Vibrational Circular Dichroism of Optically Active Substituted Allenes. Calculational Results

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Abstract: The fixed partial charge (FPC) and localized molecular orbital (LMO) models of vibrational circular dichroism (VCD) were used to generate calculated VCD spectra for comparison with the experimental spectra presented in the previous paper for 3-halo-1-alkylallenes. A transferred valence force field was set up and partially optimized for 3-bromo-1-methylallene for this purpose. For isolated modes like the C(X)-H stretch and C=C=C asymmetric stretch the FPC model gave the correct sign but poor agreement for the magnitude of $\Delta A/A$. For these bands, the VCD signs also correlate to the absolute configuration of the molecule. The sense of the calculated rotational strengths was not affected by a systematic variation of the partial charges, but the magnitudes were. On the whole, the FPC model does better than the LMO qualitatively, because the LMO fails for the lower energy modes.

In the past decade, a variety of calculational models for vibrational circular dichroism (VCD) have been developed.[1] Two of these, the fixed partial charge (FPC)[2] and localized molecular orbital (LMO)[3] models, have been shown to have some limited applicability to saturated hydrocarbon systems, particularly in the CH stretching region.[4] We have recently shown[5] that the LMO model fails in the case of cyclobutane mid-IR VCD while the FPC results were qualitatively satisfactory when a highly optimized force field was used.

It seems clear that the FPC model, due to its inherent structure, should have difficulty with the VCD of unsaturated, more electronically delocalized molecules. Good examples of this problem exist in cases such as the =C—H stretches in spirononadiene,[6] the C=O and mid-IR modes in methylcyclohexanone,[7] and the CH_2CH_2 bridge CH stretches in dihydro[5]helicene.[8] Heteroatom systems have also proven difficult for the FPC model, some examples being neopentyl-*1-d* chloride and bromide[9] and a variety of modes for epoxypropane and methylthiirane.[10] However, very recent studies of 2-methyloxetane indicate some qualitative success of the FPC model in this four-member-ring heteroatom system.[11] Detailed studies by Nafie and co-workers on alanine indicate that the LMO model can compensate for some failures of the FPC model in describing C–H and C–D stretches of deuteriated isotopomers of that molecule.[12] Therefore, it is interesting to probe the relative applicability of these two calculational models to

heteratom-containing molecular systems, such as the substituted allenes discussed in the previous paper,[13] that are intermediate in terms of delocalization between saturated hydrocarbons and aromatic systems. Allenes have the added benefit of being relatively small and conformationally rigid which provides some latitude in the range of theoretical approaches available to us.

The earlier studies of saturated hydrocarbons had a significant problem in properly accounting for overlap of nearly degenerate modes. Since VCD is a signed quantity, the frequency ordering of such modes is quite important in generating a qualitatively correct bandshape. With allenes, there are a few well-defined, relatively isolated modes available for study that should be easy to simulate calculationally and thus could provide a test of the VCD model as opposed to the force field. We have shown[13] two of these modes, the asymmetric C=C=C stretch at ~1950 cm^{-1} and the C(X)—H stretch at ~3050 cm^{-1}, to be characteristic of the configuration of the 3-halo-1-alkylallenes with both having positive VCD for the *S* configuration. Furthermore, it is reasonable to postulate that the calculated VCD for modes which are characteristic of a series of compounds would be less dependent than are other modes on the details of the force field.

There are, of course, other ad hoc models of VCD available for testing with the data from these molecules.[1] However, we will focus here on only the FPC and LMO models because we seek parallels with the more thoroughly investigated cyclobutane[4,5] and the methylcyclohexanone[7,14] studies where more complete data sets and better force fields were available. Furthermore, these other ad hoc methods typically require parameters to which we currently have no access so that their use naturally leads to added questions and less clear answers. While the FPC model requires parameters (i.e., charges) which, in fact, have no sound basis in theory, there is at least a base of experience built up as well as calculational methods of generating them in an objective (if arbitrary) manner.[4] Stephens has recently proposed a more rigorous a priori method of calculating VCD which is operationally dependent on development of very high quality wave functions[15-18] and encompasses the FPC model as a limiting case.[19] The molecules for which we have obtained experimental VCD, chloro

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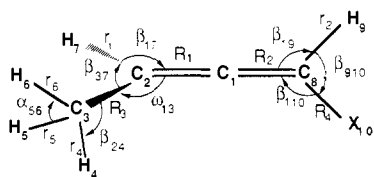
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Figure 1. Atomic numbering scheme and internal coordinate definition for (S)-1-halo-3-methylallene.

