$RuH_4(PPh_3)_3$,[21] $MoH_4(PMePh_2)_4$,[22] $WH_4(PMePh_2)_4$,[23] $WH_5(PMePh_2)_4{}^+BF_4{}^-$,[24] $WH_6(PMe_2Ph)_3$,[25] Na_2ReH_9,[26] $(Et_4N)ReH_8(PPh_3)$,[27] $ReH_5(PPh_3)_3$,[28] $Ir(CO)_2(PPh_3)_2H_2{}^+$,[29] $Ir(H_2)H(bq)(PPh_3)_2{}^+SbF_6{}^-$,[2c] and $CpRu(PPh_3)_2H$.[30]

Acknowledgment. We thank Dr. G. Hlatky for suggesting we look at the group 8 tetrahydrides, Prof. Herrman and Dr. Okuda for a kind gift of Cp^*ReH_6, and the ARO and NSF (R.H.C.) for funding.

Supplementary Material Available: A sample calculation and a calculation on Cp^*ReH_6 estimating the H_{ax}–Re–H_{eq} angle (4 pages). Ordering information is given on any current masthead page.

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Vibrational Circular Dichroism of Optically Active Allenes. Experimental Results

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Received July 16, 1987

Abstract: Vibrational circular dichroism (VCD) spectra of several substituted allenes have been measured for various characteristic fundamental vibrations. For all of the allenes studied, the VCD of the $C{=}C{=}C$ asymmetric stretch ($\sim$1950 cm^{-1}) correlates directly to the absolute configuration of the molecule, being positive for the *S* configuration. In addition, for 1-halo-3-*tert*-butylallenes, the VCD of the C(X)–H stretch ($\sim$3050 cm^{-1}) was also found to correlate to configuration but the available data set was limited. Additional VCD data for di-*tert*-butyl- and diphenylallene and a phenylallenecarboxylic acid are discussed with respect to individual bands for the sake of comparison.

Vibrational circular dichroism (VCD) has shown great potential as a new tool of use for conformational analysis.[1,2] In the past, VCD on a variety of structurally related molecules, such as substituted cyclopropanes,[3] polypeptides,[4] amino acids,[5] cyclohexyl derivatives,[6] and chiral phosphates,[7] have been measured; and empirical correlations were drawn between the respective stereochemistries and the spectra obtained. In other instances, VCD intensities have been calculated with use of various ad hoc models,[1,2,8,9] which were then compared to experimental results. These approaches parallel those traditionally used over the last 2–3 decades in the interpretation of electronic CD.

Both approaches have advantages but also corresponding limitations. For drawing empirical correlations, detailed understanding of the spectral phenomenon is not required; but a reasonable number of molecules must be studied to avoid ambiguous interpretation. Furthermore, that set should encompass a systematic variation of substituents. On the other hand, calculations can be performed on a single species at different levels of rigor. Unfortunately, the value of these various ad hoc models is far from established. For small molecules having a known geometry and an established force field, this approach appears to be attractive,[10,12] but as larger molecules are studied, more severe approximations become inevitable, and the feasibility of such calculations becomes doubtful.

Substituted allenes constitute an interesting series of molecules for chiroptical studies.[13] These molecules can be made chiral by lowering the D_{2d} allene symmetry to C_2 or C_1. Yet the structure remains small and conformationally restricted if the substituents are simple in nature.

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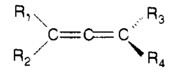
Table I. List of Substituted Allenes **A** Studied with Their Optical Rotation, Absolute Configuration, and Percent ee

compd	R_1	R_2	R_3	R_4	name[a]	measured[b] $[\alpha]_D$	absolute config	synthesized (ee), %
1	H	*t*-Bu	H	*t*-Bu	BuBu	−43	*R*	35
2	H	*t*-Bu	H	Cl	BuCl	−86	*R*	38
3	H	*t*-Bu	H	Br	BuBr	−87	*R*	38
4	H	*t*-Bu	H	I	BuI		*R*	38
3	H	*t*-Bu	Br	H	BuBr	+120	*S*	52
4	H	*t*-Bu	I	H	BuI		*S*	54
5	H	Me	Br	H	MeBr	+32	*S*	20
6	H	Me	I	H	MeI	+46	*S*	20
7	H	Ph	H	Ph	PhPh	−790	*R*	70
8	Me	Ph	Et	COOH	PMEA	−50	*R*	pure

[a] In the text the disubstituted allenes are referred by these names. Letters represent substituents but do not reflect the absolute configuration and hydrogen atoms are not specified. Bu = *tert*-butyl, Me = methyl, Cl = chloro, Br = bromo, I = iodo, Ph = phenyl. [b] For the BuI compounds, **4**, no rotations were measured due to the extensive decomposition. All measurements were done in CCl_4.

