coordinated to water molecules. All four zeolites show additional similar species which are easily removed after evacuation at room temperature. These species could not be characterized due to overlapping ESR signals with species C or I signals. The relative intensity of these species seems to depend both on the cocation present and on the Si/Al ratio.

With adsorbates other than water, the number of Rh(II) species formed in RhNa–X[1] is less compared to the other zeolites and species C seems to be the dominant species after interaction with most adsorbates. This is probably due to the inaccessibility of the Rh(II) monomers and dimers to the various adsorbates which cannot enter the β-cage except for water. In RhNa–Y, RhCa–Y, and RhCa–X, unlike RhNa–X, the paramagnetic Rh species either form dimers or other Rh(II) species in the α-cage which renders them available to interact with the various adsorbates. RhCa–Y and RhNa–Y generate a greater number of paramagnetic species than RhCa–X after adsorption of ammonia, methanol, or O_2/methanol.

The inaccessibility of the Rh species in RhNa–X is also demonstrated by ethylene adsorption. In RhNa–X the adsorption of ethylene does not induce any changes in the ESR signal,[1] whereas in RhCa–X a new ESR signal appears which decays over a period of 15 min, indicating the involvement of Rh(II) in a reaction with ethylene.[26]

It is not clear why the adduct precursors are not generated in the α-cage in RhNa–X. It may be due to crowding of the α-cage with Na^+ cocations which does not permit precursor formation there. Thus Rh(II) monomer and dimers are formed in the hexagonal prism and β-cage, respectively. It is also possible that the accessibility of site I in RhNa–X to Rh species stabilizes Rh(II) so that it does not form dimers in the larger cages.

Overall, it seems that the accessibility of the Rh(II) species to adsorbates depends on a lesser number of cocations being present which is a function of both the Si/Al ratio and the cocation charge. With a higher Si/Al ratio, as in Y zeolite, the number of cations decreases and with a larger cocation charge, as for divalent cations, the number of cations decreases. This generalization accounts for why RhNa–X behaves differently from RhCa–X, RhNa–Y, or RhCa–Y.

Conclusions

The mechanism of dehydrogenation of Fe(2-octyne)$^+$ (Scheme V) could be distinguished recently by demonstrating that the product $(FeC_8H_{12})^+$ formed is best described as **34** not by Fe$(C_4H_6)_2^+$ complexes like **31**.[21]

Exchanging Na^+ in RhNa–Y with Ca^{2+} does not seem to have a great effect on the Rh(II) species generated. The only significant differences are the following: (1) the relative concentration of species C is higher in 3 wt % RhNa–Y than in 3 wt % RhCa–Y, and (2) species H2 appears after adsorption of methanol in RhNa–Y. The exchange of Na^+ by Ca^{2+} in X zeolite as well as the increase in the Si/Al ratio from RhNa–X to RhNa–Y shows a significant affect on the accessibility of the Rh(II) species. The increase of the Si/Al ratio from RhCa–X to RhCa–Y does not show any significant changes besides the appearance of some additional species in RhCa–Y after ammonia adsorption. When the number of cations is rather large, as in the case of RhNa–X, reducing the number either by exchange with a divalent cation or by increasing the Si/Al ratio affects the formation of paramagnetic Rh species. However, when this number is not large so that the zeolite cages are less crowded with cocations, as in RhNa–Y or RhCa–X, the above change has little effect.

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Vibrational Circular Dichroism of Optically Active Cyclopropanes. 3. *trans*-2-Phenylcyclopropanecarboxylic Acid Derivatives and Related Compounds

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Abstract: Vibrational circular dichroism (VCD) data are presented for a series of (1*R*,2*R*)-*trans*-2-phenyl-1-(R-substituted)cyclopropanes where R = $COOCH_3$, $COOCD_3$, COOH, $CONH_2$, COCl, C≡N, CH_2OH, CD_2OD, CH_3, CD_3, and NH_2 (1*S*,2*R*). In addition, VCD for (1*S*,2*S*)-1-phenylpropylene oxide is presented for comparison. These data can be correlated to show certain characteristic, structure-indicating transitions common to all of the molecules. This is particularly true in the cyclopropane C–H stretching bands in the near-IR and less so of CH_2 deformations and ring modes in the mid-IR. To elucidate these comparisons it is necessary to interpret the frequency shifts of the characteristic bands as the substituent is varied. The range of compounds studied permits such an analysis for certain characteristic modes. The results for monocarbonyl and -cyano substitution further explain the presence and absence, respectively, of coupled oscillator VCD in the corresponding symmetrically disubstituted cyclopropyl compounds.

Vibrational circular dichroism (VCD) is a relatively new spectroscopic technique having demonstrated high sensitivity to conformational variation among molecules of similar structure.[1,2] Utilization of VCD for conformational analyses is just beginning to be explored. Two approaches can be followed to achieve this goal: one can correlate spectra of a series of related compounds in order to determine characteristic VCD bands, such as the topic of this paper, or one can attempt to calculate VCD by using one of the many theoretical models now available.[1-3] The latter approach demands previous evaluation of the usefulness of the calculational model with molecules of known structure. To this end, we have sought to obtain VCD of small, conformationally limited molecules on which a variety of theoretical approaches might be attempted.[4]

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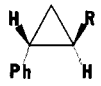
Chiral cyclopropanes form a category of natural interest to both methods of stereochemical analyses, due to their rigid structure and the common cyclopropyl (C_3H_4) ring which exists in all the molecules we have studied. One can then observe the effects of a variety of substituents on the ring VCD as well as on that of the other substituent. Such a series of compounds can also be used to study effects of mass, charge, polarizabilities, and other properties of the substituent on the VCD of the framework. In the first report in this series,[5] we studied VCD in the C–H stretch and deformation regions of symmetrically trans-1,2-disubstituted cyclopropanes derived from the diacid form. A subsequent paper[6] reported the VCD down in energy to 900 cm^{-1} and the X-ray crystal structure of a tris(*trans*-1,2-cyclopropanediyldimethylene)diborate. These plus our unpublished VCD spectra for other members of this series[7] have indicated that a $-CH_2-$ or $-CH_3$ group next to the cyclopropyl ring results in a difference in appearance for the VCD of certain characteristic modes from that first reported for molecules containing primarily –C=O containing substituents. The results herein will be used to argue that some of these modes, at least, will fit a general pattern when frequency shifts due to change in substituents are carefully taken into account.

In the present paper, we make another comparative analysis of a series of cyclopropanes, this time asymmetrically trans-1,2-disubstituted but all containing a phenyl substituent. We have also measured the VCD of *trans*-1-phenylpropylene oxide for comparison. These cyclopropyl compounds were synthesized as derivatives of *trans*-2-phenylcyclopropanecarboxylic acid which was resolved to the (–)-(1*R*,2*R*) optical isomer whose absolute configuration has been established.[8] In this report we compare



VCD, obtained over the entire currently accessible range (>4000–900 cm^{-1}) of our instrument, among the members of this series and with those of the symmetrically disubstituted cyclopropane series reported earlier.[5] This then leads us to the identification of what appear to be stereochemical marker bands for these molecules.

Experimental Section

VCD and infrared absorption spectra were recorded on the UIC spectrometer which has been described in detail elsewhere.[1,9,10] For all VCD spectra, a racemic preparation of the compound studied was used as a base line by recording its spectrum online and then digitally substracting it from that of the optically active compounds before plotting. [For the epoxide, the spectrum of the opposite enantiomer was subtracted, and the result was divided by two.] VCD spectra were calibrated with a CdS (II–IV) birefringent plate and a second grid polarizer,[9] and signs were determined by comparison to the VCD spectrum obtained from 3-methylcyclohexanone.[9–11] Single beam transmission spectra of solvents were subtracted from those of solution samples, and then the result was replotted in terms of molar extinction. Spectral grade solvents, CCl_4, C_2Cl_4, CS_2, $CDCl_3$, and Me_2SO-d_6 (Aldrich), were used without further purification.

Optical rotations of synthesized compounds were determined at room temperature with a Perkin-Elmer 241 polarimeter. ^1H NMR spectra were recorded on a Varian EM-360L or A-60 spectrometer and higher resolution infrared spectra on an IBM-32 or Digilab FTS-60 FT-IR spectrometer. Vapor phase chromatography was done on a Gow-Mac Instrument Co. Series 150 GC. Melting points were determined with a Thomas Hoover capillary melting point apparatus and are uncorrected. With two exceptions, all of the compounds studied were prepared in our laboratory according to literature methods or standard synthetic procedures from commercial starting materials. The *trans*-2-phenylcyclopropylaminesulfuric acid was obtained as a gift from Smith Klein and French Laboratories and 1-phenylpropylene oxide was purchased from Aldrich and used without further purification.

Resolution of *trans*-2-Phenylcyclopropanecarboxylic Acid. A diastereomeric salt was prepared from the commercially available trans-acid species and quinine (Aldrich) in ethyl acetate.[12] After several recrystallizations, the partially resolved acid was mixed in a 1:1 ratio with dehydroabietylamine (Aldrich) in ethyl acetate.[12] After two more recrystallizations the recovered acid had $[\alpha]_D = -302°$ ($CHCl_3$, *c* 10.2 mg/mL).