Table I. Substituted Allene Geometrical Parameters Used for G Matrix Calculations

parameter	value[a]	parameter	value[a]
r(C=C)	1.3084	r(C—F)	1.32
r(C—C)	1.501	r(C—Cl)	1.71
r(—C—H)	1.087	r(C—Br)	1.90
r(=C—H)	1.09	r(C—I)	2.15
∠X—C=C	112.00	∠C—C—H	110.60
∠H—C=C	117.00	∠C=C—H	119.00
∠C=C—C	125.20		

[a] Bond lengths are expressed in angstroms and bond angles in degrees.

and bromo substituents of methyl- and *tert*-butylallene, are too large for reliable a priori calculations in their current formulation. Nafie and Freedman have also proposed a non-Born–Oppenheimer correction to VCD theory.[20]

Given the calculational simplicity of the FPC model, it is important to explore its applicability to a variety of molecular systems in hopes of providing the stereochemist a workable, accessible tool to derive structural parameters from spectra. If the model should fail, this work will be important in defining the limits of molecular systems for which the FPC model is qualitatively applicable. Similarly, if the LMO model were to have some reliable limits of utility for stereochemical analysis, it too would be much cheaper and more accessible than are the nonadiabatic or a priori methods.[15,20]

In this paper we will present some selected calculational VCD results for the halomethylallenes and compare them to the haloalkylallene experimental results discussed in the previous paper.[13] The methyl derivatives were chosen for calculational simplicity. We have actually carried out FPC calculations for the F, Cl, Br, and I varients using transferred valence force fields (TVFF) and for the F and Cl compounds using a force field derived from CNDO level semiempirical calculations (CNDO-FF).[21] Furthermore, we have calculated LMO-VCD for the fluoro compound. Details of these theoretical methods have been previously reviewed by others.[1] Since our methods[4] have also been previously reported, it would be repetitious to include full details of the theory here. For the sake of brevity, we will focus on the 1-bromo-3-methylallene calculations in this paper; full details for the other species are available in ref 21. To facilitate discussion we will use the abbreviations of the previous paper,[13] i.e., the notation for 1-bromo-3-methylallene will be MeBr.

Calculations

Normal Coordinate Analyses. In order to calculate the VCD intensities with the FPC and LMO models it is necessary to have both a force field and geometry for the molecule. Since no haloalkylallene force fields are available, force constants from related compounds were transferred to set up an approximate TVFF for this set of molecules. The various bond lengths and angles were also approximated by transfer from propene and halogen-substituted ethylenes as well as allene (Table I). These values, in the *S* configuration, were then used for G matrix calculations (using the GMAT program[22]).

The internal coordinates and atom numbering system are described in Figure 1 and detailed elsewhere.[21] From these, a set of symmetry coordinate definitions were chosen so that the maximum number of force constants could be transferred from related molecules. This results in

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Table II. Symmetry Coordinate Definitions for 1-Halo-3-methylallene

symmetry coordinate	description in terms of internal coordinate[a]	qualitative description
S1	R_1	C=C stretch (CH₃ end)
S2	R_2	C=C stretch (X end)
S3	R_3	C—C stretch
S4	R_4	C—X stretch
S5	r_1	C—H stretch (CH₃ end)
S6	r_2	C—H stretch (X end)
S7	$(r_3 + r_4 + r_5)$	CH₃(s) stretch
S8	$(2r_3 - r_4 - r_5)$	CH₃(as) stretch
S9	$(\tau_{10823} + \tau_{10827} + \tau_{9823} + \tau_{9827})$	C=C torsion
S10	$(\tau_{4321} + \tau_{5321} + \tau_{6321} + \tau_{4327} + \tau_{5327} + \tau_{6327})$	C—C torsion
S11	ϕ_1	C=C=C linear bend 1
S12	ϕ_2	C=C=C linear bend 2
S13	$(2\omega_{13} - \beta_{17} - \beta_{37})$	C=C—C bend
S14	$(\beta_{17} - \beta_{37})$	C=C—H in-plane (CH₃ end)
S15	$(\beta_{26} + \beta_{24} + \beta_{25} - \alpha_{45} - \alpha_{56} - \alpha_{46})$	CH₃(s) deform
S16	$(2\beta_{26} - \beta_{24} - \beta_{25})$	CH₃ rock
S17	$(2\alpha_{45} - \alpha_{56} - \alpha_{46})$	CH₃(as) deform
S18	$(r_4 - r_5)$	CH₃(as) stretch
S19	$(\beta_{24} - \beta_{25})$	CH₃ rock
S20	$(\alpha_{56} - \alpha_{46})$	CH₃(as) deform
S21	γ_9	C=C—H out-of-plane (CH₃ end)
S22[b]	$\beta_{1,10}$	C=C—X bend
S23[b]	$\beta_{1,9}$	C=C—H in-plane bend (X end)
S24[b]	$\beta_{9,10}$	X—C—H bend
S25[b]	γ_7	C=C—H out-of-plane (X end)
*S22[b]	$(2\beta_{1,10} - \beta_{1,9} - \beta_{9,10})$	C=C—X bend
*S23[b]	$(\beta_{1,9} - \beta_{9,10})$	C=C—H in-plane bend (X end)
*S24[b]	γ_7	C=C—H out-of-plane (X end)