During the last 10 years the optical activity of allenes (A) has become a topic of considerable interest.[13,14] The studies presented so far concentrated on chiroptical properties induced by the electronic subsystems of the molecules and dealt with molar rotations[13-15] as well as electronic circular dichroism (CD) in the ultraviolet[13-19] and vacuum-ultraviolet spectral regions.[19]



A

In this paper we present IR absorption and VCD data on a series of 1-halo-3-alkylallenes, **1**–**6**, as summarized in Table I, which provides a systematic variation of substituent mass and electronic structure appropriate for the empirical correlation of VCD and configuration which we have made. Additionally we have included data on some phenyl-substituted molecules, **7** and **8** (Table I), which have a less systematic variation, as a test of the trends seen in the haloalkylallene series. Finally, since these molecules pose good examples of chiral cumulative π-bonded systems and are all small enough to permit calculational analysis, we will present our efforts at comparison of theoretical predictions and experimental results in the following paper. Thus this rather unique system of molecules, much like the earlier studied cyclopropanes,[3] offers an opportunity to do *both* an empirical correlation analysis as well as a calculational one.

The VCD of the allenic C=C=C stretching vibrations is of particular interest to our study. Our emphasis will be on the asymmetric C=C=C stretch which generates a rather strong IR absorption band near 1950 cm^{-1}. As this band is well separated from all the other vibrational bands, it is important for diagnostic purposes of allenes.[14] While the symmetric C=C=C stretch is often found near 1100 cm^{-1}, due to overlap with a number of other modes, its assignment is difficult.[14]

In addition to empirical correlations of the VCD of allenes to their molecular structures, it is of interest to identify correlations between VCD and the electronic structure of the molecules. Here, correlation of VCD with ^{13}C NMR features of the compounds and the electronic optical activity are sought. Relationships between electronic CD and VCD may prove to be useful for evaluation of VCD in terms of mixing of vibrational states with excited electronic states.

Experimental Section

All the compounds we have studied were synthesized at the University of Utrecht with methods that have been previously published for haloalkylallenes[20] and phenylallenes.[21-23] Infrared absorption and VCD measurements were made on the UIC dispersive instrument which has also been discussed in detail.[1] The alkyl-containing compounds used were not optically pure but had, in fact, between 20 and 54% enantiomeric excess (ee) as prepared. The two phenyl allenes we studied were much higher in ee. Additionally, some of the haloalkylallenes tended to degrade chemically with time. Both factors led to substantial problems in terms of the achievable signal-to-noise ratio (S/N) in our VCD measurements.

In Table I are listed the compounds used in this study with their ee as prepared (Utrecht), absolute configuration, and optical rotation as measured for CCl_4 solutions at room temperature with a Perkin-Elmer 241 polarimeter (UIC). The values for all but the iodo-containing compounds were consistent with the prepared ee values and expected molar rotations.

To simplify discussion in this paper, the compounds studied will be denoted by their substituents only, e.g., BuCl = 3-chloro-1-*tert*-butylallene, as defined in Table I. We sometimes had available both enantiomers of a given compound but these were always of different ee and, often, chemical purity. Still these additional samples did provide useful checks on the reliability of our final results. To simplify the comparison of VCD spectra we will present all of the data in the figures and text as appropriate for the *S* isomer, and the actual compounds used will be denoted in the figure captions and can be inferred from the data in Table I. Racemic mixtures for all except four compounds were available for use in determining VCD baselines. The exceptions are noted in the respective figure captions and in the text as the individual bands are discussed. Due to the small amount of sample available and their low ee, VCD signals were often quite small and in fact were at the limits of our detectability ($\Delta A \sim 5 \times 10^{-6}$). Hence, even though VCD was detectable for many bands, we have chosen to present and focus on only those spectral features that we feel are reliable from *both* a S/N and VCD artifact point-of-view.

Because of the problem of thermal decomposition for the haloalkylallenes, two of the samples, i.e., BuCl, BuBr (only the *R* isomers), and their racemic mixtures were purified by distillation on a vacuum line after which the clear liquid distillate sample was separated from a dark yellow residue. However, the VCD of the purified material and that of a subsequently prepared, only slightly colored sample (*S* isomer) proved to be qualitatively the same in the bands of most interest. Hence the remaining samples were used as received without further purification since this process involved some loss of sample. The BuI samples seemed to be the most highly polymerized from their appearance (bright yellow color) but were resistent to distillation as discussed above; so spectra of the impure compounds were measured in hopes of at least determining the qualitative trend. The other haloalkylallenes available (MeBr, MeI, and the *S* isomer of BuBr) were only slightly colored (yellow), were felt to be negligibly contaminated and, thus, were used without distillation.