***trans*-2-Phenylcyclopropanecarbonyl Chloride.** Following the method of Burger and Yost,[13] the acid was mixed with benzene and then refluxed with thionyl chloride. Excess $SOCl_2$ and benzene were removed by rotary evaporation, and then the product was vacuum distilled, bp 125 °C (9 mm). The ^1H NMR ($CDCl_3$) spectrum showed four bands at δ 7.14 ppm (5 H, m, phenyl H), 2.8 ppm (1 H, m, PhCH), 2.3 ppm (1 H, m, HCCOCl), and 1.8 ppm (2 H, m, CH_2). The optically active isomer had $[\alpha]_D = -328°$ (CCl_4, c 15.1 mg/mL).

Methyl *trans*-2-Phenylcyclopropanecarboxylate-d_0 and -d_3. The ester derivatives were prepared from the acid chloride and methanol-d_0 or methanol-d_3 in CCl_4 containing pyridine as a catalyst. The product was isolated by distillation, bp 117–118 °C (7 mm). The structure of the product was confirmed from its ^1H NMR ($CDCl_3$), in which the d_0 species showed δ 7.1 ppm (5 H, m, phenyl H), 3.65 ppm (3 H, s, $-OCH_3$), 2.6 ppm (1 H, m, PhCH), and 1.2–2.1 ppm (3 H, m, HCCOO and CH_2); the d_3 species had the same ^1H NMR spectrum except that the δ = 3.65 ppm peak disappeared. The optically active form of the d_0 species had $[\alpha]_D = -303°$ (CCl_4, 23.5 mg/mL), and the d_3 species had $[\alpha]_D = -295°$ (CCl_4, 18.6 mg/mL).

***trans*-2-Phenylcyclopropanecarboxamide.** The amide derivatives were prepared by mixing the acid chloride with an ice-cold 20% ammonia solution.[12] The product had a mp of 189–190 °C and its ^1H NMR spectrum (Me_2SO-d_6) showed δ 7.2 ppm (5 H, m, phenyl H), 3.3 ppm (2 H, s, amine protons), and 2.3–1.0 ppm (4 H, m, cyclopropane H). The optically active species had $[\alpha]_D = -312°$ ($CHCl_3$, c 13.5 mg/mL).

***trans*-2-Phenylcyclopropanecarbonitrile.** The nitrile derivatives were obtained by refluxing amide with thionyl chloride in benzene.[12] The product was recrystallized from petroleum ether, mp 28–30 °C. Its ^1H NMR spectrum ($CDCl_3$) had δ 7.1 ppm (5 H, m, phenyl H), 2.5 ppm (1 H, m, PhCH), 1.5 ppm (3 H, m, CH_2, CHCN). The optically active form had $[\alpha]_D = -260°$ (C_2Cl_4, c 19.3 mg/mL).

***trans*-2-Phenylcyclopropanemethanol-d_0 and -d_2.** The alcohol derivatives were prepared by reduction of acid species with $LiAlH_4$ ($LiAlD_4$). The product had bp 132–34 °C (10 mm). The ^1H NMR spectrum ($CDCl_3$) showed δ 7.1 ppm (5 H, m, phenyl ring protons), 3.5 ppm (2 H, d, CH_2–O; disappears for d_2 form), 2.8 ppm (1 H, s, OH), and 2.0–0.7 ppm (4 H, m, cyclopropane ring protons). The optically active d_0 compound had $[\alpha]_D = -84°$ (CCl_4, c 28 mg/mL) and the d_2 had $[\alpha]_D = -92°$ (CCl_4, 39 mg/mL).

***trans*-1-Methyl-2-phenylcyclopropane-d_0 and -d_3.** These compounds were prepared by reduction of *trans*-1-((tosyloxy)methyl)-2-phenylcyclopropane with lithium triethylborohydride or -borodeuteride (Super-Hydride or Super-Deuteride, Aldrich).[14] After addition of Super-Hydride, the mixture was gently heated for 3 h and then stirred under N_2 overnight at room temperature. The tosylates were prepared from *trans*-2-phenylcyclopropanemethanol (d_0, d_2) and *p*-toluenesulfonyl chloride in dry pyridine. The product had a bp of 74–76 °C (20 mm). ^1H NMR ($CDCl_3$) showed δ 7.2 ppm (5 H, m, phenyl H) and 1.8–0.6 (7 H, m, methyl and cyclopropyl); the methyl peaks centered at ~1.2 ppm and disappeared in the d_3 compound. Gas-phase chromatography on a 15% Carbowax 20M column (4 ft on Chromosorb P80/100 mesh) at 150 °C showed ~4% impurity in the d_0 sample and 7% in the d_3. At these levels the impurity is not expected to pose an interference problem for VCD measurements. The optically active isomers for d_0 had $[\alpha]_D = -108°$ (CCl_4, c 11 mg/mL) and for d_3 $[\alpha]_D = -105°$ (CCl_4, c 22 mg/mL).

***trans*-2-phenylcyclopropylamine.** This amine was obtained from the *trans*-2-phenylcyclopropylaminesulfuric acid (tranylcypromine) provided by Smith Klein and French Laboratories by mixing with 50% KOH and extracting with ether: $[\alpha]_D = -135°$ (CCl_4, c 25 mg/mL). Unfortu-

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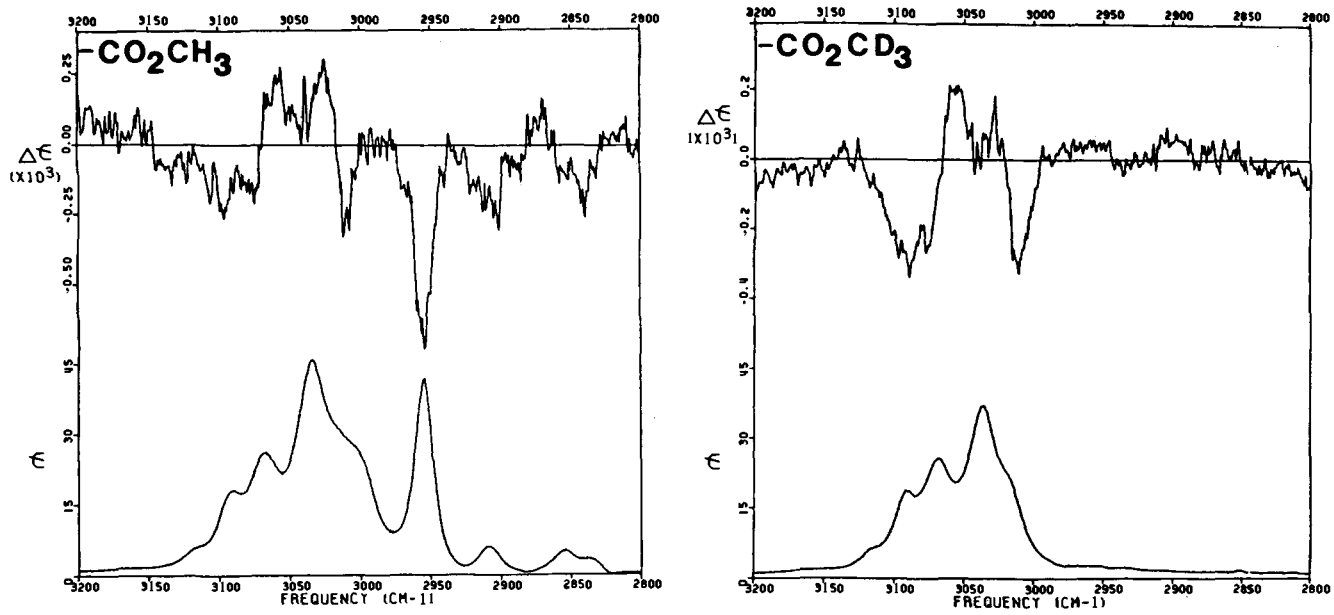

Figure 1. VCD and absorption spectra in the CH stretching region: (a) (−)-methyl *trans*-2-phenylcyclopropanecarboxylate, 0.189 M in CCl_4, PL 0.073 cm, 6 scan average, resolution ~12 cm^{-1}, with TC = 3 s and (b) (−)-methyl *trans*-2-phenylcyclopropanecarboxylate-d_3 0.104 M in CCl_4, PL 0.24 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 10 s.

nately, the amine form polymerized before the mid-IR (<1500 cm^{-1}) VCD could be run, and no additional sample was available, so that only CH stretch data are presented.

Results and Discussion

The measured IR absorption and VCD are presented, assigned, and compared in this section. For ease of discussion we will divide the spectra into four sections which we, arbitrarily, denote as the C–H stretch, functional group bands (C=O, C≡N), C—H deformation, and framework region after their most common features. As compared to our earlier study,[5] these molecules have two common groups to give rise to characteristic VCD, the cyclopropyl ring, and the phenyl ring. In all cases, due to our synthetic procedures, these groups have the same absolute configuration and, thus, are expected to evidence some VCD bands of the same sign for all the molecules, if those bands are stereospecific.

