorption spectra of (+)-dimethyl *trans*-1,2-cyclopropanedicarboxylate in the CH stretching region: (a) d_0 ester, 0.90 M in CCl_4, path length (PL) = 0.15 cm, average of 3 scans with 10-s time constant (TC); (b) d_2 ester, 0.094 M in CCl_4, 4 scan average, above 2970 cm^{-1} PL = 0.15 cm and TC = 3 s, below 2970 cm^{-1} PL = 0.070 cm and TC = 10 s.

Comparison of Figure 1a with Figure 1b shows the effect of isotopic substitution of the hydrogen atoms at the trans-1,2 positions on the cyclopropane ring. The VCD spectrum of the d_2 ester shows the disappearance of the strong negative feature in the ring C–H stretching region at about 3070 cm^{-1}. The apparent positive shoulder at 3080 cm^{-1} also disappears. This same effect is observed for the d_6 and d_8 ester derivatives as shown in Figure 2. In these two species the ring C–H modes have been isolated by replacement of the CH_3 groups of the methyl ester substituents with CD_3 groups. Figure 3 shows the VCD for a few cyclopropane derivatives that have the same absolute configuration

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[8] T. Shono, T. Morikawa, R.-I. Okayama, and R. Oda, *Makromol. Chem.*, **81**, 142 (1965).

[9] N. C. Craig, T.-N. H. Chao, E. Cuellar, D. E. Hendriksen, and J. W. Koepke, *J. Phys. Chem.*, **79**, 2270 (1975).

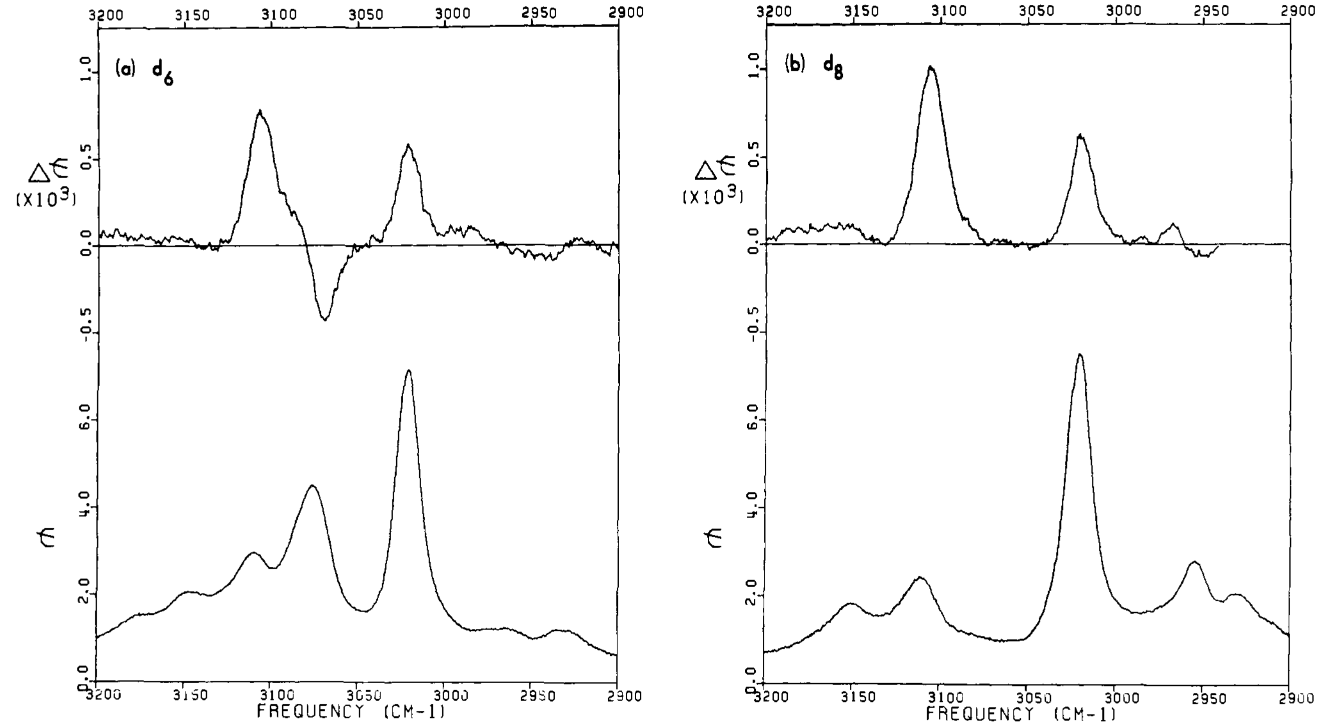

Figure 2. VCD and absorption spectra in the CH stretching region of (+)-dimethyl *trans*-1,2-cyclopropanedicarboxylate with d_3 methyl groups: (a) d_6 ester, 0.115 M in CCl_4, PL = 0.30 cm, 2 scan average with TC = 3 s; (b) d_8 ester, 0.050 M in CCl_4, PL = 0.35 cm, 2 scan average with TC = 10 s.

and have sign patterns similar to that of the dimethyl ester. The poor signal-to-noise ratios in the diamide and diacid spectra (Figure 3a and 3b, respectively) are due to solvent interference. Acetone-d_6 and Me_2SO-d_6, neither of which is completely transparent in this region, were used because these species are not soluble in $CDCl_3$ or CCl_4. The VCD of the diphenyl ester derivative (Figure 3c), on the other hand, is complicated by overlap of signals from the phenyl C–H stretching modes. Qualitatively, the VCD spectra are all similar to that of the ester with the same + − + sign pattern for the major features.

The diacid chloride derivative gives a partially altered sign pattern in the VCD even though it also has the same absolute configuration as the esters. Shown in Figure 4 is the comparison of the d_0 and d_2 species. As with the dimethyl ester derivatives the VCD and absorption features at the middle frequencies are no longer observed after isotopic substitution of the trans-1,2 H atoms. Although positive VCD features associated with the highest and lowest frequency absorbances remain qualitatively unchanged from the dimethyl ester, the middle VCD feature is here also positive. The two central features are more clearly distinguishable than for the esters and are apparently shifted to lower frequencies by about 10 cm^{-1}. (The very small negative band at 3130 cm^{-1} appears to be reproducible and may be due to conformer equilibrium.)

However, as shown in Figure 5, the trans-dinitrile derivative gives a very different VCD spectrum from the previous examples. Whereas for all the above mentioned compounds there was a large positive VCD feature associated with the highest energy absorption band assigned to the apex CH_2, the band at 3120 cm^{-1} in the d_0 dinitrile spectrum has a negative VCD peak. This and the lowest frequency band (3030 cm^{-1}) are also somewhat higher in energy than the corresponding ester bands. The largest VCD feature is positive and corresponds to a strong absorption band at 3055 cm^{-1}. This is similar to what is observed for the diacid chloride derivative but very different from the other derivatives. Results for the d_2 dinitrile show that this strong central band disappears in both the VCD and absorbance spectra and can be associated with the trans C–H stretches. However, the remaining d_2 VCD is so weak ($\Delta\epsilon \lesssim 10^{-4}$) that the features found may be unreliable and hence are not reproduced here.