Since the amount of sample used was very small compared to that of the solvent (spectral grade CCl_4 or CS_2 from Aldrich), the volume of solution was assumed to be equal to that of the solvent; and the concentration was determined to be ~±10% for purposes of determination

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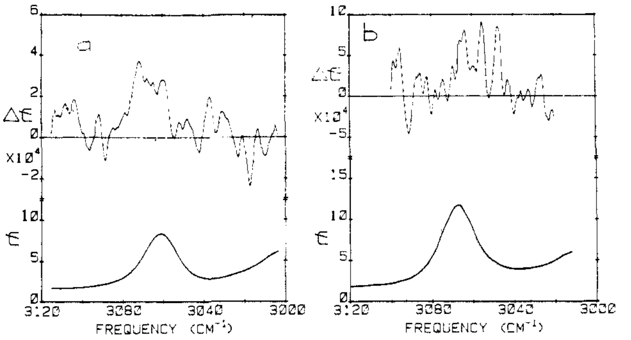

Figure 1. Absorption and VCD spectra of (*S*)-3-halo-1-*tert*-butylallenes for the C(X)–H stretch. Instrument resolution is ~15 cm^{-1} and time constant is 3 s. Plots are smoothed by using 6-cm^{-1} interval. (a) BuCl, concentration 0.032 M in CCl_4, path length 0.5 cm, peak absorbance 0.13, six scans averaged, BuCl racemate baseline, spectrum measured for *R* isomer. (b) BuBr, concentration 0.043 M, path length 0.2 cm, peak absorbance 0.09, six scans averaged, (*R*).

of the ε and Δε values. In the case of the BuI samples, the decomposition was so extensive that ε could not be reliably approximated. Hence data are presented for those samples only in terms of *A* and Δ*A*. Since our samples are not 100% optically pure and the VCD signal observed is only due to the enantiomeric excess, the plotted VCD data are corrected by scaling (i.e., the plotted VCD is Δε/ee). The actual maximum absorbances that we could achieve are noted in the figure captions. In summary, both the limited absorbance *and* the ee restrict the resultant VCD S/N. Thus some data of obvious interest for empirical correlation, although sought, could not be measured due to sampling constraints.

The absorption and VCD measurements for these compounds can be grouped into four parts: C—H stretching region (~3000 cm^{-1}); C=C=C asymmetric stretching region (~1950 cm^{-1}); mid-IR from 1500 cm^{-1} down to 1250 cm^{-1}, where the various CH deformation modes occur; and the fingerprint region 1250 cm^{-1} down to 950 cm^{-1}. In addition to these, compounds containing phenyl and/or COOH have absorption bands in the 1500–1800-cm^{-1} region. However, this latter region yielded little measurable VCD for our samples. For the halogen-substituted allenes there are no bands from 1900 cm^{-1} down to 1500 cm^{-1}. Furthermore, little reliable VCD could be obtained for these molecules in either the mid-IR or fingerprint regions.

Both a variable pathlength cell (Wilks) with CaF_2, NaCl, or KBr windows and a fixed pathlength (0.5 cm) brass cell with CaF_2 or BaF_2 windows were used for containing the samples.[16] For the first three regions noted above, i.e., from ~3000 cm^{-1} down to 1250 cm^{-1}, CaF_2 cells were used with CCl_4 solutions. Since CCl_4 strongly absorbs in the region ~1600 cm^{-1}, chloroform was substituted for scans at this frequency. For the fingerprint region, NaCl or KBr cells were used with CS_2 solutions.

Results and Discussion

For samples where both enantiomers were available (e.g., *R* and *S* isomers of BuBr), data for only one of them is presented. Here experimental VCD plots are all replotted to be appropriate for the *S* configuration. The correlations will be discussed in the following paragraphs by region as noted above.

C–H Stretch. In the C–H stretching region, VCD for BuCl, BuBr, and BuI, could be measured for only the highest energy C–H stretch which corresponds primarily to motion of the hydrogens on the allenic carbon bound to the halogen.[24,25] The absorbance spectra in the balance of the region are dominated by strong methyl CH stretches from the *tert*-butyl group for which we have detected no measureable VCD. For BuCl the amount of racemate was sufficient to be used for determination of the VCD baseline, and the result is shown in Figure 1. However, for the BuBr and BuI samples, sufficient amounts of the respective racemates were not available to match the absorbance. In fact, VCD spectra of both of these compounds indicated very weak positive VCD for the C(X)–H stretch in the *S* isomer (Figure 1). However, the signals were often smaller than the baseline absorption artifact. It should be noted that these artifacts are not constant, but change with alignment and hence vary over an extended period. Since an exact match between sample and baseline absorbances was not possible, these latter results cannot be viewed as definitive or quantitatively useful. We can say that Δε/ε ~ 10^{-5} is an *upper bound* on the signals measured and that they were reproducibly positive for the *S* and negative for the *R* configuration under a variety of different sample preparations. The exceptions always corresponded to signals less than the noise level.

For the MeBr and MeI compounds, VCD for the whole C–H stretching region from 3100 cm^{-1} down to 2800 cm^{-1} was measured. Since the racemate of these latter two samples was unavailable, there was a problem matching the absorption satisfactorily for VCD baseline purposes. Furthermore, primarily due to the very small sample amount and low ee (20%) available, the S/N obtained for these two compounds in the C–H stretching region proved to be quite bad. In particular, no clear VCD could be found for the highest energy C(X)–H stretch in MeBr and only a broad very weak positive VCD, seemingly uncorrelated to the absorbance band, was seen in MeI. In both cases, only an absorbance of ≲0.1 was achievable for the C(X)–H band. Finally, in the BuBu compound, we were unable to detect any C–H stretch VCD. Here the *tert*-butyl vibrations overlap both allenic =C—H stretches making comparison to the above noted C(X)–H results impossible.