To aid assimilation of these data, we make some general remarks here. The carbonyl containing compounds tend to form a sub group that evidences clear band shape similarities not always obvious in the C≡N, NH_2, CH_2OH, and CH_3 species. The magnitudes of ϵ vary substantially with respect to our earlier study. Those assignable to substituent modes are, as expected from the 2 to 1 reduction in effective concentration, somewhat smaller in these phenyl-substituted compounds than was found earlier in the symmetrically disubstituted cyclopropanes.[5] In general the $\Delta\epsilon$, or VCD, values are substantially less for these asymmetrically 1-phenyl-substituted molecules than was seen for the 1,2 symmetrically disubstituted cyclopropanes in the CH stretching region, but the two are comparable in the deformation region.

Deuteriation of these phenyl-substituted molecules is not so facile as for the diester precursor of the previously studied series, so we must rely here more on assignment by analogy to the results of other workers. Additionally, the phenyl and cyclopropyl groups have several interfering VCD and absorption bands so that clear separation and assignment is sometimes impossible. Finally, some data is not accessible due to solvent absorption interference. This is particularly true for the acid and amide substituents.

C–H Stretching Region. In the region from ~3000 to 3150 cm^{-1} occur the four cyclopropyl CH stretching modes.[15] The five phenyl C–H stretches also occur in this region and hence cause unavoidable overlap and mixing. These cyclopropyl frequencies are also somewhat affected by substituent, being on average a bit higher for —C≡N[5] and lower for —CH_2—.[6] The absorption spectra in this region are dominated by the characteristic three bands of the phenyl group near ~3030, ~3070, and ~3090 cm^{-1}.[16] The cyclopropyl bands, being weaker, are evidenced as shoulders to higher and lower energy of these peaks.

From several VCD studies of phenyl ethyl compounds[10,17,18] and our previous cyclopropane studies,[5] we would expect the phenyl C–H modes to give rise to small but measureable VCD, due to interaction with a chiral center, and the cyclopropyl CH modes, on the other hand, to yield more intense VCD. This supposition has guided some of our interpretation of the VCD in this region. Of course, substituent CH_3 and CH_2 modes are expected to be lower in energy (2850–3000 cm^{-1}) and the N–H and O–H stretches to be much higher than the phenyl and cyclopropyl CH modes.

With the above in mind, we compare the CH stretching VCD of the methyl *trans*-2-phenylcyclopropanecarboxylate-d_0 and -d_3 in Figure 1. The amide-substituted phenylcyclopropane yielded a similar, though broadened, VCD pattern while the corresponding acid VCD was very broad and reduced in signal to noise ratio (S/N) by intermolecular hydrogen bonding. A remarkable similarity in the −,+,− pattern seen in the 3000–3100-cm^{-1} region with that noted earlier in the cyclopropane diester, diacid, and diamide species[5] is evident in this monosubstituted series. But, here, the central positive feature, in addition, is more complex and corresponds to two or more bands, and the overall $\Delta\epsilon$ values are substantially lower. The lowest energy negative component of this triple sign VCD pattern corresponds to a shoulder on the low energy side of the most intense phenyl CH absorption peak. Higher resolution FTIR scans of this region show that the shoulder in the d_0 compound has two components, the lower of which disappears in the d_3 compound. Higher in energy lie two distinct positive VCD bands, the lower of which (~3025 cm^{-1}) still lies significantly lower in energy than the most intense phenyl CH mode at ~3035 cm^{-1}. The next higher positive mode lies at ~3060 cm^{-1} which is slightly lower in energy than the next most

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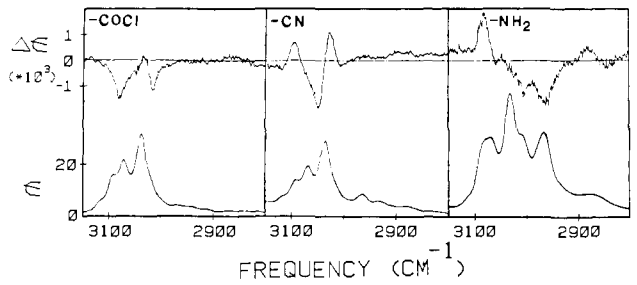

Figure 2. VCD and absorption spectra in the CH stretching region: (a) (−)-*trans*-2-phenylcyclopropanecarbonyl chloride, 0.282 M in CCl_4, PL 0.073 cm, 8 scan average, resolution ~12 cm^{-1}, with TC = 3 s; (b) (−)-*trans*-2-phenylcyclopropanecarbonitrile, 0.135 M in C_2Cl_4, PL 0.243 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 10 s; (c) (−)-*trans*-2-phenylcyclopropylamine, 0.163 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 10 s.

intense phenyl CH mode. (Such a clear correlation of VCD and absorption is not possible for the amide and acid spectra due to bandshape broadening.) The highest energy VCD band is negative and broad, overlapping the remaining phenyl and cyclopropyl absorption bands.

Below this region at ~2955 cm^{-1}, the methyl asymmetric CH_3 gives rise to an intense negative VCD in the ester-d_0 compound. While only of ancillary interest to this paper, it is interesting to note that both the sign[19] and the magnitude of the VCD are consistent with that observed earlier[5] for the diester-d_0 compound. However, since ϵ for the CH_3 mode in this phenyl-substituted cyclopropane is half that in the diester,[5] $\Delta\epsilon/\epsilon$ has in fact doubled.

The 3000–3100-cm^{-1} region described above can be assigned to a mixture of cyclopropyl and phenyl CH stretching modes. The negative VCD band at ~3010 cm^{-1} is almost certainly the cyclopropyl symmetric CH_2 stretch. Its consistency through the series we examine here (vide infra) is the best evidence for such an assignment, and the parallel result seen in the symmetrically disubstituted cyclopropanes[5,19] provides additional evidence for its assignment. The two positive bands could be interpreted as arising from the trans 1,2-C*–H of the cyclopropyl group or from phenyl C–H modes. If the former assignment were used, the splitting of the near degenerate trans 1,2-CH's would be enhanced over that seen in the previous work[5] due to the asymmetric 1,2 substitution. These modes may, indeed, be coupled to phenyl CH modes which might cause the phenyl CH's to have the opposite sense VCD as the cyclopropyl C*–H. This could explain the negative going dip at 3030 cm^{-1} and the negative band at 3070 cm^{-1} which appear to correspond to the two most prominent phenyl CH absorption bands. The width of the high energy negative VCD band is explained by additional VCD arising from the asymmetric cyclopropyl CH_2 stretch which is expected to be near 3100 cm^{-1}. In the diester compounds it was possible to demonstrate that the cyclopropyl symmetric and asymmetric CH_2 stretches had the same sign VCD which is consistent with what we observe here.

In Figure 2 are compared similar VCD for the COCl, C≡N, and NH_2 and in Figure 3 for the CH_2OH, CD_2OH, CH_3, and CD_3 phenylcyclopropyl compounds. At first glance these look quite different from Figure 1 and, in the case of Figure 2, from each other. However, some remnants of the above delineated pattern are detectable. For COCl, we see essentially the same −,+,− pattern except that now the central positive feature is only a single feature having become very weak and narrow. The high-energy negative VCD band has grown in intensity and developed a low-energy negative shoulder at the position where the esters and amide had their high-energy positive band. This is consistent with the positive VCD band seen in the ester compounds at ~3050 cm^{-1} having changed the sign to negative when the ring is substituted with an acid chloride. A similar occurrence was earlier noted for the diacid chloride as compared to the diester cyclopropane[5] and was there attributed to a possible alteration in the coupling between the trans C*–H's on the cyclopropyl ring as influenced by the COCl group. But in that case, no negative band remained. This suggests an assignment of the higher C*–H as being that one associated with the COCl substituent. The lowest energy positive feature (~3030 cm^{-1}) seems to be retained in the –COCl VCD but is quite weak, possibly due to overlap with negative bands from both above and below in frequency. The cyclopropyl symmetric CH_2 stretch has shifted up in energy to ~3020 cm^{-1} (lowest energy negative VCD correlated to the barely apparent shoulder on the low-energy phenyl CH absorption) further exacerbating this cancellation effect. One other problem with this analysis is that the cyclopropyl asymmetric CH_2 stretch VCD (~3120 cm^{-1}) has apparently disappeared or changed sign.