[a] For internal coordinates see Figure 1. All symmetry coordinates were normalized, but the normalization constants are not included here for sake of simplicity. [b] The first 25 symmetry coordinates were used with the TVFF. The last four of these were replaced by the three symmetry coordinates indicated by asterisks for use with the CNDO force field.

a total of 25 symmetry coordinates (one redundant) as defined in Table II.

The force constants themselves were then transferred from four molecules: allene,[21,25] propene,[23] ethylene chloride,[24] and formyl chloride.[26] It was assumed that there was no interaction between the methyl and halogen parts of the molecules, and such force constants were thus constrained to zero. The force constants are labeled with use of a notation based on the symmetry coordinate numbering system in Table II.

A total of 85 force constants are taken for the calculations for MeBr which are available in ref 21 along with modifications for the other halomethylallenes. By using FTIR data obtained at 1-cm⁻¹ resolution (IBM-IR/32) for MeBr and MeI in CCl₄ and CS₂ solvents, a partial refinement was attempted for 10 of the possible 25 diagonal force constants, using 13 observed frequencies for MeBr. For another point of view, CNDO force fields (CNDO-FF) were calculated for the fluoro- and chloromethylallenes and scaled[27] by comparison with the corresponding diagonal TVFF force constants.[21]

FPC-VCD calculations were carried out by using the above force fields with the procedures described earlier.[4] Two sets of partial charge parameters were chosen, one empirically derived from bond dipoles[21] and the other a CNDO calculated set of charges. To test the sensitivity of rotational and dipolar strengths with respect to the partial charges used, the values in the MeBr empirical set for the hydrogens were varied from −0.3 to 0.3 and those for the terminal allenic and methyl carbons from 0.7 to −0.8, without changing the partial charges on the central allenic carbon and on the Br. Additionally, the mass effect on the FPC-VCD was studied by replacing the methyl hydrogens with a pseudo-atom of mass 15 to mimic the *tert*-butyl situation for better comparison to the majority of our experimental results.[13,21] LMO calculations were carried

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Table III. Calculated and Observed Frequencies Along with FPC–VCD Results for 1-Bromo-3-methylallene Using TVFF

frequency (cm^{-1})		FPC^a [(esu·cm)^2]		
obsd	calcd	D ($\times 10^{39}$)	R ($\times 10^{45}$)	PED^b
	91.1	65.10	−19.51	S22(34) + S12(24)
	159.9	20.90	−74.75	S10(59) + S25(11) + S11(10)
	196.4	35.97	339.16	S10(34) + S9(18) + S11(11)
	264.8	20.30	332.70	S13(34) + S11(31) + S9(16)
	423.9	10.88	−163.39	S12(47) + S4(22)
	562.2	10.13	−7.01	S13(38) + S11(28)
655.0	648.9	9.71	−153.55	S4(58)
705.0	702.6	23.26	−743.08	S25(47) + S21(16)
	851.9	1.59	−3.40	S16(31) + S3(21) + S1(13)
895.0	895.0	23.31	138.55	S21(27) + S19(24) + S9(19)
	968.4	4.96	141.11	S16(38) + S23(23) + S14(11) + S17(12)
	1023.6	4.43	656.48	S19(25) + S21(18) + S23(17) + S16(14)
1074.0	1063.1	14.98	−225.52	S19(34) + S3(30) + S13(18) + S16(12)
1126.6	1130.8	8.80	217.08	S14(54)
	1335.9	14.47	−194.59	S14(27) + S2(25) + S1(17) + S15(12)
1373.0	1381.0	62.59	95.29	S15(91) + S3(18) + S13,15(16) + S3(11)
1440.0	1444.3	22.52	334.50	S17(50) + S20(36)
1454.5	1449.1	22.03	−392.21	S20(60) + S17(30)
1954.1	1954.0	2.24	17.28	S1(52) + S2(51)
2896.5	2900.0	5.29	−20.75	S7(100)
2925.9	2920.1	22.95	−23.46	S18(97)
2953.9	2954.7	23.01	−92.92	S8(96)
2994.9	2995.1	3.27	21.84	S5(98)
3064.0	3067.3	1.14	21.40	S6(97)

^{a} D and R are dipolar and rotational strengths, respectively, expressed in units of (esu·cm)^2. FPC calculations were done using TVFF with the following empirical charges: C_1, 0.05; C_2, 0.3; C_3, 0.7; H_{4-6}, −0.3; $H_{7,9}$, −0.1; C_8, 0.81; X, −0.76. ^{b} Potential energy distribution (PED) description from TVFF calculations (×100). Only coordinates with PED greater than 0.10 are listed.

out for only the fluoro varient by using a modified CNDO program gratiously provided to us by Prof. P. L. Polavarapu.