For **2**–**4**, the halo-*tert*-butyl compounds, the C(X)–H stretching frequency has a complex correlation with halogen, being highest at 3069 cm^{-1} for BuBr, middle at 3061 cm^{-1} for BuCl, and lowest at 3056 cm^{-1} for BuI. Similarly, in the methyl compounds, the MeBr frequency (3064 cm^{-1}) is higher than the MeI frequency (3045 cm^{-1}). In these latter two, the frequency position of the C(X)–H stretch decreases on going from *t*-Bu to Me substitution. For the *tert*-butyl compounds the variation of the allenic C(X)–H frequency corresponds to that observed for the monosubstituted allenes $H_2C{=}C{=}CHX$.[14] The same irrgular trend within a series of halogen compounds, as is observed for the C(X)–H stretching frequency, is found for the one-bond carbon–proton NMR coupling constants ^1J(C–H).[26]

The experimental VCD for the C(X)–H band appears to correlate directly to the absolute configuration of the molecule for our set of data with the *S* configuration exhibiting a positive monosignate VCD. The other allenic =C—H stretching frequency is expected to lie near 2990 cm^{-1}, but the close lying aliphatic C–H stretching modes of *tert*-butyl and methyl make its VCD measurement impossible for the samples at hand.

The MeBr and MeI (**5**, **6**) results neither contradict nor support the C(X)–H pattern due to the lack of measurable signal in that band at 3050 cm^{-1}. Lower in energy, a consistent pattern was seen for the remaining C–H stretching bands in both these molecules. A negative VCD band occurs at ~3000 cm^{-1} followed by a weak positive VCD at ~2980 cm^{-1}. These bands (3000–2800 cm^{-1}) are dominated by methyl C–H stretches, which are undoubtably mixed with the allenic =C—H on the alkyl end. This coupling presumably gives rise to their observed VCD which, due to its dependence on a unique structural element, will not be generalizable for allene VCD.[25]

By way of comparison, the VCD of PhPh (**7**) is presented in Figure 2 for the entire CH stretching region (3200–2900 cm^{-1}). Here the phenyl =C—H stretches overlap those of the allenyl =C—H and prevent the relatively easy assignment possible for the haloalkylallenes. The absorption spectrum, in fact, contains a series of resolved peaks characteristic of the phenyl group. This band structure is apparently superimposed on the broad, positive VCD seen over the same frequency region. The apparent shift in baseline to negative Δε was reproducible so we have not corrected for it, but this may be due to some impurity in the racemic baseline sample which is suggested by extra aliphatic C–H peaks in its absorption spectrum. Corresponding to the above haloalkylallene pattern, at ~3060 cm^{-1} a positive VCD is found for the *S* isomer. There also appears to be a small negative VCD

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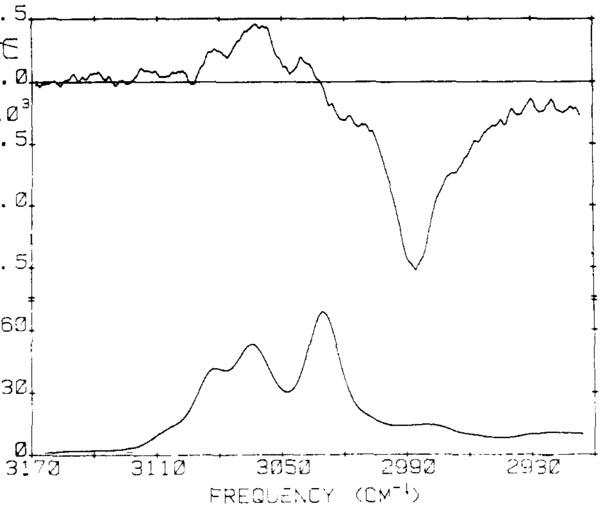


Figure 2. Absorption and VCD spectra of (*S*)-1,3-diphenylallene in the C–H stretching region. Concentration 0.025 M in CCl_4, path length 0.15 cm, resolution ~ 15 cm^{-1}, time constant 10 s, peak absorbance 0.23, four scans averaged. PhPh racemate was used for VCD baseline, data obtained for *R* absolute configuration.

associated with the band at ~ 3020 cm^{-1} and a much larger negative VCD for the very weak absorption band at ~ 2980 cm^{-1}. The pattern at ~ 3060 and 3020 cm^{-1} appears to be a bisignate VCD somewhat obscured by the large negative VCD feature at 2990 cm^{-1}. The asym C–H is generally assigned to be higher in energy than the sym C–H mode[27] and, in fact, that sense of coupling also contributes to the C(X)–H band seen in the haloalkylallene compounds.[24,25] Thus the pattern at this stage appears to be that the asym C–H stretch yields positive VCD for the *S* isomer. We have no explanation for the large negative VCD at 2990 cm^{-1} unless this is the sym =C—H coupled to a phenyl =C—H mode at 3030 cm^{-1}.