On the first inspection, the —C≡N substituted phenylcyclopropane VCD (Figure 2) appears to be just opposite in sign pattern from that seen above (Figure 1) for the esters. Such an assessment of the VCD cannot be positively ruled out. However some parallel with the above pattern can be found if we recall that cyanocyclopropyl C–H stretches lie somewhat (~20 cm^{-1}) higher in energy than those in the ester cyclopropyl compounds,[5,15] but that the phenyl bands will be at about the same energy in both. Hence, we expect some relative shifting of their VCD features. Thus it is possible that the large negative band at ~3050 cm^{-1} is an overlap of the above noted negative VCD for the shifted cyclopropyl CH_2 symmetric stretch and the coupled phenyl and C*–H(CN) stretch modes. This would, however, be a very large shift from the above pattern. From the dicyano study,[5] it is clear that only the C*–H modes give rise to large VCD, the symmetric CH_2 mode being exceptionally weak in both absorption and VCD. Hence the CH_2 mode may have simply disappeared under the positive VCD at 3030 cm^{-1}. The lower energy (~3030 cm^{-1}) positive VCD most probably is then due to the C*–H next to the phenyl since it has not shifted from the above discussed molecules. The higher energy (~3095 cm^{-1}) positive VCD could be attributed to the cyclopropyl asymmetric CH_2 stretch paralleling the assignments below for $-CH_2-$ substituted phenylcyclopropanes. While, at present, the assignment of the cyanophenylcyclopropane results remains somewhat unclear, comparison to the dicyanocyclopropane VCD indicates that, at somewhat higher frequencies, a similar sign pattern was found for the C*–H and asymmetric CH_2 (3050, 3095 cm^{-1}) thus confirming their origin in cyclopropyl modes. While this cyano compound is clearly the worst fitting of the series to the concept of stereochemically sensitive cyclopropyl CH stretch VCD, that failure probably is due to the unusually weak VCD and IR absorption of the symmetric CH_2 stretch.

The cyclopropylamine CH VCD (Figure 2) can be seen to follow the same pattern when the frequency shifts due to amine substitution are taken into account. Following Kalasinsky et al.,[20] we attribute the lowest energy band (~2970 cm^{-1}) and its associated negative VCD to the C*–H (NH_2) stretch which is drastically shifted from its position at ~3050 cm^{-1} in the previous compounds. Thus this mode has the opposite sign from that seen in the esters but the same as that in the cyano compound. The absorption shoulder at ~3010 cm^{-1} and its associated negative VCD can be assigned to the cyclopropyl symmetric CH_2 stretch paralleling the analysis of the ester spectra. The high-energy positive VCD at ~3085 cm^{-1} correlates to the highest energy phenyl CH absorption but probably arises from the underlying cyclopropyl asymmetric CH_2 stretch. For this band, the NH_2 result again appears to follow the cyano pattern rather than that of the ester. This parallel adds evidence that the C*–H(CN) band in the cyano compound above is also negative and helps explain the large 3050-cm^{-1} negative band in that spectrum. Thus, by looking at all of the spectra together, a more uniform understanding has developed. The NH_3^+ substituted cyclopropane results are too broad (due to overlaping NH_3^+ bands) for comparison.

(19) Note that the cyclopropane spectra presented here are for (1*R*,2*R*) and those published previously[5] were (1*S*,2*S*) so that a sign flip between the two studies would be expected for any band which is an indication of absolute stereochemistry.

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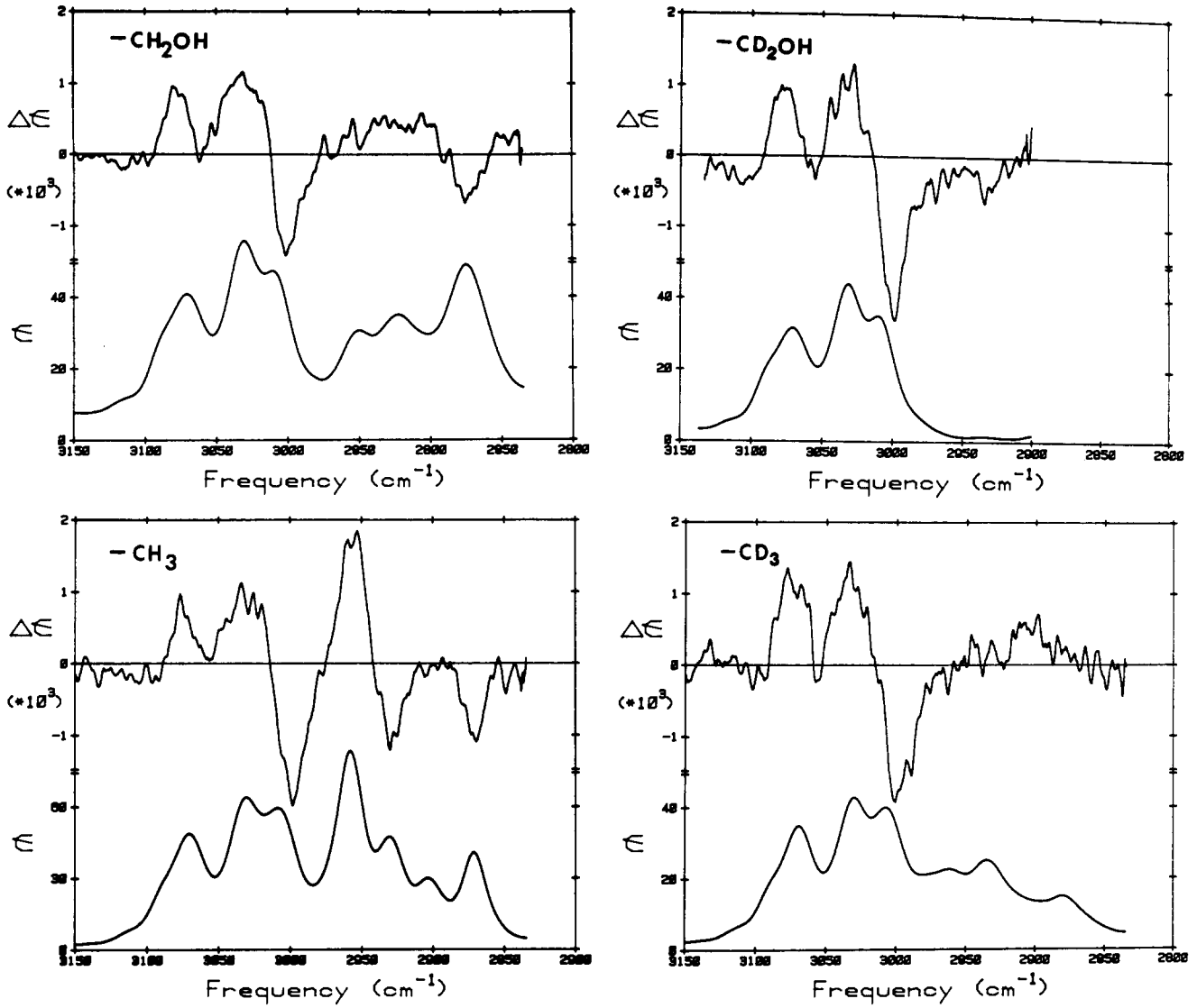

Figure 3. VCD and absorption spectra in the CH stretching region: (a) (−)-*trans*-1-methyl-2-phenylcyclopropane-d_0, 0.09 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 3 s; (b) (−)-*trans*-1-methyl-2-phenylcyclopropane-d_3, 0.16 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 3 s; (c) (−)-*trans*-2-phenylcyclopropanemethanol-d_0, 0.010 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 3 s; (d) (−)-*trans*-2-phenylcyclopropanemethanol-d_2, 0.198 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~12 cm^{-1}, with TC = 3 s.

In summarizing the COCl, CN, and NH_2 results, it is clear that the apparently simple overall pattern for the phenyl and cyclopropyl CH stretches seen in the esters does not carry through to these species. However, the symmetric cyclopropyl CH_2 stretch does seem to be uniformly negative for all these examples (with the possible exception of C≡N, due to lack of intensity). On the other hand, the trans C*–H's seem to be quite sensitive to the nature of the substituent, and the asymmetric CH_2 also changes sign in the NH_2 and C≡N cases.

The VCD of the CH_2OH, CD_2OH, CH_3, and CD_3 substituted phenylcyclopropanes (Figure 3) are remarkably similar when attention is focused on the cyclopropyl and phenyl CH stretches from 2980–3100 cm^{-1}. A regular −, +, + pattern is seen with increasing vibrational frequency. From earlier work[6,7,15] it is clear that the cyclopropyl frequencies in these compounds should be lower than those in the esters and that the cyclopropyl symmetric CH_2 stretch (~3000 cm^{-1}) should be more intense than the asymmetric. This explains the well-resolved intense shoulder (~3010 cm^{-1}) on the 3030-cm^{-1} phenyl CH absorption band which, along with its negative VCD, can be assigned to the cyclopropyl symmetric CH_2 stretch paralleling all the above results. The positive VCD lying higher in energy overlaps but is broader than the phenyl CH and probably has contribution from an underlying cyclopropyl C*–H mode. The next positive VCD band lies between the two higher energy phenyl IR bands and most probably has a large contribution from the underlying CH_2 asymmetric stretch. As such its sign directly parallels the NH_2 and C≡N results above after taking into account the expected frequency shifts. By comparison, (−)-1-phenylpropylene oxide[21] shows positive VCD at ~3060 cm^{-1} and negative VCD at ~3020 cm^{-1}. Presumably these latter two bands are primarily due to mutual coupling of the trans C*–H modes in the epoxide ring.