Since the central features in the VCD of the diacid chloride and dimethyl ester derivatives were removed by deuteration at the trans position with little qualitative change in the remaining VCD, it might be expected that these bands would show up as C–D stretches with the same sign pattern. Figure 6 shows the VCD spectra of these two molecules in the C–D stretching region. It should be pointed out that there is a strong atmospheric CO_2 absorption from 2375 to 2300 cm^{-1} making measurements in this region difficult due to the long light path of our VCD instrument. As expected, these ring C–D stretching modes are higher in energy than the methyl group C–D stretches. (The highest absorpton band in the d_6 ester was found at 2275 cm^{-1}.) The acid chloride species which lost a positive feature in its C–H stretching VCD spectrum now shows a positive VCD peak for the C–D stretching mode (Figure 6a). Similarly the dimethyl ester species shows a negative VCD peak for the C–D stretch at 2320 cm^{-1} corresponding to the C–H stretch which had a negative VCD peak (Figure 6b). (Due to the lower extinction and limited amount of d_2 ester sample, a positive peak corresponding to the positive shoulder found in the CH region could not be identified.)

CH_2 Deformation Region. The region from 1500 to 1250 cm^{-1} is where C–H bending and CH_2 scissoring modes are typically found and is sometimes also the location of CH_2 twisting and ring breathing modes for cyclopropanes.[3] Figure 7 shows the results in this region for the isotopically substituted dimethyl ester species. One should note that both the absorbance and VCD are larger in this region than in the C–H stretching region. The d_0 and d_2 species (top) have CH_3 groups on the ester substituents while the d_6 and d_8 species have CD_3 groups. The d_0 and d_6 species (left) have four H atoms on the cyclopropane ring while the d_2 and d_8 species (right) have only an apex CH_2 group. When top to bottom and left to right are compared, the effects of the different isotopic substitutions can be identified. Deuteration of the methyl group causes the disappearance of a negative-then-positive sigmoidal VCD feature around 1440 cm^{-1} and implies that it is due to the asymmetric methyl deformation. This feature is larger in the d_0 species than in the d_2 presumably because of overlap or interaction with the negative VCD feature which is found in the d_6 species but not in the d_8 form. Except for slight shifts in frequency, the bands below 1420 cm^{-1} are unaffected by the deuteration of the methyl groups.

Isotopic substitution of the ring trans H's causes the positive-

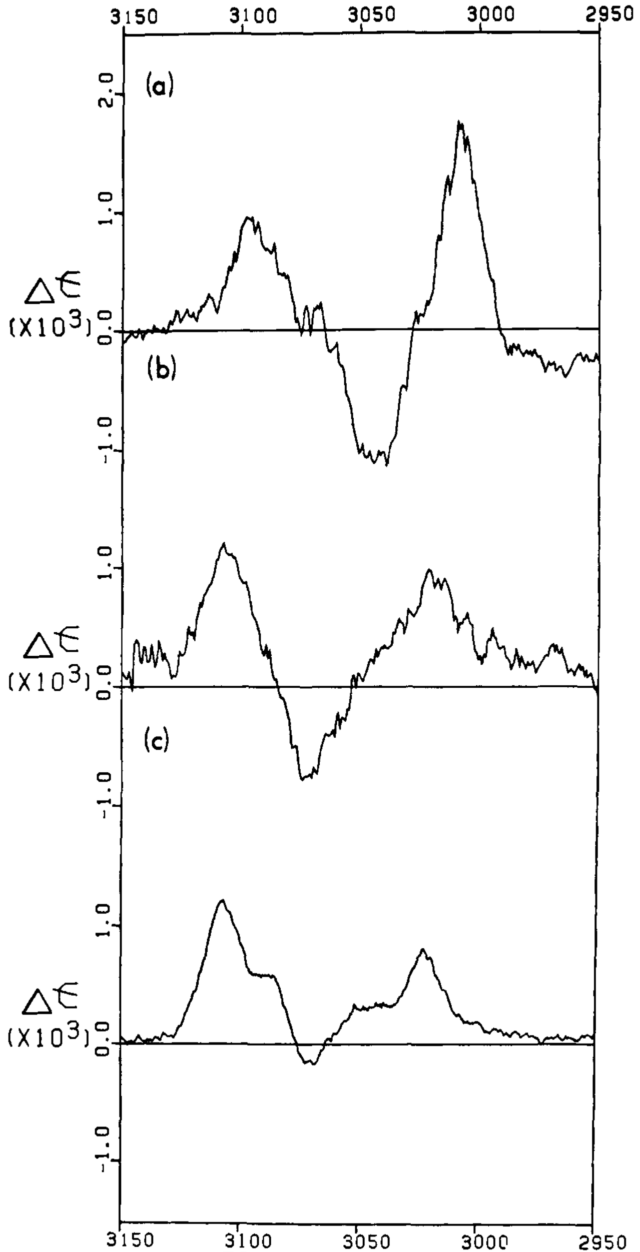

Figure 3. VCD spectra in the CH stretching region: (a) (+)-*trans*-1,2-cyclopropanedicarboxamide, 0.080 M in Me$_2$SO-d_6, PL = 0.075 cm, 5 scan average with TC = 10 s; (b) (+)-*trans*-1,2-cyclopropanedicarboxylic acid, 0.060 M in acetone-d_6, PL = 0.10 cm, 4 scan average with TC = 10 s; (c) (+)-diphenyl *trans*-1,2-cyclopropanedicarboxylate, 0.054 M in CCl$_4$, PL = 0.25 cm, 16 scan average with TC = 3 s.

then-negative sigmoidal VCD feature around 1400 cm^{-1} to be replaced by a positive-only feature near 1375 cm^{-1} which appears to be the CH$_2$ scissor mode. The strong absorptions below 1350 cm^{-1} with their associated large positive VCD are replaced by a large absorption below 1300 cm^{-1} for which VCD could not be measured due to the current instrumental cutoff.

The comparison of the d_0 and d_2 forms of the diacid chloride derivative is shown in Figure 8. The absorption with positive VCD around 1430 cm^{-1} is qualitatively unaffected by the deuterium exchange of the trans H's and appears to be the CH$_2$ scissor mode which is significantly shifted from the ester frequencies. The band with negative VCD around 1380 cm^{-1} disappears and is replaced by an absorption band of nearly the same intensity at lower frequency but having only very weak VCD associated with it. The band at 1300 cm^{-1} with strong positive VCD is shifted to lower frequency out of the VCD range of our instrument.

The VCD of dinitrile derivatives in this region is shown in Figure 9. The absorption intensities are substantially weaker than found for the acid chloride spectra. The VCD spectrum is slightly shifted to higher energy but is qualitatively very similar to that of the acid chloride derivative having a positive feature around 1445 cm^{-1} and a negative one at 1380 cm^{-1} that shifts to 1325 cm^{-1} upon deuteration. (Measurements below 1350 cm^{-1} and at 1425 cm^{-1} were complicated by interference from the chloroform solvent for the d_0 as were measurements at 1380 cm^{-1} by CDCl$_3$ for the d_2.) This behavior and the sign of the VCD parallel the acid chloride results and suggest a similar assignment.