The results of the various calculations are summarized as follows: For MeBr, some observed and calculated (from the TVFF) frequencies are given in Table III along with dipole strengths (D) and rotational strengths (R) from the FPC. The MeF, MeCl, and MeI results of interest will be discussed separately as needed for comparison and are available in ref 21.

Results and Discussion

C(X)–H Stretch. In the normal coordinate calculations, when the methyl hydrogens were each replaced by mass 15 to mimic *tert*-butyl (without changing the force field), the allenic C(X)–H stretching frequency and potential energy distribution (PED) remained almost the same. The PED's of the various haloallenes for this mode were all dominated by S6, the C(X)–H stretch, with values ranging from 94 to 97, showing it to be relatively independent of the alkyl and halogen groups on the allene. Thus, it is reasonable to compare the calculated VCD for the C(X)–H stretches on the halomethylallenes with the experimental VCD we have obtained for the halo-*tert*-butylallenes.

Experimentally, the S isomer of BuCl had positive VCD with $\Delta A/A$ of ca. +4 × 10^{-5} for the C(X)–H stretch. That of BuBr and BuI were similar but somewhat smaller and distorted by artifact.[13] This should be comparable to the calculated $4R/D$ value if the absorption and VCD have the same bandshape. With use of the TVFF, the MeBr calculated value is about equal to the experimental one while the MeI and MeF calculated $\Delta A/A$ values are higher than any we have observed and the MeCl values are somewhat small, analogous to previous FPC results.[28] The

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CNDO–FF VCD ($4R/D$) of this band is smaller than the TVFF result by a factor of 2–5 for both MeCl and MeF but remains positive. In terms of frequencies, the TVFF values for the C(X)–H stretch for these molecules are in reasonable agreement with our experimental results, but the CNDO-FF frequencies are much poorer. In fact, for MeF with the CNDO-FF, this band is calculated to lie below the CH$_3$ stretches in obvious disagreement with our data for the other haloalkylallenes, yet the VCD sign pattern is conserved. The C(X)–H calculated frequencies and $4R/D$ values are condensed in Table IV.

Taken together, these results imply a sensitivity to force field and charge parameters for this mode that was not expected. It seems clear that even though the FPC model with the TVFF yields the correct VCD sign for all species and gives the right magnitude (as compared to BuBr data), in fact, the FPC does not adequately reflect the nature of the VCD measured in that its sensitivity to halogen alteration is much higher than our experimental results[13] would have led us to believe. As a warning to the reader, it should be noted that the C(X)–H data we have measured are at the limits of our detectability and hence are quantitatively much less reliable than the C=C=C stretch VCD data, for example.

One might be concerned that a problem arises from calculating VCD for the methyl compounds and comparing it to VCD data for the C(X)–H stretch obtained from only the *tert*-butyl compounds. To test this possibility, calculations were done with the mass of the CH$_3$ hydrogens increased to 15. We find only a small effect on the VCD of the C(X)–H in terms of $\Delta A/A$. However, the other allenic =C–H stretch changes sign to negative. This implies that while coupling between CH$_3$ and C(X)–H is not very important, that between the alkyl =C—H and the CH$_3$ does influence the VCD. This is reasonable considering their geminal connectivity. Calculated values for ϵ and $\Delta\epsilon$ both increased by ~60% for the C(X)–H on this mass increase.

On the other hand, variation of halogen mass, but use of the same MeBr TVFF and charges, resulted in a less than a 20% change for the C–H stretch R and D values in all cases except that of the fluoro compound. There the rotational strengths of both allenic =C—H's decreased by nearly a factor of $^2/_3$, presumably due to kinetic effects. The variation seen with change in halogen for the calculations that we have done (Table IV) is thus probably due to force field effects, not mass effects. Another concern is that the arbitrary charge distribution could have led to the observed deviation of our calculated VCD from the experimental result. As a test, we recalculated MeBr with various charge sets appropriate to the other halogens. This led to virtually identical results for the I, Br, and Cl charge sets but a significant decrease in R for the fluoro case. Thus the charge *and* mass effect together should reduce the calculated MeF C–H VCD; but, in fact, the MeF value we calculated increased over that of the MeBr case (Table IV). This again indicates that the main difference in the two is in the force field.