In the methylphenylcyclopropanes, the methyl CH_3 asymmetric stretch at 2955 cm^{-1} gives rise to a positive VCD, and a weak band (presumably due to a Fermi resonance) at 2930 cm^{-1} gives a negative VCD. A somewhat similar pattern is found for the (1)-1-phenylpropylene oxide[21] except that the CH_3 modes appear to be split leading to a more complex pattern.

Finally, the CH_2 group on the methyl alcohol substituent gives rise to weak VCD with a broad positive band correlating to two absorption bands at 2950 and 2930 cm^{-1} and a sharp negative band at 2880 cm^{-1}. This latter is presumably the symmetric CH_2 stretch which would be expected to interact with the adjacent C*–H bond on the cyclopropyl ring.[15] Weak negative VCD at ~2850 cm^{-1}

(21) Note that (−)-phenylpropylene oxide is (1*S*,2*S*) but has the same absolute configuration as the (1*R*,2*R*)-phenylcyclopropanes discussed in this paper.

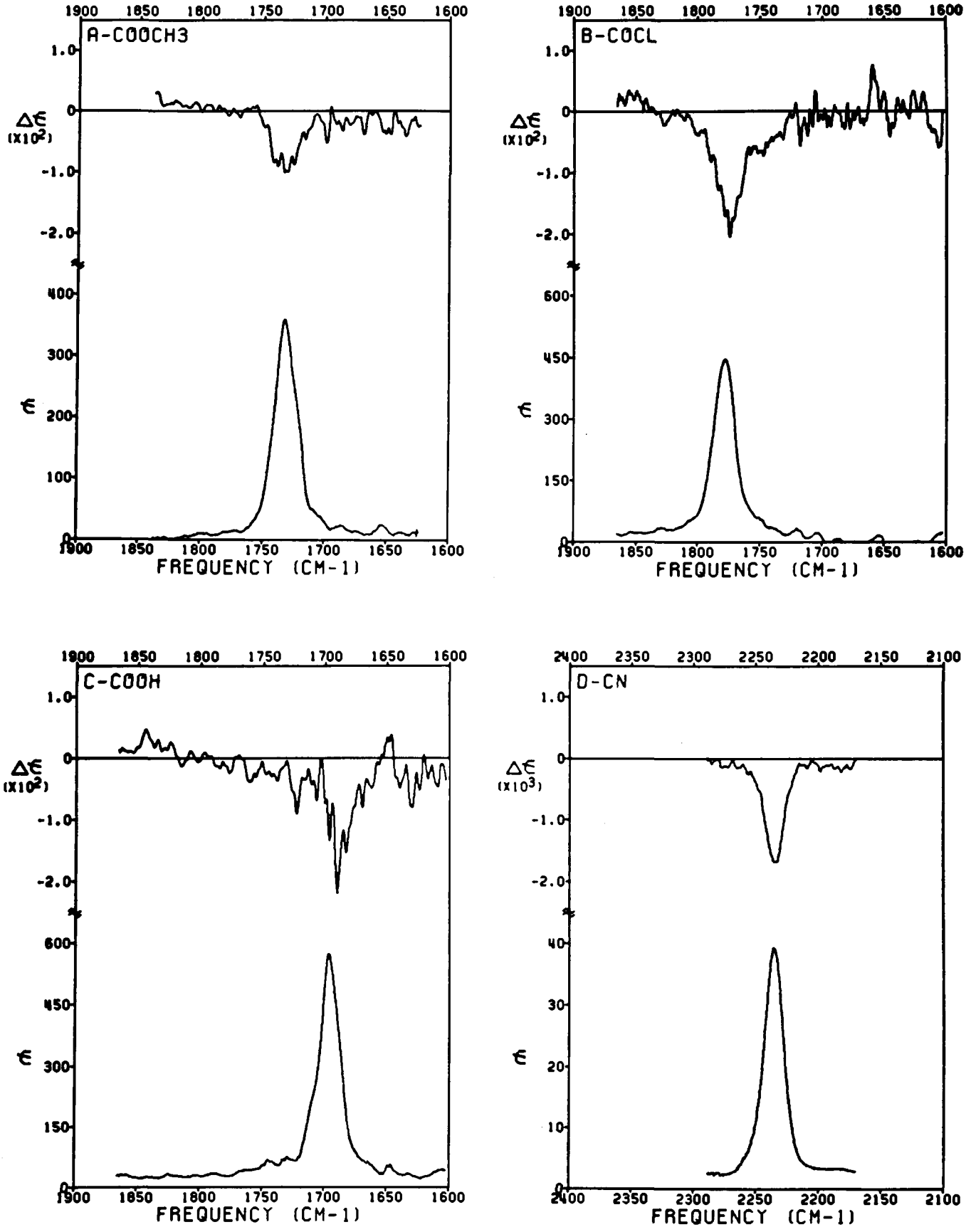

Figure 4. VCD and absorption spectra in carbonyl and nitrile stretching region: (a) (−)-methyl *trans*-2-phenylcyclopropanecarboxylate, 0.028 M in CCl_4, PL 0.043 cm, 6 scan average, resolution ~11 cm^{-1}, with TC = 10 s; (b) (−)-*trans*-2-phenylcyclopropanecarbonyl chloride, 0.014 M in CCl_4, PL 0.043 cm, 6 scan average, resolution ~11 cm^{-1}, with TC = 10 s; (c) (−)-*trans*-2-phenylcyclopropanecarboxylic acid, 0.015 M in CCl_4, PL 0.043 cm, 6 scan average, resolution ~11 cm^{-1}, with TC = 10 s; (d) (−)-*trans*-2-phenylcyclopropanecarbonitrile, 0.135 M in C_2Cl_4, PL 0.073 cm, 10 scan average, resolution ~12 cm^{-1}, with TC = 3 s.