C=O and C≡N Functional Groups. The VCD and absorption spectra for the carbonyl functional group C=O stretch of the dimethyl ester derivative are shown in Figure 10a. There is a strong absorbance band at 1730 cm^{-1} with at least two reproducible shoulders apparent under higher resolution conditions. The associated sigmoidal VCD signal which goes first positive then negative is quite large in magnitude, although $\Delta\epsilon/\epsilon$ is in the usual range. The acid chloride species gives a similar although weaker VCD for its C=O stretch (Figure 10b) at 1785 cm^{-1}.

The spectrum for the C≡N stretch in the dinitrile is shown in Figure 11. The strong absorption at 2255 cm^{-1} gives rise to a positive VCD peak that is weaker than the C=O stretching VCD but stronger than the C—H stretching VCD signals.

Discussion

CH Stretching Region. As seen in the previous section, deuteration of the trans ring protons makes assignment of the C-H stretching region quite straightforward. The higher and lower energy bands at 3110 and 3020 cm^{-1} for the acid chloride and at 3107 and 3021 cm^{-1} for the esters correspond to the antisymmetric and symmetric stretches, respectively, of the apex CH$_2$ group. The center frequencies 3080 and 3050 cm^{-1} in the acid chloride and 3087 and 3071 cm^{-1} in the ester correspond to the trans CH stretches. The latter pair are significantly overlapped and were resolved by fitting Gaussian line shapes to both the VCD and the absorption spectra. These assignments agree with those made for *trans*-1,2-difluorocyclopropane.[9]

In both of these, acid chloride and ester, the VCD associated with each mode is not qualitatively changed by deuteration but is merely shifted in frequency. This result would imply that the apex and trans CH stretches are fairly independent of each other. However, the two molecules give rise to significantly different intensity patterns for both the apex and trans CH stretches and to oppositely signed VCD for the trans modes. This coupled with the nonconservative nature of the VCD (especially for the acid chloride) implies that the VCD is, however, dependent on interaction with the substituent group.

On the other hand, the VCD changes drastically for the dinitrile on deuteration, suggesting the possibility of significant apex-trans CH interaction. Here the bulk of the intensity appears in the trans C-H stretch at 3053 cm^{-1} (only one band is resolved). The CH$_2$(as) and -(s) apex modes appear at 3120 and 3036 cm^{-1}, respectively. The d_2 results show virtually no CH stretching VCD, suggesting that the observed d_0 spectra may be entirely due to the trans CH's or to the apex-trans interaction. Since the dinitrile is only soluble in CHCl$_3$, these peaks are at the limits of our detectability with a single beam instrument. We have confirmed the frequencies with Raman measurements.

This difference for the dinitrile may be due to conjugation of C≡N with the cyclopropane ring.[10] As a π acceptor, C≡N can cause distortion of the cyclopropane ring such that, in the monosubstituted case, the adjacent C—C bonds are lengthened and the opposing one shortened relative to cyclopropane.[10c] Ab initio calculations are consistent with this geometry and evidence a charge flow from the ring to the substituent.[10d] This variation in charge and subsequent variation in C-H bond strength, as evidenced by the higher frequencies in the nitrile compared to the ester and acid chloride, could well be the cause of the significantly different observed VCD for the dinitrile. The sp hybridization

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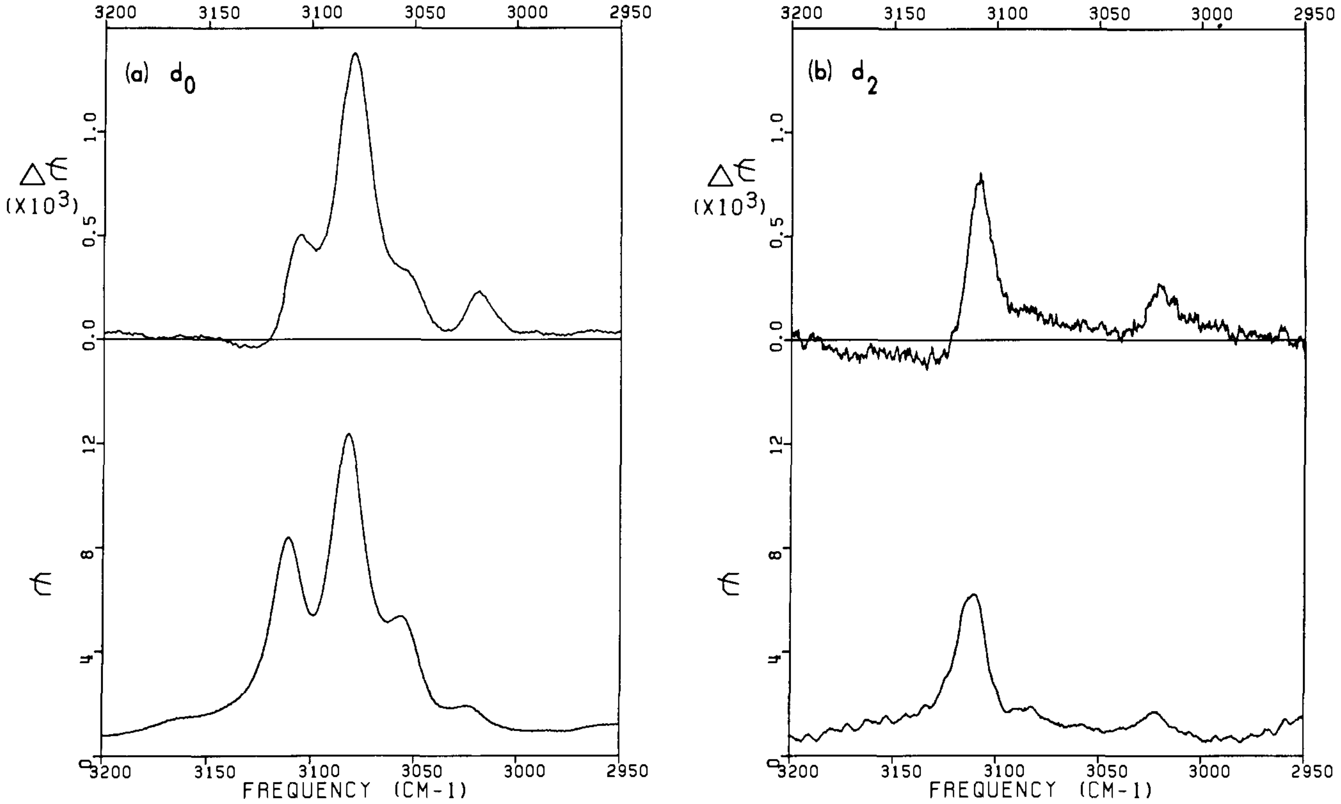

Figure 4. VCD and absorption spectra of (+)-*trans*-1,2-cyclopropanedicarbonyl dichloride in the CH stretching region: (a) d_0 acid chloride, 0.213 M in CCl_4, PL = 0.30 cm, 5 scan average with TC = 10 s; (b) d_2 acid chloride, 0.123 M in CCl_4, PL = 0.30 cm, 2 scan average with TC = 3 s.