C=C=C Asymmetric Stretch. All of the compounds **1–8** have the characteristic C=C=C asymmetric stretching band around 1950 cm^{-1}. Racemates were used for determining the VCD baseline for all compounds except MeBr and MeI for which 1,1-dimethylallene was used. In Figure 3 are presented the absorption and VCD spectra for the BuCl, BuBr, MeBr, MeI, PhPh, and PMEA substituted allenes as measured in this region. With regard to the other available samples, BuBu gave positive VCD (for the *S* isomer) but had very low S/N with $\Delta A/A \cong +6 \times 10^{-6}$ and $A = 0.34$. Both of our BuI samples did not exhibit any measureable VCD in this region. We feel that the samples were substantially degraded by the time we could attempt to measure the spectra because, even using the entire sample, only a very weak absorbance ($A < 0.1$) could be seen in this region.

The 1950-cm^{-1} asym C=C=C stretching frequency does not seem to be greatly affected by substituents. Earlier studies[27] comparing IR frequencies of a large number of substituted allenes have indicated that allenes with alkyl substituents or σ-inductive groups have this band near 1960 cm^{-1}, whereas allenes with phenyl groups have it around 1940 cm^{-1}. Since these molecules were part of that earlier study, it is not surprising that our results follow the same pattern.[14] Because the vibration of this mode is thought to involve primarily the central carbon atom, the substituents on the terminal carbon atoms do not greatly affect its frequency. The ϵ value for this band over this series of compounds ranged from ~ 60 (in PMEA) to ~ 10 for the halomethylallenes. These absorption intensities also follow the known pattern of increasing absorption intensity with increasing degree of substitution ($\epsilon \approx$ 10–30 for disubstituted, $\epsilon \approx$ 40–60 for tri- and tetrasubstituted allenes).[28]

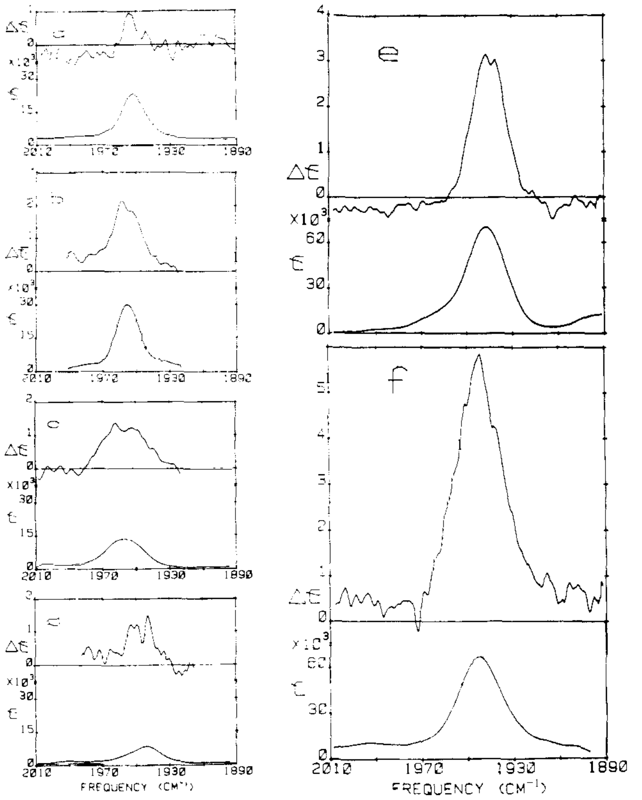
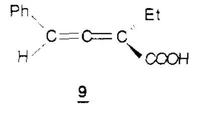


Figure 3. Absorption and VCD spectra of all substituted allenes for the C=C=C asymmetric stretch. Resolution ~ 15 cm^{-1} and time constant 10 s. Plots are typically the average of six scans (except PhPh and PMEA) and are smoothed taking 6-cm^{-1} intervals. All VCD plots are presented for *S* absolute configuration. (a) BuCl, concentration 0.021 M in CCl_4, path length 0.5 cm, peak absorbance 0.24, BuCl racemate baseline, data obtained for *R* isomer. (b) BuBr, concentration 0.029 M in CCl_4, path length 0.14 cm, peak absorbance 0.13, BuBr racemate baseline. (c) MeBr, concentration 0.126 M in CCl_4, path length 0.092 cm, peak absorbance 0.16, 1,1-dimethylallene baseline. (d) MeI, concentration 0.127 M in CCl_4, path length 0.092 cm, peak absorbance 0.1, 1,1-dimethylallene baseline. S/N poor due to low absorbance. (e) PhPh, concentration 0.025 M in CCl_4, path length 0.2 cm, peak absorbance 0.16, PhPh racemate baseline, data obtained for *R* isomer. (f) PMEA, concentration 0.01 M in CCl_4, path length 0.15 cm, peak absorbance 0.1, PMEA racemate baseline, data obtained for the *R* isomer. Note change in absorption scale.

The experimental VCD observed for this band was in all cases monosignate and characteristic of the absolute configuration of the molecule, i.e., *S* absolute configuration gave positive VCD. After correcting for ee, all compounds measured had the same order of magnitude for $\Delta\epsilon$ ($\sim 10^{-3}$) with $\Delta\epsilon/\epsilon$ values varying from $\sim 6 \times 10^{-5}$ for the halo species to $\sim 10^{-4}$ for the phenyl-containing ones.