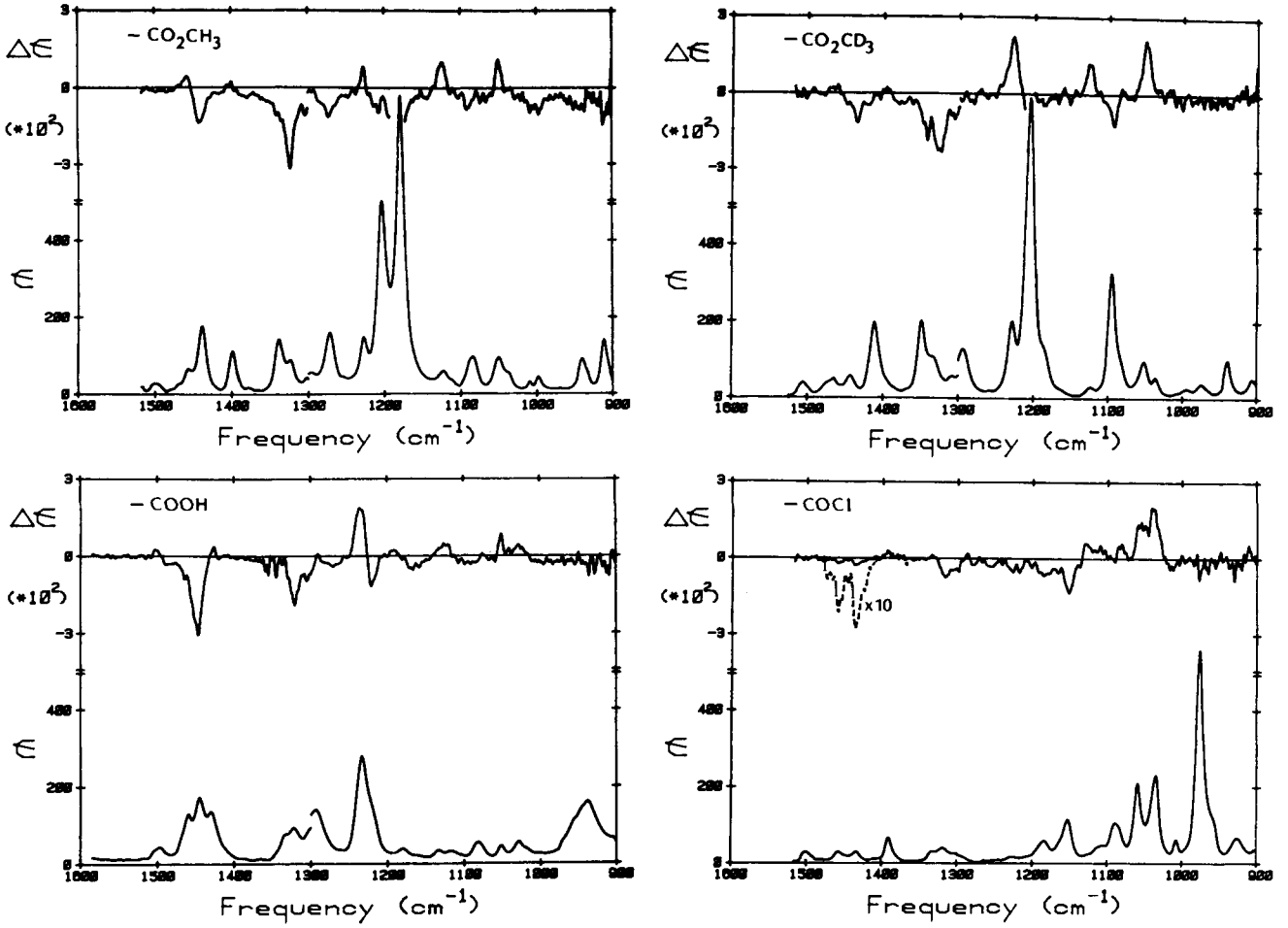

Figure 5. VCD and absorption spectra in the CH_2 bending and framework region: (a) (−)-methyl *trans*-2-phenylcyclopropanecarboxylate, region above 1300 cm^{-1}, 0.095 M in CCl_4, PL 0.043 cm, 6 scan average, resolution ~10 cm^{-1}, with TC = 10 s and region below 1300 cm^{-1}, 0.107 M in CS_2, PL 0.009 cm, 6 scan average, resolution ~6 cm^{-1}, with TC = 3 s; (b) (−)-methyl *trans*-2-phenylcyclopropanecarboxylate-d_3, region above 1300 cm^{-1}, 0.104 M in CCl_4, PL 0.043 cm, 4 scan average, resolution ~10 cm^{-1}, with TC = 10 s and region below 1300 cm^{-1}, 0.0864 M in CS_2, PL 0.008 cm, 6 scan average, resolution ~6 cm^{-1} with TC = 3 s; (c) (−)-*trans*-2-phenylcyclopropanecarboxylic acid, region above 1300 cm^{-1}, 0.077 M in C_2Cl_4, PL 0.063 cm, 6 scan average, resolution ~10 cm^{-1}, with TC = 3 s and region below 1300 cm^{-1}, 0.031 M in CS_2, PL 0.048 cm, 6 scan average, resolution ~6 cm^{-1}, with TC = 3 s; (d) (−)-*trans*-2-phenylcyclopropanecarbonyl chloride, region above 1300 cm^{-1}, 0.282 M in CCl_4, PL 0.043 cm, 6 scan average, resolution ~10 cm^{-1}, with TC = 3 s and region below 1300 cm^{-1}, 0.107 M in CS_2, PL 0.008 cm, 6 scan average, resolution ~6 cm^{-1} with TC = 3 s.

is also seen for the (−)-phenylpropylene oxide[21] symmetric CH_3 stretch.

It would seem that of these C–H stretching bands, which result from relatively local motion, some should evidence VCD that is characteristic of local stereochemistry. In particular, this appears to be the case for the lowest energy cyclopropane C–H mode in all but the C≡N case. A survey of our earlier published spectra[5,6] indicates that the lowest energy cyclopropyl C–H stretching mode was also consistent in sign in those symmetrically substituted cyclopropanes, but, in that case, the VCD shown was positive because the (1*S*,2*S*) isomer was used.[19] The vibration giving rise to this band is primarily due to the apex cyclopropyl–CH_2 symmetric stretching and, as such, might be reasonably expected to experience similar perturbations in both classes of molecules.

It is not clear why the asymmetric stretch, expected to be highest in energy, is not similarly consistent. Our assignments indicate that the sign of this mode changes between the C=O containing and the $-CH_2-$, NH_2, and C≡N substituted groups of compounds. On the other hand, the trans C*–H is expected to be more strongly affected by the character of the substituent and may be significantly shifted in energy by it. Since we are here studying asymmetrically substituted molecules, it is possible that the relative ordering of the cyclopropyl modes is altered by substituent thus distorting the pattern.

Another question is why C≡N differs so much from the others. Perhaps its π system has a strong interaction with the ring psuedo-π system.[15,22] This has been previously proposed as the source of considerable distortion of the cyclopropyl ring from equilateral geometry[23] and changes in the vibrational frequency patterns.[24,25] At any rate, this lone deviation from the clear systematic trend for the symmetric CH_2 mode seems to be attributable to a lack of intensity. The frequency and sign pattern data for all of these molecules are summarized in Table I.

Functional Groups. In Figure 4 are shown the VCD and absorption of the C=O stretching bands of the COOH, $COOCH_3$, and COCl derivatives as well as of the C≡N stretch of the cyano compound. All give rise to monosignate, negative VCD correlated to the absorption band. The acid VCD is, however, significantly displaced to lower energy from the absorbance maximum. While these should not necessarily be quantitatively comparable to the same bands for the symmetrically disubstituted molecules, such a comparison is potentially useful for evaluation of the application of the coupled oscillator model[26] used in that study.[5,7]

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(24) Schrumpf, G.; Dunker, H. *Spectrochim. Acta* **1985**, *41A*, 841–845, and references therein.
(25) El-Azhary, A.; Keiderling, T. A.; Alper, J. S.; Lowe, M. A., to be submitted for publication.
(26) Holzwarth, G.; Chabay, I. *J. Chem. Phys.* **1972**, *57*, 1632. Faulkner, J. R. Ph.D. Thesis, University of Minnesota, 1976. Su, C. N. Ph.D. Thesis, University of Illinois at Chicago, 1981.

In the cyano case, in particular, both molecules have a single band in the C≡N stretching region with $\Delta\epsilon/\epsilon \sim 4 \times 10^{-5}$ of a single sign reflecting the chirality [(−) for R or (+) for S]. Since the coupling signal in the dicyano compound is predicted to be significantly smaller than this "intrinsic" monocyano signal, it is clear why no coupled oscillator VCD was seen for the dicyano species.[5] Additionally, a substantial shift in absorption frequency is seen comparing the dicyano (~2250 cm^{-1}) to monocyano (~2240 cm^{-1}) compounds. This is further evidence of a strong interaction of the -C≡N group with the cyclopropyl ring. Such a shift has been seen before with other cyanocyclopropanes.[15,24]

In the (1*S*,2*S*) diester[19] a bisignate signal of $\Delta\epsilon/\epsilon = 6 \times 10^{-5}$ in the negative and 9×10^{-5} in the positive lobe was found, while here for the (1*R*,2*R*) monoester only a negative monosignate $\Delta\epsilon/\epsilon \sim 3 \times 10^{-5}$ is seen with no significant frequency shift from the absorption maximum. This difference in magnitude and shape is consistent with a coupled oscillator contribution to the VCD being superimposed on a relatively small local chirality effect.[26] Comparing $\Delta\epsilon/\epsilon$ values helps correct for possible effects of the polarizability of the phenyl group on intensity and normalizes for the number of oscillators. A similar analysis for the acid chloride can be postulated but is not so successful quantitatively as it is qualitatively. The diacid chloride C=O absorption band additionally evidenced considerable broadening[5] not seen in the monoacid chloride implying that a mixture of conformations is present in the former case. However, the monoacid chloride (Figure 4) VCD result does have a prominent shoulder and a shift away from the absorption maximum. The phenyl group will probably alter the relative population of cis and trans C=O conformers (with respect to the ring) as compared to the diacid chloride case. Thus quantitative comparison becomes quite difficult.

CH_2 Deformation Region. In the spectral region from 1525 to 1250 cm^{-1} we expect to find the CH_2 scissor, CH deformation, and sometimes the CH_2 twist and ring breathing modes of the cyclopropane somewhat overlapped with phenyl C=C stretching modes. Furthermore, the modes in this spectral region show a greater tendency to shift with substituent and, presumably, to become strongly mixed. Hence the clarity of assignment and universality of configuration dependent marker bands is expected to be less in this region. However, in this region, near 1450 cm^{-1}, is found the most consistent VCD feature found for this series of substituted cyclopropanes.

Phenyl C=C stretching modes are also expected above 1550 cm^{-1}. To measure VCD in that region requires a change of solvent from the CS_2 and CCl_4 used[6] in the region below 1500 cm^{-1}. For several of the molecules studied, insufficient sample was obtained to obtain VCD for this phenyl C=C region. For those compounds for which we did attempt VCD, no signals above the noise and artifact level[1] were found.