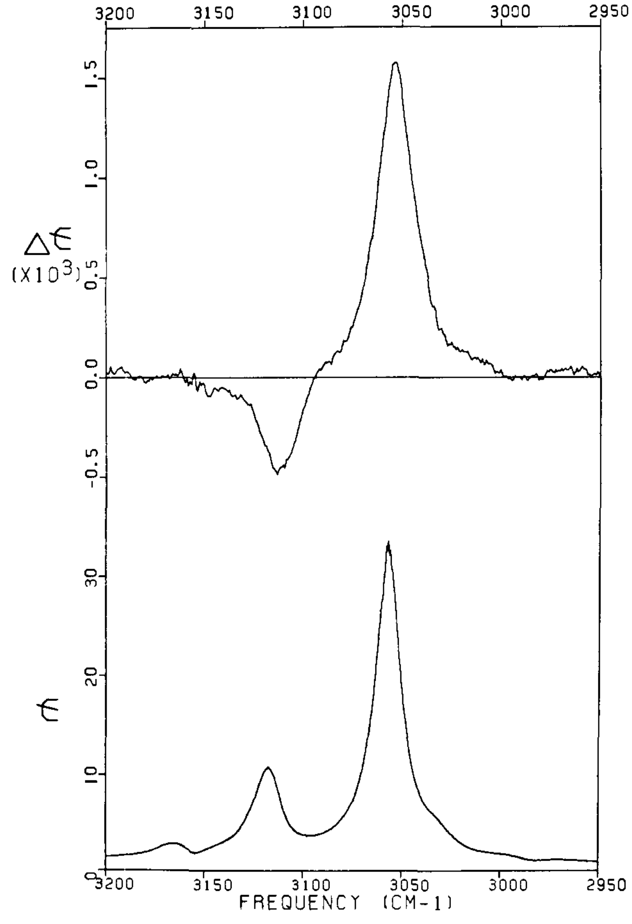

Figure 5. VCD and absorption spectra of (+)-*trans*-1,2-cyclopropanedicarbonitrile in the CH stretching region: 0.110 M in $CDCl_3$, PL = 0.15 cm, 4 scan average with TC = 10 s.

and subsequent linear geometry may also be a source of different effects of conjugation on the VCD between C≡N and COCl.

These concepts were tested with a series of fixed partial charge (FPC) calculations[11] on a model compound by using pseudoatoms for the substituents. A cyclopropane valence force field[12] was used with initial charges derived from a CNDO calculation[13] and with various masses for the pseudoatom substituents. In agreement with the ester VCD, a consistent sign pattern: + + − + from high to low energy resulted for the range of pseudoatom charges and masses used. Even when the pseudoatom was converted to a carboxylic acid or nitrile group,[14] this pattern remained and proved insensitive to conformational variation. However, small changes of the CH stretching or the CH—CH interaction force constants could induce large intensity changes and even alteration of the sign pattern. This is consistent with effects of conjugation being important factors in the observed difference of VCD for nitrile, ester, and acid chloride species.

CH Deformations. In the 1500–1250-cm^{-1} region the assignments are not so simple as in the stretching region since CH_2 twisting and scissoring, CH deformation, CH_3 deformation, and ring breathing motions all contribute to the modes in this region and appear to be substantially mixed. Deuteration experiments have permitted identification of features primarily due to the CH_3(as) deformations (~1450 cm^{-1} in d_0 and d_2) and the CH_2 scissor mode (1410–1370 cm^{-1}) for the ester, as indicated in the results section. Other bands have significant, though small, deuteration shifts and may involve motion of the trans hydrogens.

The large negative VCD at ~1450 cm^{-1} in the d_0 ester has a counterpart in the d_6 but not in the d_8 case. Hence it must be a non-CH_3 mode which has contributions from the trans C—H and overlaps the CH_3(as) modes. Previous assignments have attributed a 1457-cm^{-1} band to ring breathing of the difluoro-

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(14) Only diagonal force constants, chosen to reproduce the observed frequencies, were used for substituent groups.

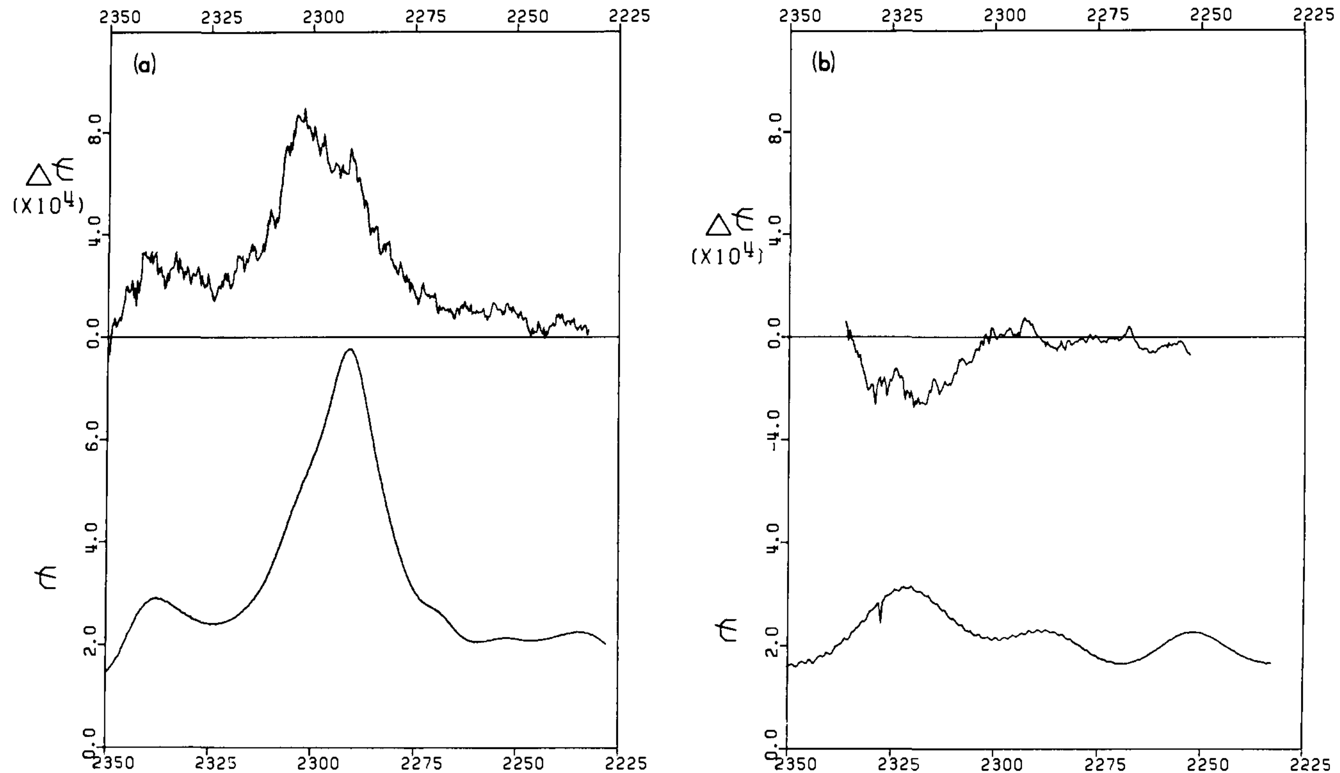

Figure 6. VCD and absorption spectra in the C–D stretching region: (a) d_2 acid chloride, 0.123 M in CCl_4, PL = 0.30 cm, 2 scan average with TC = 10 s; (b) d_2 ester, 0.094 M in CCl_4, PL = 0.435 cm, 2 scan average with TC = 30 s. Atmospheric CO_2 interferes above 2330 cm^{-1}.