CH$_3$ Stretches. Now let us consider the rest of the C–H stretching region by focusing on the CH$_3$ modes. As noted in our previous paper,[13] the initial problem is that more absorption bands are observed experimentally than can be calculated. This may be due to CH$_3$ Fermi resonance (with the CH$_3$ deformation modes). The qualitative patterns seen in the MeBr calculated absorption spectrum are reflective of the experimental results. This assigns the 2960- and 2925-cm^{-1} bands as components of the CH$_3$(as) stretch and 2895 cm^{-1} as the CH$_3$(s) stretch, while 3060 and 2990 cm^{-1} would be the C(X)—H and =C—H allenic stretches, respectively.[21] The 2865-cm^{-1} band would be ascribed to resonance with combinations of methyl deformation modes in such an assignment. As expected,[4,7] the FPC model is poor in terms of absorption intensities, especially for the CH$_3$(s) stretch.

As for the VCD, the two MeBr CH$_3$(as) modes are not calculated to have a bisignate spectrum and as such do not behave as a perturbed degenerate oscillator. As a result, using the TVFF, the CH$_3$ VCD for MeBr is calculated to be net negative with its relative intensity distribution being quite dependent on the charge scheme used. Experimentally, a very noisy negatively biased couplet was seen at ~2970 cm^{-1} with the dominant negative

Table IV. FPC and LMO-VCD Summary for 1-Halo-3-alkylallenes in C(X)-H Stretch

parameters[a]	substituent in H(X)C=C=CRH X	R	freq calcd[b] (cm^{-1})	experiment[b] ν	ε	Δε	Δε/ε	calculation 4R/D
	F	Me						
FPC(TE)			3112.8					1.59 × 10^{-4}
FPC(CE)			2975.4					0.32 × 10^{-4}
LMO(T)			3112.8					1.40 × 10^{-4}
	Cl	t-Bu		3062	6.6	4 × 10^{-4}	6 × 10^{-5}	
	Cl	Me						
FPC(TE)			3044.9					8.9 × 10^{-6}
FPC(CE)			2961.0					3.2 × 10^{-6}
	Br	t-Bu		3068	10.0	∼3 × 10^{-4}	∼3 × 10^{-5}	
	Br	Me						
FPC(TE)			3067.3					7.50 × 10^{-5}
	I	Me						
FPC(TE)			3038.4					1.40 × 10^{-4}

[a] FPC(TE) and FPC(CE) refer to FPC calculations with TVFF and CNDO-FF, respectively using empirical charges. LMO(T) and LMO(C) refer to LMO calculations with TVFF and CNDO-FF, respectively. All calculations were for the methyl derivatives. [b] The observed frequencies of the absorption maxima and VCD are given for 3-halo-3-*tert*-butylallene (*S* absolute configuration). The Br value has a significant error and the I result was adversely affected by sample decomposition (ε and Δε units in L mol^{-1} cm^{-1} and ν in cm^{-1}).
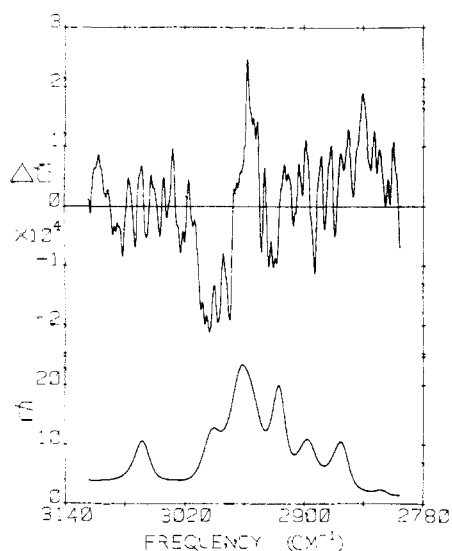

Figure 2. Absorption and VCD spectra of MeBr in the CH stretching region. Concentration 0.045 M in CCl$_4$, path 0.5 cm, resolution 12 cm^{-1}, time constant 3 s, peak absorbance 0.5, six scans averaged, corrected for ee ∼20%. VCD baseline obtained with acetonitrile. Note that the noise level varies from ±0.5 to ±1.0 × 10^{-4} in Δε. VCD bands judged to be reproducible are the negative at ∼2980 cm^{-1}, the positive at ∼2960 cm^{-1}, and, perhaps, the broad positive at ∼2840 cm^{-1}.

intensity more correlated to the 2995-cm^{-1} band, which is assigned to the =C—H rather than the CH$_3$ bands. The data for MeBr are illustrated in Figure 2 and indicate the S/N limitations faced with the samples at our disposal. Hence, while the *net* calculated CH-VCD was in agreement with respect to sign with our experiment for all cases, it correlates in detail to what appears to be the wrong band. Agreement in *net* sign for near degenerate bands is often the limit of accuracy one can expect for the FPC model.[29]