These results provide a clear comparison of the VCD for a variety of allenes due to the unique nature of this vibrational mode which is at a frequency rarely overlapped by any other organic group frequencies and is far enough from other modes to limit mixing. That relative purity of normal mode is further evidenced by the close overlap of VCD and absorption bandshapes which indicates that few other modes are available to perturb the observed result. The PhPh and PMEA compounds, **7** and **8**, provide a nice extension of this correlation under conditions of very good S/N ratio due to their high optical purity. Such a correlation can be further extended by noting that (*S*)(+)-1-ethyl-4-phenylbuta-2,3-dienoic acid (**9**) also shows positive VCD for its asym C=C=C stretch which appears at 1945 cm^{-1} and has a $\Delta A/A \sim 5 \times 10^{-5}$.[29]



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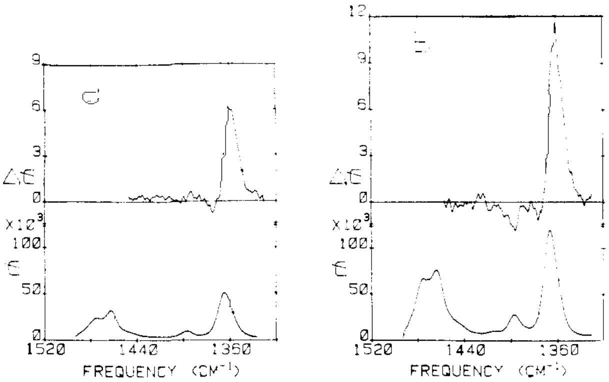

Figure 4. Absorption and VCD of haloalkylallenes in the mid-IR (~ 1400 cm^{-1}): (a) BuCl, (b) BuBr. Resolution ~12 cm^{-1}, time constant 10 s. Plots are averages of six scans and are smoothed by using a 6-cm^{-1} interval.

The allenic asymmetric C=C=C stretching vibration is thought to involve primarily motion of the central carbon atom. Therefore to relate the C=C=C VCD features to electronic characteristics it is meaningful to put the emphasis on electronic features of the allenic central atoms. One such feature would be the ^{13}C chemical shifts of the central atom.

For the (*S*)-haloalkylallenes the VCD is in the range of $\Delta\epsilon = +1\text{-}2 \times 10^{-3}$. It increases distinctly for the (*S*)-phenylallanes ($\Delta\epsilon \approx +4 \times 10^{-3}$ for PhPh and $\Delta\epsilon \approx +6 \times 10^{-3}$ for PMEA). This trend seems to parallel the ^{13}C chemical shifts of the C-2 atoms, where one observes $\delta_{C\text{-}2}$ = 199–206 ppm for the halogenoallenes,[20] $\delta_{C\text{-}2}$ = 207.9 ppm for PhPh,[30] and $\delta_{C\text{-}2}$ = 210.8 ppm for PMEA.[26] Trends between ^{13}C resonances $\delta_{C\text{-}2}$ of allenes and optical activity have also been noted using their respective optical rotations.[13b]

It is also interesting to compare the VCD results with those previously established in electronic CD for allenes and phenylallene excited states.[16-19] Though the electronic CD of the 53–56000 cm^{-1} (40000 cm^{-1} for phenylallenes) excitations is positive for allenes with the (*S*) configuration, as is the VCD of the C=C=C asym stretch, the substituent effects on the VCD differ in one important respect from those observed for the electronic CD. For both kinds of CD phenomena one observes an increase in the CD going from BuCl to BuBr and, finally, to PhPh. However, in electronic CD, PMEA exhibits the by far smallest CD ($\Delta\epsilon_{el} \approx +4$ for (*S*)[16]) for this series of allenes and PhPh shows the largest effect ($\Delta\epsilon_{el} \approx +108$ for (*S*)[17]) while, in VCD, PMEA has the largest $\Delta\epsilon$.

Also the relative changes of $\Delta\epsilon/\epsilon$ are quite different for both kinds of phenomena. For the VCD these vary from 0.3 to 1.7 $\times 10^{-4}$. The $\Delta\epsilon/\epsilon$ values are approximately equal for the phenylallenes studied. For the electronic CD, PMEA actually has an electronic $\Delta\epsilon/\epsilon$ value of $\approx 3 \times 10^{-4}$ for (*S*),[16] which is comparable to its VCD $\Delta\epsilon/\epsilon$ value. However, the electronic $\Delta\epsilon/\epsilon$ values of the other compounds we have studied here are larger by an order of magnitude ($\approx 1\text{-}4 \times 10^{-3}$).[17,19] As a result, it turns out that, apart from the relationship of the signs to the absolute configurations, there is no obvious correlation between the electronic CD and VCD of the allenic skeleton. Therefore, it remains to be tested whether the observed correlation of the VCD to the ^{13}C resonances of the allenic central atoms is more than accidental.