cyclopropane;[9] but the deuteration results and lack of intensity argue against such an assignment here. Similarly the large positive VCD at 1340 cm^{-1} must also have trans C—H contribution, but the apparent large increase in intensity and small shift indicate that it is much more complex. The small shift to *higher* energy in d_6 and d_8 as compared to d_0 and d_2, respectively, also implies interaction with the CH_3(s) modes which overlap. The small 1310-cm^{-1} d_0 and d_6 absorption band that corresponds to large positive VCD shifts to 1290 cm^{-1} in the d_2 and d_8 (overlapped by the shifted 1340-cm^{-1} mode) and appears to be primarily a CH_2 mode which may involve twisting motions. Finally, the d_0 and d_6 band around 1275 cm^{-1} gets overlapped by the shift of the above intense (1340 cm^{-1}) band upon deuteration to d_2 and d_8. This band could be due to the C—O stretch in analogy to a similar assignment for the monoester.[15]

In the acid chloride, the band at 1430 cm^{-1} has positive VCD and does not shift with deuteration; hence it is assigned to the apex scissor mode. This band lies at substantially higher energy than found for the ester (~1400–1370 cm^{-1}). In the latter case it appeared to be affected by the CH_3(s) modes which occur at the same frequency and appear to be responsible for the deuteration shifts. Hence comparison of d_0 and d_2 acid chloride to the d_6 and d_8 esters is most appropriate. In this light, it is clear that the VCD of this mode in both molecules has the same sign.

The bands at 1380 and 1300 cm^{-1} appear to shift to much lower energy upon deuteration and hence must have a large C—H contribution. A new band appears at 1330 cm^{-1} in d_2 which may be related to the d_0 1380-cm^{-1} band, but its lack of VCD indicates that the character of the mode is substantially different from the d_0 mode or that it overlaps a mode with oppositely signed VCD. These two acid chloride d_0 bands (1380 and 1300 cm^{-1}) have the same VCD sign pattern and deuteration behavior as found for the 1440- and 1345-cm^{-1} bands in the d_6 ester but are significantly lower in energy. This is in contrast to the apex mode (1430 cm^{-1}) which was higher in energy than in the ester.

These frequency shifts are consistent with the effects of a change in conjugation of the ring with change in the substituent group. Such an interaction would affect the apex and trans positions in the opposite manner. These results parallel the VCD changes noted above for the stretching region in the ester as compared to the acid chloride.

The shoulder at 1280 cm^{-1} occurs at an energy similar to that thought to be a CH_2 twist in the ester. It is possible that upon deuteration of the ring this mode interacts with lower energy modes to shift up and become the 1330-cm^{-1} band.

In the d_0 dinitrile, the positive VCD peak at 1445 cm^{-1} and the negative one at 1380 cm^{-1} are similar to features observed in the same region in the acid chloride. However, solvent interference and the very low extinction values prevent accurate absorption determination in this region and severely hinder VCD measurements. Dinitrile absorption intensities are drastically reduced from those of the ester and acid chloride, and the VCD is consequently also much smaller. The apex mode is shifted up in energy to 1445 cm^{-1} from acid chloride value (~1430 cm^{-1}). This may explain the lack of a large intensity band in the cyano compound to correlate to the 1300-cm^{-1} acid chloride VCD and absorption band. This mode may be shifted down in energy out of the range of this experiment, in the same sense as discussed above, due to substituent–ring conjugation changes.

In summary, the effect of changing the substituent group from methyl ester to acid chloride to nitrile seems to be to raise the frequency of the CH_2 scissor mode while lowering the frequencies of the trans CH bends. As a result, there is apparently more mixing of the trans CH bends with the CH_2 scissors in the ester case, while there is more mixing of the CH bends with lower frequency modes like CH_2 twist in the acid chloride case. The correlation with conjugation effects may evidence a new application of VCD to monitor bonding aspects of these three-member ring systems. Another substituent effect is the reduction in overall absorption intensities by about a factor of 5 in going from ester to acid chloride while the VCD intensities remain much the same. If the substituent group is nitrile, the absorbance is even less. This may be related to the loss of conformational mobility also occurring in this series.

The preliminary FPC calculations mentioned above also provide predictions of the VCD in the 1500–1250-cm^{-1} region which we have measured. To the transferred cyclopropane force field were

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[15] D. L. Powell, P. Klaboe, and D. H. Christensen, *J. Mol. Struct.*, **15**, 77 (1973).