In summary, while the FPC model succeeds in qualitatively describing the C(X)H VCD, it fails to adequately explain the observed VCD of the methyl C-H stretching modes. Given its qualitative success with CH$_3$ stretches in a variety of other systems,[7,12,30,31] the model may be considered to be inadequate for

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aliphatic (CH$_3$) stretches adjacent to an allenic functional group. On the other hand, we have earlier found the benzylic CH$_3$ groups gave systematic VCD if they are viewed as acting as part of a CH$_3$-C*H chromophore and that the sign pattern of that VCD could be calculated in the FPC model.[30] Similar success was found for alanine-*N*-d$_3$ but not for its other deuteriated isotopomers which, of necessity, drastically alter the CH$_3$-C*H group.[12] In those cases, the CH$_3$(as) stretches yielded a strong, calculated VCD couplet but were nearly degenerate, which leads to substantial intensity cancellation. In the MeBr allene case, the CH$_3$(as) modes are calculated to be split by ∼30 cm^{-1} and a strong couplet is not calculated. Other examples of success with CH$_3$ groups in the FPC model are primarily due to strong dipolar coupling in hydrocarbon ring systems.[4,7,31]

LMO calculations were only possible for MeF. For the C(X)-H stretch in MeF with the TVFF, the LMO yields a value for 4R/D of ∼1.4 × 10^{-4} and corresponding the FPC has 4R/D ∼ 1.6 × 10^{-4}, in exceptional agreement. The LMO D and R values are 3-4 times higher than those of the FPC. However, in the other modes, there are very large differences between the two calculations. The most interesting concerns the other allenic =C—H stretch which has, in the LMO, negative VCD with 4R/D = -1.8 × 10^{-4}, but in the FPC its VCD is positive with 4R/D = +0.72 × 10^{-4}. Thus the LMO result is analogous to a coupling of C(X)—H and =C—H, while the FPC is not. It is interesting to note that the FPC charges can be altered to yield the LMO sign pattern. With use of the CNDO derived charges, the =C—H and highest energy CH$_3$(as) component have negative VCD with the MeF TVFF. However, the absorption intensity distribution with these charges is highly anomalous.[21] Finally, it might be noted that the LMO D values are approximately equal for all five CH stretches[21] in sharp contrast to the experiment. The FPC too strongly weights the CH$_3$ with respect to the =C—H in terms of dipolar intensity, but this is probably an artifact of charge selection. A referee has noted that the LMO sign pattern in MeF is just what one obtains from coupled oscillator considerations of the C(X)H and =C—H modes in symmetric and antisymmetric combinations.

C=C=C Asymmetric Stretch. As might have been expected, due to its unique nature, the C=C=C(asym str) was the most consistent of all the FPC-VCD calculated modes. In agreement with experiment, this mode was calculated to have positive VCD for all charge sets, force fields, and mass distributions used in our study. With the TVFF and empirical charges (Table III), 4R/D is 0.31 × 10^{-4} for MeBr with values varying by only ∼10% for the other haloalkylallenes. With the CNDO-based charges, the 4R/D value obtained was about the same but R and D separately were sharply reduced. Sensitivity tests via variation of the empirical charges for MeBr, as indicated in the calculational section, caused a change of 4R/D by as much as a factor of 10, but the value obtained was always positive.

Table V. FPC and LMO–VCD for 1-Halo-3-methylallene in the C=C=C(as) Stretch

parameters[a]	substituent in H(X)C=C=CRH X	H	freq calcd (cm^{-1})	experiment[a] ν	ϵ	$\Delta\epsilon$	$\Delta\epsilon/\epsilon$	calculation 4R/D
	F	Me						
FPC(TE)			1980.5					2.88 × 10^{-5}
FPC(CE)			1990.9					1.80 × 10^{-5}
LMO(T)			1980.5					-8.70 × 10^{-6}
	Cl	t-Bu		1959	23.0	1.0 × 10^{-3}	4.5 × 10^{-5}	
	Cl	Me						
FPC(TE)			1977.9					3.00 × 10^{-5}
FPC(CE)			1913.0					4.50 × 10^{-6}
	Br	t-Bu		1965	30.0	2.1 × 10^{-3}	7.0 × 10^{-5}	
	Br	Me		1954	12.0	1.4 × 10^{-3}	1.2 × 10^{-4}	
FPC(TE)			1954.0					3.10 × 10^{-5}
	I	Me		1944	8.9	1.3 × 10^{-3}	1.5 × 10^{-4}	
FPC(TE)			1948.5					3.10 × 10^{-5}

[a] Abbreviations and units as in Table IV. The observed frequencies listed correspond to the absorption maxima of the compound. Observed and calculated VCD data are given for *S* absolute configuration of the molecule.