The mid-IR VCD of the esters (d_0 and d_3), acid, and acid chloride are in Figure 5. Due to solubility problems, we could not obtain similar amide VCD. The corresponding cyano and phenylpropylene oxide results are in Figure 6, and the CH_2OH, CD_2OH, CH_3, and CD_3 mid-IR spectra are in Figure 7. Due to polymerization, we could not measure the amide sample in this region, and, due to insufficient sample, data below 1300 cm^{-1} were not obtained for the CH_3 and CD_3 substituted phenylcyclopropanes. Immediately a common VCD pattern becomes apparent. All the spectra, including that of the epoxide, evidence substantial negative peaks at ~1460–1430 cm^{-1}. Additionally, several of the compounds have intense negative VCD at ~1325 cm^{-1}, with the $-CH_2-$ and $-CD_2-$ type systems being the exceptions. While the higher energy band may be due to CH_2 or CH_3 deformation modes of the methyl-type substituents, these if present are undoubtedly mixed with phenyl ring C=C modes[27] which provide the consistency in VCD for this band through the series of phenylcyclopropanes. It has previously been shown in a series of phenylethyl compounds that these benzene modes can substantially mix with CH_3 deformations when separated by a single chiral carbon atom.[17,28] In that situation a substantial VCD can result in the phenyl mode. Most of the 1450-cm^{-1} bands observed in this work evidence a split sign pattern in the VCD implying interaction between various modes which, by analogy to the phenylethyl case,[17] could be with cyclopropyl C*–H deformations. Typically this is associated with the presence of some weak positive VCD either higher or lower in energy from the main negative band. That cyclopropyl modes may also contribute to the 1450-cm^{-1} bands is suggested by its parallel in the VCD of the symmetrically disubstituted cyclopropanes[5] which also show a consistent 1450-cm^{-1} band (there positive[19]) for all except some of the diesters.

The cyclopropyl CH_2 scissor mode is expected to lie somewhere between 1450 and 1380 cm^{-1} and to be fairly sensitive to ring substitution. Without deuteriation data, its assignment is difficult. For the ester, this band occurs at ~1400 cm^{-1} (~1410 cm^{-1}, d_3) and has only very weak positive VCD. By analogy to the symmetrically disubstituted species, bands at ~1440 cm^{-1} for CN[24,25] and ~1430 cm^{-1} for COCl[5] substituted phenylcyclopropanes can

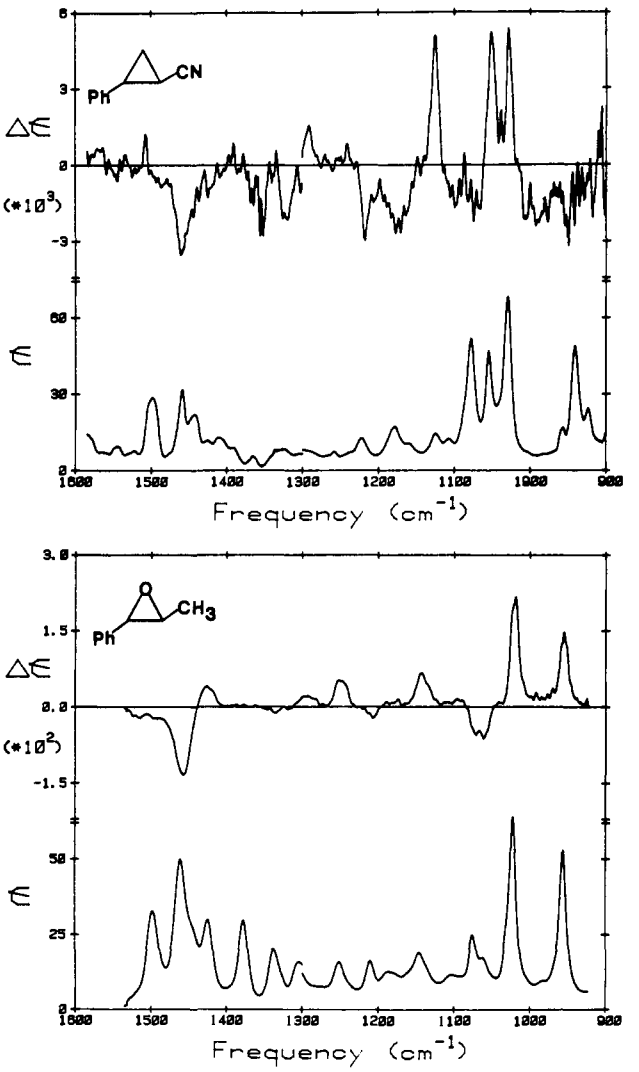

Figure 6. VCD and absorption spectra in the CH_2 bending and framework region: (a) (−)-*trans*-2-phenylcyclopropanecarbonitrile, region above 1300 cm^{-1}, 0.135 M in C_2Cl_4, PL 0.063 cm, 6 scan average, resolution ~10 cm^{-1}, with TC = 3 s and region below 1300 cm^{-1}, 0.032 M in CS_2, PL 0.098 cm, 6 scan average, resolution ~6 cm^{-1}, with TC = 3 s and (b) (−)-1-phenylpropylene oxide, region above 1300 cm^{-1}, 0.179 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~10 cm^{-1}, with TC = 10 s and region below 1300 cm^{-1}, 0.13 M in CS_2, PL 0.052 cm, 4 scan average, resolution ~6 cm^{-1} with TC = 10 s.

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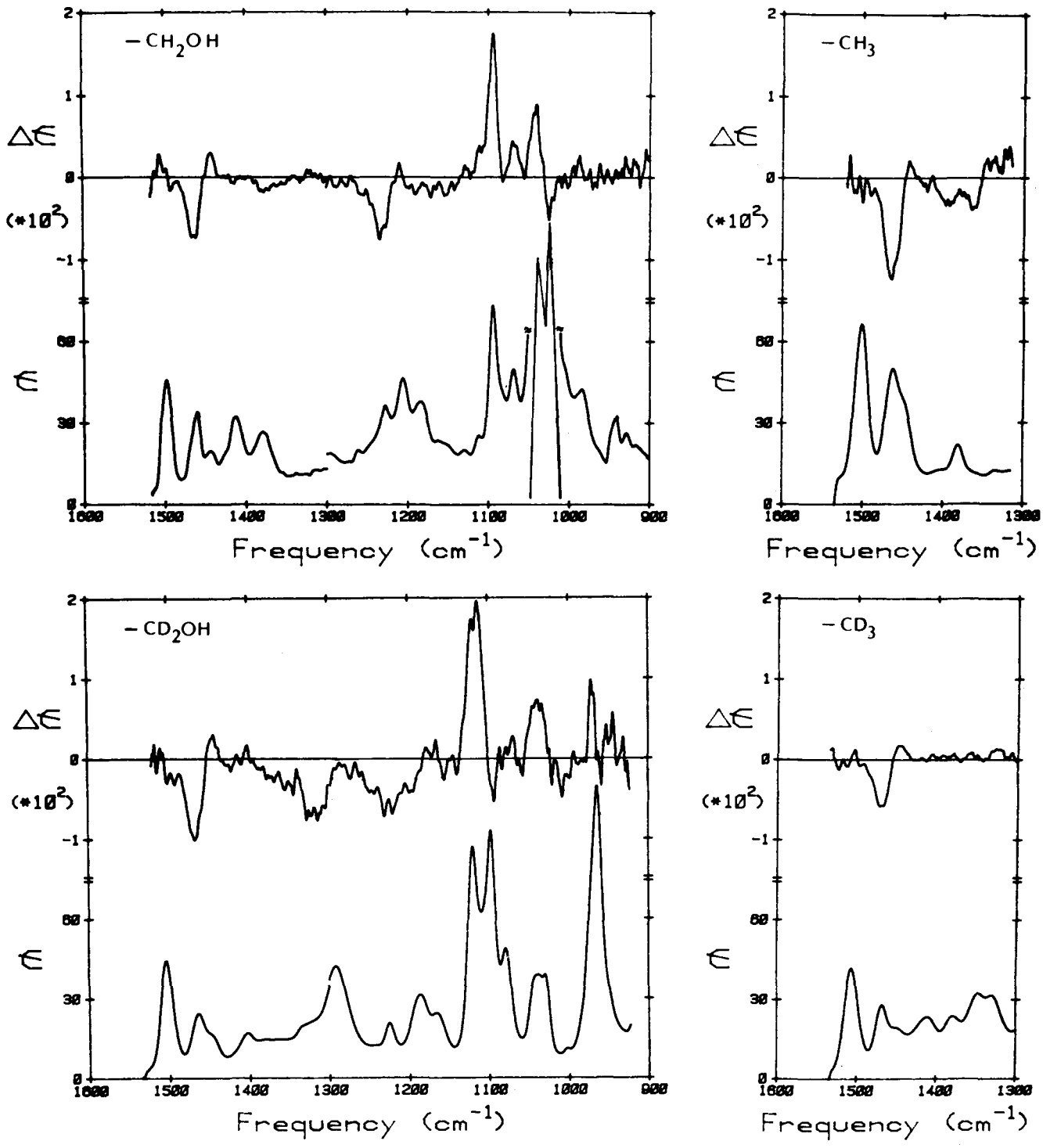