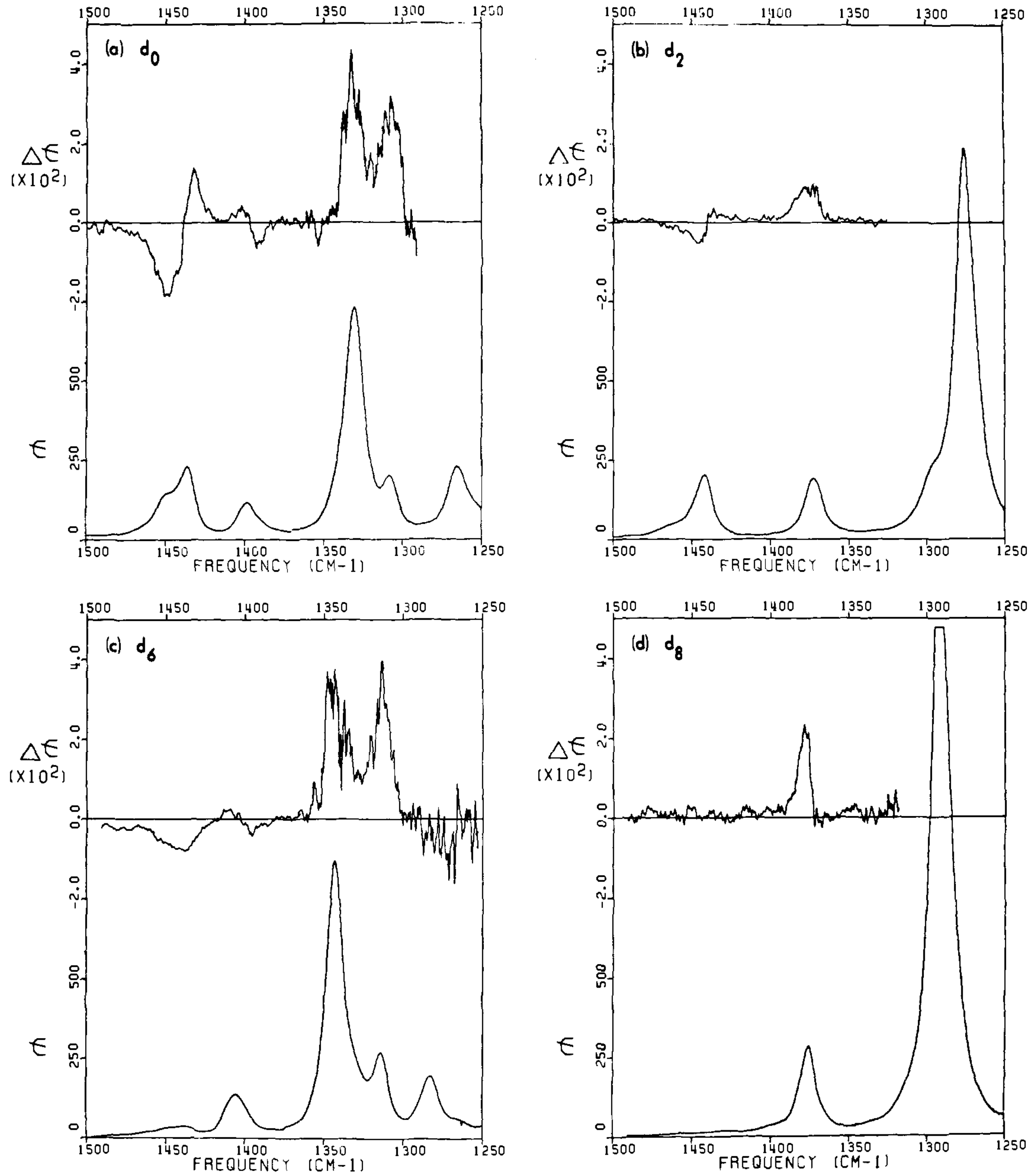

Figure 7. Comparison of the VCD and absorption spectra of the isotopically substituted esters in the CH_2 bending region: (a) d_0 ester, 0.114 M in CCl_4, for 1500–1360 cm^{-1} PL = 0.02 cm, 6 scan average with TC = 10 s, and for 1360–1290 cm^{-1} PL = 0.005 cm, 4 scan average with TC = 30 s; (b) d_2 ester, 0.094 M in CCl_4, PL = 0.14 cm, 2 scan average with TC = 30 s; (c) d_6 ester, 0.115 M in CCl_4, for 1500–1360 cm^{-1} PL = 0.04 cm, 6 scan average with TC = 10 s, and for 1360–1250 cm^{-1} PL = 0.01 cm, 6 scan average with TC = 10 s; (d) d_8 ester, 0.157 M in CCl_4, PL = 0.015 cm, 6 scan average with TC = 10 s.

added parameters for COOH substituents as a model of the molecules studied here. Due to the approximate nature of the force field, the calculations do not accurately mimic the sign patterns found in this region but do give some insight into the problem. In particular, we have found that the calculated 1500–1250 cm^{-1} VCD is very sensitive, in terms of relative magnitudes, to the conformation of the acid group with respect to the ring. The conformer with both C=O groups cis to the ring gives an intensity pattern more paralleling the experiment than does the trans conformer. This result is consistent with data that indicate both the monoacid chloride[3] and the monoester[15] species have a dominant cis conformer. If this tentative interpretation is shown to be valid by subsequent detailed calculation, it will evidence another utility of VCD as a conformational probe.

C=O and C≡N Stretches. A more direct look at the conformation of these C=O bonds is, in principle, given by analysis of their stretching VCD near 1750 cm^{-1}. However the FPC calculations for both the cis-cis and trans-trans isomers predict the same sign pattern (with a positive lobe higher in energy than an equally large negative one) which is in agreement with the experimental results for both the ester and acid chloride (Figure 10). Only if a trans-cis isomer were present would a different FPC sign pattern result.

Careful inspection of the ester absorption band reveals two shoulders which indicate the presence of at least three bands. Since only two bands near 1730 cm^{-1} are expected for two ester groups, there may be an equilibrium between conformers. Temperature dependence studies could indicate the nature of such an equilibrium but, with our presently available signal-to-noise ratio, would probably be inconclusive.

Due to its large transition dipole moment, the C=O stretching VCD of the esters lends itself to analysis with the degenerate coupled oscillator model.[16] Paralleling the FPC result, both the trans-trans and cis-cis conformers are predicted to give rise to a sigmoidal band with a negative lobe to lower energy. While this sign agrees with the experimental result, it does not permit easy

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(16) G. Holzwarth and I. Chabay, *J. Chem. Phys.*, **57**, 1632 (1972).