Mid-IR. Below 1500 cm^{-1} down to 1300 cm^{-1}, VCD was measured for the haloalkylallenes (Figure 4), BuBu and PhPh (Figure 5), and PMEA (Figure 6). For MeBr and MeI, use of 1,1-dimethylallene for obtaining the VCD baseline proved to be inadequate.

For the haloalkylallenes, in the region from 1500 cm^{-1} down to 1320 cm^{-1}, three prominent absorption bands are seen. Two bands at 1460 and 1480 cm^{-1} in the *tert*-butyl compounds can be assigned to local asymmetric deformations (e-type modes) of CH_3.[31] The band around 1365 cm^{-1} could belong to the symmetric deformation of the CH_3 groups, but in view of its intensity, some mixing with other modes may be important. An additional weak band around 1400 cm^{-1} is observed, which also belongs to one of the symmetric methyl deformations of the *tert*-butyl.[31]

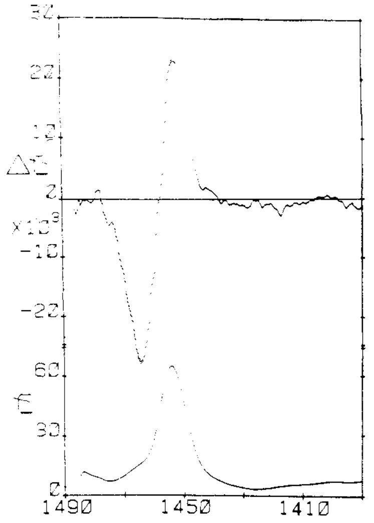

Figure 5. Absorption and VCD of (*S*)-1,3-diphenylallene in the mid-IR (~1450 cm^{-1}). Concentration 9.4 mM in CCl_4, path length 0.2 cm, resolution 12 cm^{-1}, time constant 10 s, peak absorbance 0.12, four scans averaged, PhPh racemate baseline, data for *R* isomer.

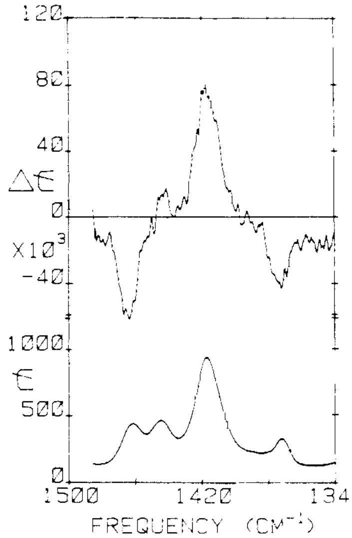

Figure 6. Absorption and VCD of (*S*)-1-ethyl-4-phenylpenta-2,3-dienoic acid (PMEA) in the mid-IR. Concentration 0.01 M, in CCl_4, path length 0.04 cm, resolution 12 cm^{-1}, time constant 10 s, peak absorbance 0.32, four scans averaged, PMEA racemate baseline, data obtained for *R* isomer.

For the halo-*tert*-butylallenes, the *S* configuration gave a reproducible, positive VCD for the 1365-cm^{-1} band; but all of the other features had VCD signals significantly below our reliability limits. In BuBu a weak couplet was seen centered at 1400 cm^{-1} and correlated to two weak absorption bands at 1405 and 1390 cm^{-1}.

For the diphenylallene, the 1450-cm^{-1} band corresponding to a phenyl ring deformation gave a bisignate VCD, negative to higher frequency, for the *S* isomer (Figure 6). The absorption maximum appears to line up with the positive peak of the VCD, and an absorption shoulder to higher frequency, ~1470 cm^{-1},

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correlates to the negative peak. No VCD was detected for the ~1600-cm^{-1} band corresponding to the alternate ring deformation mode.[32]

In an effort to explain this result, a degenerate coupled oscillator (DCO) calculation was undertaken for the VCD resulting from the coupling represented by the in-phase and out-of-phase phenyl ring modes.[33] The transition electric dipole moment was considered to lie along the 1–4 axis of the phenyl ring. For the *S* absolute configuration of the molecule, the rotational strength (R^+) was calculated to be -1.2×10^{-43} (esu·cm)^2 with dipolar splitting energy (V_{ab}) equal to 0.12 cm^{-1}. Taking the half-width to be that seen in the absorption spectrum at $1/e$ of ϵ_{max} (~7 cm^{-1}) and assuming that the actual splitting was equivalent to $2V_{ab}$, $\Delta\epsilon$ was calculated to be -0.97×10^{-4} for the higher energy component. [Calculations for the perpendicularly polarized phenyl deformation gave a slightly larger $R^{\pm} \sim 1.7 \times 10^{-43}$ (esu·cm)^2 but calculated V_{ab} and consequently $\Delta\epsilon$ to be vanishingly small.] Though the sense of rotational strength calculated agrees with that seen in the experiment, its intensity is more than two orders of magnitude lower than seen experimentally ($\Delta\epsilon = -2.5 \times 10^{-2}$). While this may indicate that the DCO model is inadequate to explain the origin of this VCD it is more likely that dipolar coupling is not a sufficient mechanism for determination of the splitting of the two modes of interest. The latter effect has been noted in several other molecules as the source of inadequate DCO magnitudes.[34] Splittings are best determined from experimental data for these purposes.