Figure 7. VCD and absorption spectra in the CH_2 bending and framework region: (a) (−)-*trans*-2-phenylcyclopropanemethanol-d_0, region above 1300 cm^{-1}, 0.189 M in CCl_4, PL 0.053 cm, 6 scan average, resolution ~10 cm^{-1}, with TC = 3 s and region below 1300 cm^{-1}, 0.084 M in CS_2, PL 0.033 cm, 6 scan average, resolution ~6 cm^{-1} with TC = 3 s. The band between 1000 and 1050 cm^{-1} has been truncated and shifted for clarity. (b) (−)-*trans*-2-phenylcyclopropanemethanol-d_2, region above 1300 cm^{-1}, 0.16 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~10 cm^{-1}, with TC = 10 and region below 1300 cm^{-1}, 0.16 M in CS_2, resolution ~6 cm^{-1}, PL 0.05 cm, 4 scan average, with TC = 10 s. (c) (−)-*trans*-1-methyl-2-phenylcyclopropane-d_0, region above 1300 cm^{-1}, 0.09 M in CCl_4, PL 0.05 cm, 4 scan average, resolution ~10 cm^{-1}, with TC = 10 s and region below 1300 cm^{-1}, 0.09 M in CS_2, PL 0.08 cm, 4 scan average, resolution ~6 cm^{-1} with TC = 10 s; (d) (−)-*trans*-1-methyl-2-phenylcyclopropane-d_3, region above 1300 cm^{-1}, 0.16 M in CCl_4, PL 0.052 cm, 4 scan average, resolution ~10 cm^{-1}, with TC = 10 s and region below 1300 cm^{-1}, 0.144 M in CS_2, PL 0.052 cm, 4 scan average, resolution ~6 cm^{-1} with TC = 10 s.

probably be similarly assigned but have negative VCD. In $-CH_2-$ substituted cyclopropanes, a band at ~1400 cm^{-1} can be assigned to the cyclopropane CH_2 but has an inconsistent VCD (Figure 7). That no pattern for the VCD of this scissor mode was found in this series is in sharp contrast to the situation noted at 3010 cm^{-1} for the symmetric CH_2 stretch.

The relatively consistent 1320-cm^{-1} negative VCD noted earlier most likely correlates to a cyclopropyl trans C*–H deformation. This assignment is consistent with the positive VCD[19] found between 1300 and 1350 cm^{-1} for the d_0 symmetrically disubstituted compounds. It also explains why the band is so sensitive to substituent. The $-CH_2-$ and CH_3 group deformations (Figure 7) would be expected to interact strongly with vibrations of this bond on an adjacent carbon and thus be the cause of the observed shift of the negative VCD band up in energy to ~1370 cm^{-1}. On deuteriation, this latter interaction is lost as is, apparently, the

Table I. Summary of Absorbance and VCD Bands in the 3200–2900-cm^{-1} Region[a]

R	configuration	solvent	infrared (cm^{-1})	VCD (cm^{-1})
COOH	(−)-(*R*,*R*)	$CDCl_3$	br band from 3200–2900	br negative band from 3200–2800
$COOCH_3$	(−)-(*R*,*R*)	CCl_4	3118 (sh), 3090, 3070, 3033, 3015 (sh), 3000 (sh), 2955	(−)3085, (+)3060, (+)3025, (−)3010, (−)2953
$COOCD_3$	(−)-(*R*,*R*)	CCl_4	3118 (sh), 3090, 3070, 3035, 3015 (sh)	(−)3090, (+)3060, (+)3030, (−)3010
COCl	(−)-(*R*,*R*)	CCl_4	3116 (sh), 3092, 3072, 3035, 3015 (sh)	(−)3080, (+)3035, (−)3015
$CONH_2$	(−)-(*R*,*R*)	Me_2SO-d_6	3190, 3090, 3060, 3034, 3008	(−)3190, (−)3090, (+)3060, (+)3036, (−)3008
CN	(−)-(*R*,*R*)	C_2Cl_4	3118 (sh), 3092, 3070, 3036, 3015 (sh)	(−)3120, (+)3100, (−)3050, (+)3030, (−)3010
NH_2	(−)-(*S*,*R*)[b]	CCl_4	3118 (sh), 3084, 3070, 3033, 3010, 2970	(+)3084, (−)3008, (−)2966
CH_2OH	(−)-(*R*,*R*)	CCl_4	3118 (sh), 3090 (sh), 3070, 3032, 3010	(−)3110, (+)3080, (−)3050, (+)3035, (−)3000
CD_2OH	(−)-(*R*,*R*)	CCl_4	3118 (sh), 3090 (sh), 3070, 3032, 3010	(−)3110, (+)3080, (−)3056, (+)3032, (−)3000
CH_3	(−)-(*R*,*R*)	CCl_4	3110 (sh), 3090 (sh), 3070, 3030, 3010, 2960, 2930	(−)3100, (+)3075, (+)3030, (−)3000, (+)2955, (−)2930
CD_3	(−)-(*R*,*R*)	CCl_4	3116 (sh), 3090 (sh), 3070, 3030, 3010	(−)3100, (+)3075, (−)3058, (+)3034, (−)3000
epoxide	(−)-(*S*,*S*)	CCl_4	3118 (sh), 3090, 3070, 3035, 2985, 2970, 2930	(−)3110, (+)3060, (−)3040, (+)3000, (−)2980, (+)2960, (−)2920

[a] All values from UIC VCD instrument using ~12-cm^{-1} resolution. [b] Same absolute configuration.

Table II. VCD Stereochemical Marker Bands for Phenylcyclopropanes

VCD freq (cm^{-1})	VCD sign	assignment
3000–3010	−	cyclopropyl-CH_2 symmetric stretch
~1450	−	phenyl deformation
~1320	−	C*–H deformation (not universal)
~1030–1150	+	unknown (not universal)

VCD. The negative VCD band is only hinted at in phenylpropylene oxide at ~1340 cm^{-1}.

A somewhat lower energy, ~1300 cm^{-1}, and consistently positive band (for 1*S*,2*S*)[19] also occurred in the diester and diacid chloride spectra previously published.[5] Subsequent spectra measured with our extended wavelength capabilities, unavailable for the earlier study, indicate this band also is present in the isotopic variants of the diesters and the dicyano compounds.[7,25] From the deuteriation studies, assignment as the C*–H deformation seems reasonable[24,25] and correlates well with the above assignment for the phenylcyclopropyl results. Mixing in of the ring breathing mode or CH_2 twist mixed with C*–H deformation is also possible. While other peaks occur in both VCD and absorption spectra over this region, none are systematic of the series or give significant VCD, except the ~1450- and ~1320-cm^{-1} bands discussed above.

Framework Vibrations. In the region below 1300 cm^{-1} many different types of modes occur which are undoubtedly strongly coupled. Assignment and determination of consistent frequency patterns are difficult as a result. However, some common features are evident. Between roughly 1030 and 1150 cm^{-1} there are several VCD peaks in each spectrum, except that of the epoxide, with a *net* positive VCD. Typically two or more positive peaks are seen with a separation of ~70 cm^{-1} (Figures 5–7). In the case of the esters and acid, only weak absorption is seen in this region; but, in the others, one or more moderately intense absorption peaks are seen to correlate with the observed VCD. The VCD consistency of these bands argues for assignment to cyclopropyl or phenyl modes. However, their modest sensitivity to substituent might suggest the former, in which case a ring deformation may be the underlying part of the VCD. Such an assignment is further strengthened by the systematic presence of negative VCD in our (1*S*,2*S*)[19] symmetrically disubstituted compounds.[7]

The phenylpropylene oxide (Figure 6) does have a distinctive VCD in this region, but it does not correlate to the above, providing further evidence of a cyclopropyl origin for those bands. This epoxide result does have VCD features similar to the *S*-(−)-propylene oxide results[29] such as the 1250 cm^{-1} (+) and 1150 cm^{-1} (+); but the significance of these is unclear at present.[30]

Most of the spectra also have a VCD band at ~1230 cm^{-1}, but it is not consistent in sign among the compounds studied and virtually disappears for the acid chloride case. Hence this lower energy region, while rich in spectral features, is poor for stereochemical correlation when viewed on an overall rather than well-assigned peak basis.

Conclusion

In summary, we have presented the VCD and absorption spectra of a series of *trans*-2-phenyl-1-(R-substituted)cyclopropanes of the same absolute configuration. Our results indicate that localized bands can sometimes be a convenient marker for absolute stereochemistry. This was shown in detail for the CH stretching region and more cursorily for some bands in the mid-IR. Significant changes are noted, in particular, on change from a C=O to a CH_2 group adjacent to the cyclopropane ring.

The clearest marker band was the CH_2 (cyclopropyl) symmetric stretch at ~3010 cm^{-1} which yielded consistently negative VCD for the (1*R*,2*R*) configuration while other CH stretches were more substituent dependent. A phenyl deformation at 1450 cm^{-1}, possibly mixed with some cyclopropyl mode, was similarly uniformly negative. Typically, the C*–H deformation at ~1320 cm^{-1} was negative while the 1050–1150-cm^{-1} region was positive. These consistencies are summarized in Table II and correlate well with our previous study of symmetrically disubstituted cyclopropanes.[5] The modes which are consistent tend to be C–H or substituent based which implies that the C_3 ring itself is not a good isolated chromophore for use in stereochemical analysis. That the cyclopropyl CH vibrations may be better for such correlation may be due to their frequency stability which greatly aids their identification in the spectra and hence facilitates their use as marker bands. The effects of substituent on VCD need extensive study, and our current work is directed along this line. By default it will also generate further tests of the correlations proposed above.

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