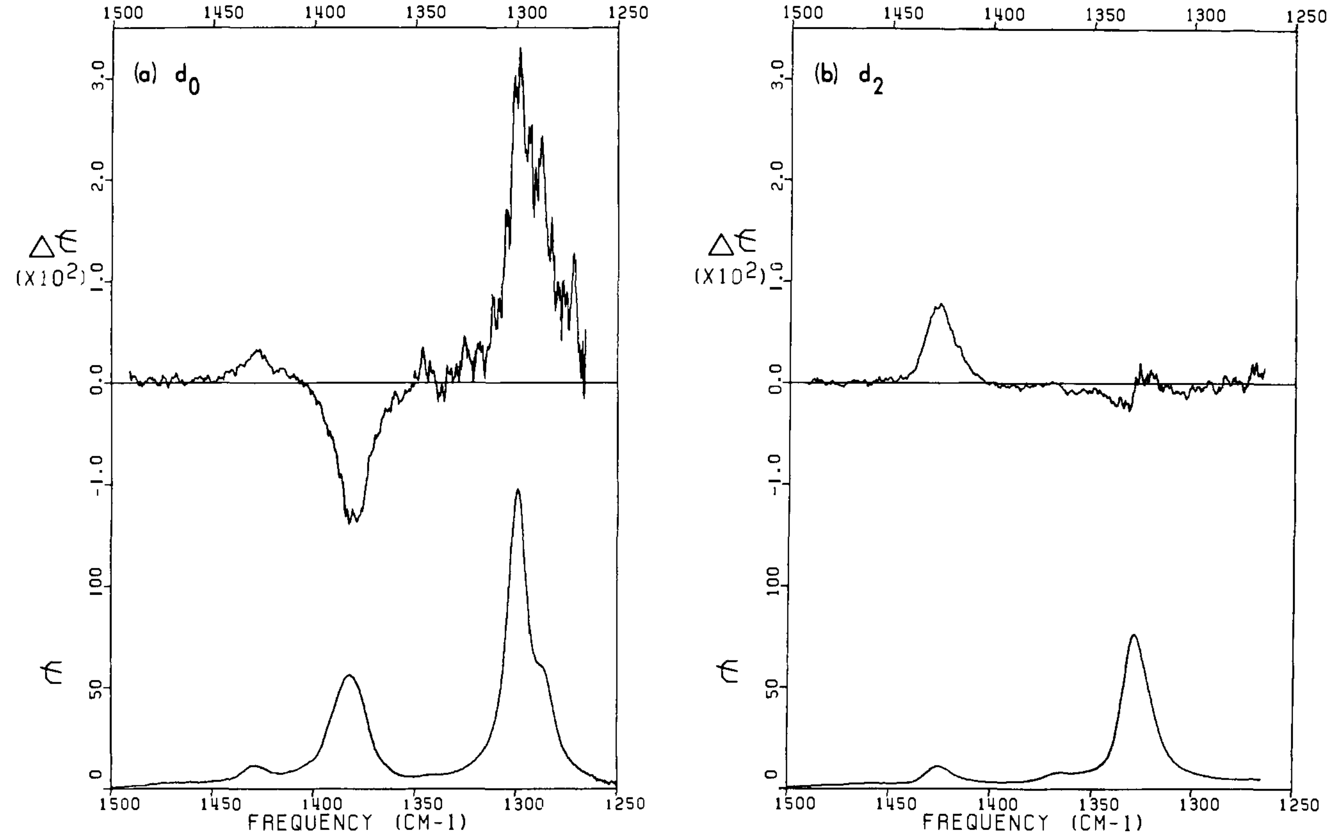

Figure 8. VCD and absorption spectra of the acid chloride species in CH_2 bending region: (a) d_0 acid chloride, 0.115 M in CCl_4, for 1500–1350 cm^{-1} PL = 0.075 cm, 2 scans with TC = 10 s, and for 1350–1250 cm^{-1} PL = 0.015 cm, 4 scan average with TC = 10 s; (b) d_2 acid chloride, 0.205 M in CCl_4, PL = 0.05 cm, 4 scan average with TC = 10 s.

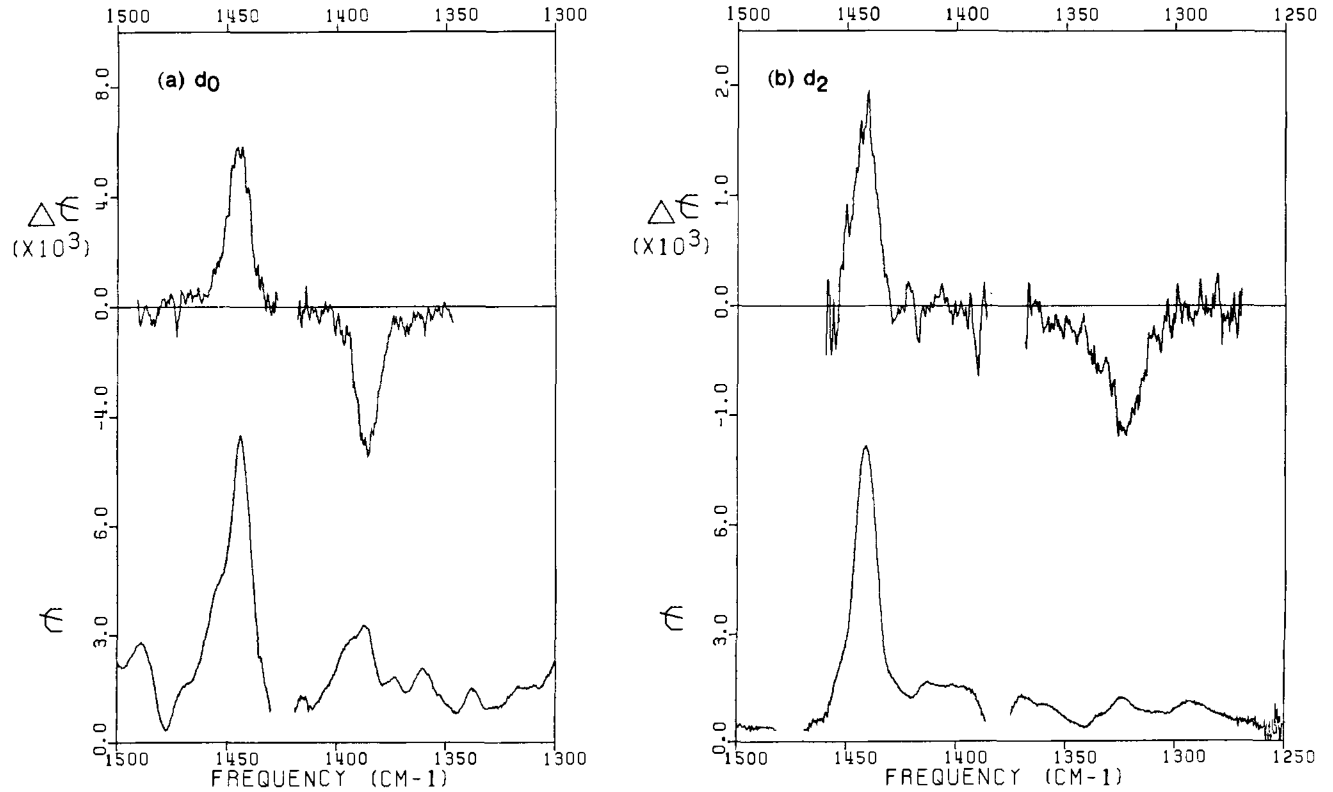

Figure 9. VCD and absorption spectra of dinitrile species in CH_2 bending region: (a) d_0 nitrile, 0.200 M in $CHCl_3$, PL = 0.025 cm, 4 scan average with TC = 10 s; (b) d_2 nitrile, 0.22 M in $CCl_4/CDCl_3$ (2:1 mixture), PL = 0.10 cm, 4 scan average with TC = 10 s. A $CHCl_3$ absorption interferes at 1425 cm^{-1} and $CDCl_3$ absorptions interfere at 1475 and 1380 cm^{-1}.

distinguishability of the two conformers. The mixed trans-cis conformation does have oppositely signed coupled oscillator VCD and is thus eliminated. The magnitude of the line shape corrected VCD predicted with this model for the trans-trans case has a peak of $\Delta\epsilon \approx 0.1$ while the cis-cis has only a peak at $\Delta\epsilon \approx 0.01$. This derives primarily from a large difference in the predicted splitting of the symmetric and antisymmetric bands and would imply that the trans-trans conformer is dominant in solution. Such a con-