Here it is important to note the apparent inability of the FPC model *as we have parametrized it* to predict the C=C=C(asym str) dipolar strength, *D*. The values for MeBr in Table V suggest that ϵ for the C=C=C(asym str) should be an order of magnitude below those found for the methyl group whereas experimentally they are only a factor of 2–3 smaller. However, the calculations also suggest that the C(X)—H mode should be only somewhat weaker than the C=C=C. Since this is, in fact, what is observed, one may view the calculations as being satisfactory for =C(X)—H and C=C=C but *too high* for CH$_3$. To further probe this effect, we varied the central carbon charge from –0.55 to +0.45 and balanced it by equivalent alteration of the two terminal allenic carbon charges. This process varied the *D* value for the C=C=C by two orders of magnitude but the *R* value changed by only less than an order of magnitude. This type of charge alteration, because it involves only changes for a linear part of the molecule, apparently affects the electric dipole moment primarily. Thus, shifting the charge parameter of the central carbon to a more negative value *decreases* $\Delta A/A$ for the C=C=C(asym str) band while it makes the *D* values more reasonable. Clearly the arbitrary nature of the charge parameters in a complex, heteroatom-containing system makes quantitative FPC–VCD a hopeless task. Our results for allene and its deuterio-isotopomers follow this same pattern of the asym C=C=C str having a low calculated *D* value.[21,29]

Experimentally, $\Delta\epsilon/\epsilon$ for this mode ranged from (0.5 to 1.5) × 10^{-4} with the MeBr and MeI values being higher than the halo-*tert*-butylallene values. The order of magnitude range of our calculated values for the C=C=C(as) in comparison to the exceptional stability (factor of 3) of the corresponding experimental ones could, in principle, be attributed to our choice of charge parameters. As shown above, 4R/D can be varied dramatically by changing the allenic carbon charges. Due to its unique nature, the VCD of the C=C=C(asym str) probably arises from the overall charge distribution of the molecule. Since the normal mode primarily involves motion of only the central carbon atom,[32] it must generate a magnetic moment (in an FPC sense) from interaction with a virtually fixed charge distribution. As such, the fact that this mode involved nearly pure allenic motion is consistent with its VCD being a useful stereochemical delimiter as was found experimentally in the previous paper.[13] Furthermore, the observation that the FPC-calculated VCD for this mode is generally lower in magnitude than was found experimentally in the halo-alkylallenes (especially when reasonable *D* values are attained) is consistent with the patterns typically found for FPC calculations on isolated modes in highly polarizable molecules.[28] The results for the C=C=C(asym str) are summarized in Table V.

On the other hand, the LMO–VCD calculation with the TVFF indicates a *negative* VCD for the C=C=C(asym str) in MeF

(*S* configuration) contrary to all of our experimental and FPC calculated results on substituted allenes. A 4R/D ($\sim \Delta\epsilon/\epsilon$) value resulted that is somewhat smaller but comparable to that obtained with the FPC calculations discussed above. Such a failure to reproduce what would appear to be the most characteristic VCD of the haloalkylallene series indicates a significant problem with the LMO model. This is somewhat analogous to our earlier findings in the cyclobutane case where the LMO gave quite good results for the CH and CD stretching VCD[4] but qualitatively poor calculated VCD for the lower energy mid-IR modes.[5]

Mid-IR. The FPC and LMO calculations, of course, have no problem in generating calculated VCD for the mid-IR modes. However, there are no experimental data to which the calculations can be compared. The MeBr and MeI mid-IR VCD could not be measured due to VCD artifact interference.[13] The BuCl and BuBr compounds gave a significant VCD band at 1370 cm^{-1}, but this probably originates in the butyl CH$_3$ deformations and would not be reflected in our calculations. At best we can compare the calculations among themselves.

The three CH$_3$ deformation modes (1449, 1444, and 1381 cm^{-1}) are consistently calculated with the partially optimized MeBr and MeI TVFF and empirical charges (see Table IV). The next lower transition at $\sim$1330 cm^{-1} has a significant C=C=C(sym-str) contribution and is calculated to be strongly negative. The same pattern holds for the MeF TVFF results using the FPC model; but, in analogy to what happens in other spectral regions, the LMO–VCD pattern is opposite in sign for the CH$_3$ deformations. Without experimental data, no conclusion as to the value of these mid-IR calculations is possible. For further comparison the reader is referred to ref 21.

Conclusion

Our data demonstrate that substituted allenes provide a system where a clear difference exists between LMO and FPC calculated VCD. The two calculational models are most alike in the CH stretching region where modes correspond to relatively pure symmetry coordinates but deviate sharply in the lower energy, more highly mixed modes. At present, it appears that the much more approximate FPC model does a better *overall* job of giving a *qualitative* representation of the VCD spectra.