Since the calculated DCO sign pattern is correct and the two phenyl groups are coupled electronically across the allene linkage,[13,17,18,30] it is interesting to speculate whether such an effective, off-diagonal interaction in the force field leads to an enhancement in the apparent VCD associated with these modes. To test this concept, we simulated the calculated VCD by varying the splitting between two oppositely signed gaussian bands correctly scaled to the calculated $R^{\pm}$ values. It was not possible to obtain the observed peak-to-peak separation (~11 cm^{-1}) and the observed $\Delta\epsilon_{max}$ by constraining the simulation to the observed absorption band half-width and the computed $R^{\pm}$ values. All of these calculated spectra were, in fact, a factor of 3 or more higher in VCD intensity than seen experimentally. While this is certainly better than the deviation obtained by using the dipolar coupling model, it is less than satisfactory for using such an empirical curve fitting approach. The intensity relationships seen experimentally between the strong 1450-cm^{-1} peak and its weak 1465-cm^{-1} shoulder are, however, consistent with a positive $V_{ab} \sim 7$ cm^{-1}. (Recently, Polavarapu has demonstrated that inclusion of charge flow between the oscillators can alter the expected intensity ratios but should not affect the VCD sense.[35] Our DCO analysis assumes that the perpendicular components of these E-type pseudo-benzene modes remain essentially degenerate with the parallel ones. However, this is probably not realistic given the apparent phenylallene coupling noted earlier in the frequency trends of the C=C=C stretches.

At present a simple DCO calculation appears to be inadequate to explain the PhPh 1450-cm^{-1} VCD. As an alternative, these modes may be vibronically coupled to excited electronic states of the phenyl groups ($^1E_{1u}$-like). Since the electronic states are strongly dipole coupled (as seen in UV–CD[17]), this vibronic coupling could give rise to the VCD seen in Figure 6 via a vibronic coupling mechanism analogous to that which we have shown to be important in the magnetic VCD of substituted benzenes.[36]

For PMEA, which has an acid group, the C=O stretching mode is at 1675 cm^{-1} and has only a very weak, negative VCD ($\Delta\epsilon/\epsilon \lesssim 10^{-5}$). Again, no VCD was detected for the ~1600-cm^{-1} phenyl band. Since this compound has both methyl and phenyl groups, the bands at 1470 and 1450 cm^{-1} may be due to both the ring deformation and the CH_3 deformation.[31,32] The corresponding VCD has a large negative signal at higher energy with a small positive VCD toward lower energy (*S* isomer) which is consistent with the results above for the diphenyl compound. The band at ~1420 cm^{-1}, giving a strong positive VCD, may be due to the ethyl CH_2 deformation or to some combination including the methyl deformations. The band at 1370 cm^{-1} should be the symmetric deformation of one of the CH_3 groups. Little correlation of the observed VCD for this mode with that of other allenes can be made since both the methyl and ethyl functional groups may contribute.

Below 1300 cm^{-1} down to 900 cm^{-1} the VCD signals of all the compounds were of very low S/N. Even the more optically enriched PhPh did not yield reasonable low-frequency VCD. For PMEA, there is a strong absorption band around 1290 cm^{-1} and weaker bands below 1240 cm^{-1}. The 1290-cm^{-1} band gives a large positive VCD and a small negative peak toward lower energy,[24] probably due to another underlying band around 1260 cm^{-1}. This intense feature probably derives in large part from the C–O stretch of the acid group. Below 1290 cm^{-1} the VCD spectrum has several features corresponding to the absorption bands. In this region of highly mixed modes, little can be said with respect to the significance of these bands. For purposes of empirical correlation of classes of molecules, such "fingerprint" modes are unlikely to be of any real help in determining the absolute configuration or conformation of the molecules since they are most likely specific to the molecule studied. While the symmetric C=C=C stretch is also expected in this region, we have not been able to assign it to a consistent frequency.

Conclusion

In summary, the absorption and VCD spectra of several substituted allenes have been measured on samples of both *R* and *S* absolute configurations. Our results indicate that some of the VCD features associated with relatively well-defined local modes appear to be stereosensitive. The clearest marker band was the C=C=C asymmetric stretch of the allenic framework. Its IR frequency position was relatively constant around 1950 cm^{-1} for the various substituents we studied, and its VCD was monosignate and positive for the *S* absolute configuration. Furthermore the VCD magnitude was relatively independent of the different substituents to which we had access. For the 1-halo-3-alkylallenes, the C(X)–H stretch was isolated in frequency and its VCD appeared to be again characteristic of the absolute configuration of the molecule, being monosignate and positive for the *S* absolute configuration. For this same set of molecules it is possible that the 1370-cm^{-1} band, positive for *S*, is also characteristic. However, insufficient data are accessible to justify such a conclusion. Below 1250 cm^{-1} the modes are unique for each given compound and are likely to be strongly coupled. Thus it is not surprising that they were not useful for correlation to configuration.

Acknowledgment. This research was supported in part by a grant to T.A.K. from the National Science Foundation (CHE-84-12087) for which we are most grateful.

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