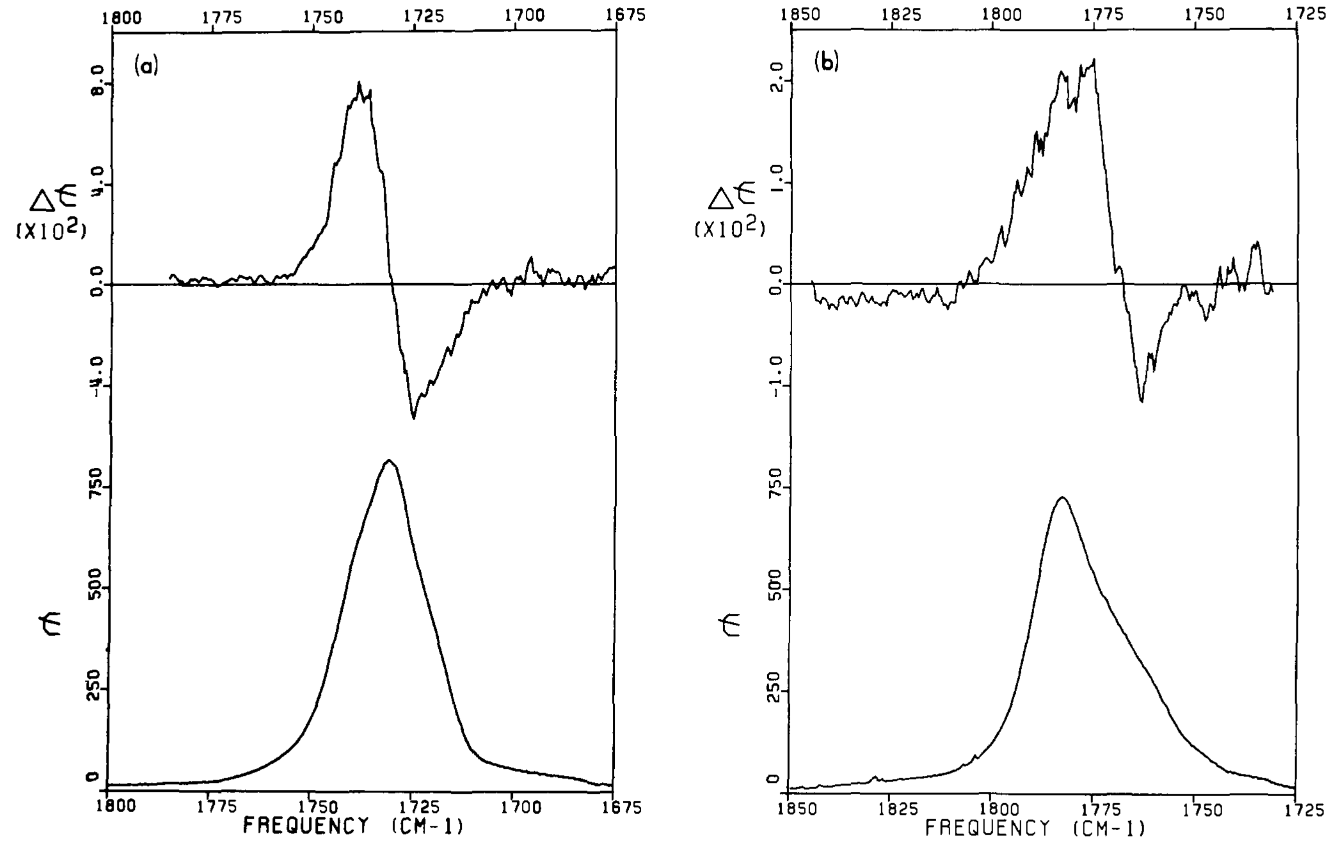

Figure 10. VCD and absorption spectra in the C=O stretching region for two substituted cyclopropanes: (a) dimethyl ester, 0.004 M in CCl_4, PL = 0.15 cm, 2 scan average with TC = 10 s; (b) acid chloride, 0.0046 M in CCl_4, PL = 0.15 cm, 6 scan average with TC = 10 s.

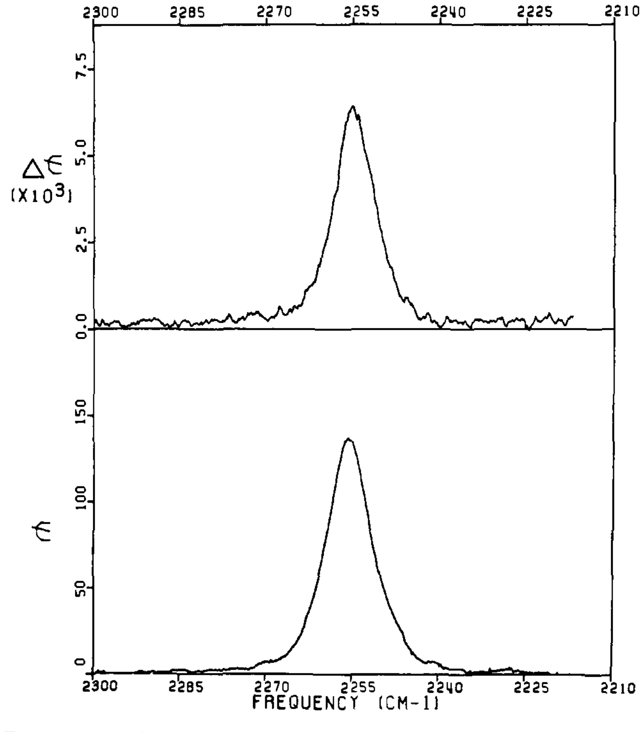

Figure 11. VCD and absorption spectra in C≡N stretching region for (+)-*trans*-1,2-cyclopropanedicarbonitrile: 0.044 M in $CHCl_3$, PL = 0.10 cm, 3 scan average with TC = 10 s.

clusion would be at variance with expectations based on the monoester conformational study[15] and with the above FPC results and is probably not warranted until an explanation for the shoulders on the absorption bands is in hand.

Similar calculations for the dinitrile show that the coupled oscillator contribution to the C≡N VCD would be ~20 times smaller than the observed monosignate signal and, hence, would be unobservable. This exceedingly small effect is primarily a result of a small splitting due to the nearly parallel orientation of the dipoles.

Conclusion

In this paper we have presented the VCD of a series of trans-1,2-disubstituted cyclopropanes in the CH stretching and deformation regions. The former data are seen to correlate well with theoretical predictions on the basis of the FPC model using a transferred force field. The latter modes, however, appear to be strongly interacting; and such a simple FPC treatment fails to adequately account for the observed mid-IR VCD. In both regions substituent effects on the VCD appear to correlate with predicted changes in the charge delocalization with the ring. In this respect, VCD may eventually prove to be a useful probe for such effects. In addition, VCD of the C=O stretches of both the ester and acid chloride agree with predictions based on the coupled oscillator model and may, in other systems, provide data on the conformation of such groups with respect to the ring.

In summary, this work provides data for a set of molecules on the basis of a small rigid framework that should be of theoretical interest. The VCD is interpretable by comparison of spectra of the different molecules and deuterated variations and, in part, is fit by FPC calculations. Future work will concentrate on extending the range of substituents and on developing an optimal force field to better test the available theoretical models.

Acknowledgment. We wish to thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the UICC Biomedical Research Fund for support of this work. We are grateful to Professors J. Kagan, P. R. Young, and W. R. Synder for helpful conversations regarding synthetic techniques and to Professors V. J. Tekippe and L. L. Abels for aid in obtaining Raman spectra.