The main conclusion of this work is a somewhat negative one. The LMO model, while perhaps conceptually more attractive than the crude FPC model, has now failed in two cases to adequately reproduce the qualitative aspects of VCD measured in the lower energy, heavy atom modes. A similar problem has also arisen for 1,3-dideuterioallene which indicates that this difficulty is not attributable to halogens as being a special case.[29] For the lower energy modes, the FPC model was found to be qualitatively superior even though it was quantitatively poorer. These transitions involve vibrational modes for which one might naively expect the LMO to be superior to the FPC model. The two cases, i.e., cyclobutane and alkylhaloallenes, are significantly different in electronic structure. This leads us to the suggestion that where

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the FPC is proven inadequate to represent mid-IR VCD, the LMO will *not* be a useful alternative for stereochemical analysis.

Finally, it should be clear that these substituted allenes form a class of molecules with stereoelectronic effects of interest for study with VCD. Yet, at the same time, they are not ammenable to the more quantitatively reliable, large-basis-set type calculations of Stephens and co-workers.[18] Thus the applicability of simpler, though deficient, VCD models remains a viable problem for future research. Its solution will be needed to attain extensive stereo-

chemical utility for VCD with even these relatively small molecules.

Experimental and Theoretical Study of the Structures and Optical Rotations of Chiral Bicyclic Ortho Esters
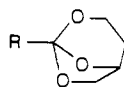
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Abstract: Syntheses are described for three rigid (−)-1-R-2,7,8-trioxabicyclo[3.2.1]octanes (R = H, 1; R = Me, 2; R = Ph, 3) in high enantiomeric purity. The crystal and molecular structure of (−)-3 was determined by X-ray means. A crystal of (−)-3 grown from Et_2O-n-C_6H_{14} belonged to the space group $P2_1$ having cell constants $a = 7.8520$ (9), $b = 10.493$ (1), and $c = 6.1048$ (6) Å and $\beta = 107.02$ (1)°. The cell volume was 481.35 (9) Å^3 with 2 molecules per unit cell. The final conventional residual index was 0.0612. From the crystallographic data, four refined structural models of 3 were generated, which differed only in their degree of geometric optimization. Whereas model 1 is unstrained, models 2–4 are increasingly restrained to ideal geometry in order to correct the systematically short bonds associated with an unrestrained refinement. Molar rotations were calculated from classical dipole interaction theory with the structural parameters from the four models of 3 and atom polarizabilities derived earlier. The calculated molar rotations for 3 were correct in sign and insensitive to rotations of the phenyl group about the C–C bond. The differences between the calculated values and the experimental rotation decreased to within a factor of 4 concomitantly with the increased level of geometric optimization of the models. The difference between the theoretical and experimental values is attributable to small uncertainties in atom coordinates and atom polarizabilities. Similar results were obtained for 1 and 2 with the structural models obtained for 3. The identical signs and similar magnitudes of rotations for 1–3 appear to stem primarily from the chiral gauche arrangement of the butane fragment.

Ortho esters **1–3** are nearly rigid chiral molecules derived from optically active 1,2,4-butanetriol. The lack of conformational freedom in these molecules confers on them special theoretical interest, because it is possible to make meaningful theoretical calculations of their optical activity without resorting to rather uncertain conformational averaging. These molecules are also amenable to the classical dipole interaction theory,[3] which has been applied successfully to a variety of optically active molecules, ranging from the simplest known case of $CHFClBr^{3-5}$ to complex helical polypeptides.[6] In the simplest molecular model treated by this theory, the atoms are regarded as isotropic units that interact with each other only by way of the fields of their induced electric dipole moments in the field of a light wave. This approach works well for essentially saturated molecules, presumably because the high degree of electron localization implicit in the model is most nearly valid for such molecules. We employ this approach for the ortho esters **1–3**, since the chiral bicyclic moiety in each

1. R = H
2. R = Me
3. R = Ph

is saturated. Moreover, these esters can be synthesized in enantiomerically pure form for reliable optical rotation measurements, and **3** gave crystals suitable for X-ray diffraction determination of the required structural parameters.

To predict the optical rotation at the sodium D line (5893 Å), the theory requires the polarizabilities and coordinates of all atoms in the molecule. The atom polarizabilities have been obtained semiempirically from observed molecular polarizabilities of simple compounds at the sodium D line.[7] In most previous studies of this type, reasonably accurate atom coordinates were generated from bond lengths and bond angles obtained from various sources. Compounds **1–3** must be approached differently because their bicyclic configuration is strained, rendering accurate predictions of their structures from "standard" bond lengths and bond angles unfeasible. The approach adopted in this study was to determine the structure of a single crystal of a pure enantiomer of one of the ortho esters (**3**) by X-ray diffraction and then to utilize the coordinates so found for the bicyclic moiety in calculating the

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