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Molecular Orbital Calculations on the Optical Rotatory Properties of Chiral Allene Systems

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The chiroptical properties associated with the $\pi \rightarrow \pi^*$ transitions in dissymmetric allene systems are calculated and relationships between the chiroptical observables and the stereochemical and electronic structural features of these systems are examined. The calculations are based on the INDO and CNDO/S semiempirical molecular orbital models for the electronic structure of the molecular systems and excited states are constructed in the virtual orbital-configuration interaction approximation. The dipole strengths, rotatory strengths, and dissymmetry factors for the three lowest energy $\pi \rightarrow \pi^*$ transitions are computed and reported for eleven chiral allene structures. Relationships between absolute configuration and the signs of the $\pi \rightarrow \pi^*$ rotatory strengths are examined and discussed.

Key words: Chiral allene systems – Allene systems, chiroptical properties of ~

1. Introduction

The electronic structure and spectroscopic properties of allene systems have received considerable attention in recent years. Semiempirical self-consistent-field molecular orbital (SCF-MO) calculations have been carried out by a number of workers in attempts to characterize the ground state electronic structure and the ultraviolet absorption spectra of allene and allene derivatives [1–5]. Additionally, *ab initio* SCF-MO calculations have been carried out on the ground state properties of allene by Buenker [6]; and Schaad, Burnelle, and Dressler [7] have calculated the excited state properties of allene using virtual orbitals generated from an *ab initio* Gaussian SCF calculation on the ground state. Medium resolution vacuum ultraviolet absorption spectra of allene and methyl-substituted allenes in the vapor phase have recently been reported by Russell and coworkers [8], and Heilbronner and coworkers [9] have reported the photoelectron spectra of a series of methyl-substituted allenes and of tetramethyl-bisallenyl.

The optical activity of chiral allene systems and the problem of assigning absolute configurations to these systems have been of considerable interest for many years [10, 11]. A number of empirically and semiempirically based spectra-structure relationships and rules for assigning absolute configurations have been proposed for chiral allene derivatives [10b, 10f–h] and Ruch [12] has used dissymmetrically substituted allene derivatives to demonstrate the applicability of the general theory of chirality functions to the optical rotatory properties of molecular systems.

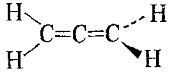
In the present study we report direct calculations on the chiroptical properties of dissymmetric allene systems. These calculations are based on the CNDO (complete neglect of differential overlap) and INDO (intermediate neglect of differential overlap) semiempirical SCF-MO models and the virtual orbital-configuration interaction method for constructing electronic excited states. Similar calculations done in our laboratory [13] and by others [14] (on various classes of molecular systems) have demonstrated their utility in developing reliable spectra-structure relationships and in ascertaining the mechanism whereby a chromophoric unit in a chiral molecule acquires optical activity. Due to the approximations inherent in the semiempirical SCF-MO models and in the virtual orbital-configuration interaction methods employed in these direct calculations, the results are not expected to be inherently more accurate or reliable than those obtained using, for example, independent systems type perturbation models. However, the direct calculational approach provides an alternative representation which is especially appropriate for molecules having "extended" chromophoric units, cyclic systems in which ring strain may influence spectroscopic properties, and molecules not easily partitioned into weakly coupled fragments (weakly coupled with respect to their spectroscopic states). In the direct calculational approach, electronic wave functions are calculated for the entire molecule and these molecular (rather than fragment or subsystem) wave functions are then used to calculate, directly, the rotatory strength parameters.

The principal objective of the present study was to determine if *direct* calculations of the chiroptical properties of chiral allene systems based on a semiempirical molecular orbital model could be used to develop reliable spectra-structure relationships for these systems. Furthermore, such calculations are expected to provide a basis on which the merits and shortcomings of the variously proposed sector rules and spectra (chiroptical) interpretations of optically active allene systems may be evaluated. In most instances, previously proposed spectra-structure relationships for chiral allene systems have been based on semiempirical and semiquantitative considerations. The calculations presented here yield quantitative results for specific systems.

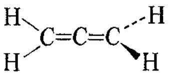
2. Structures

Eleven chiral structures and one achiral structure (unsubstituted and undistorted allene) were examined in the present study. These twelve structures are shown in Fig. 1. Structure I has exact D_{2d} symmetry, whereas the point group symmetry of structure II is D_2. Structure II is simply unsubstituted allene with a torsional distortion (6° twist angle) applied about the C=C=C bond axis. Structures III and IV each have C_2 symmetry with the C_2 axis perpendicular to the C=C=C bond axis. Structures V and VI also have C_2 symmetry, but in these cases the C_2 axis lies along the C=C=C bond axis. The remaining structures, VII-XII, are devoid of any symmetry.

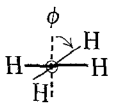
Structures II and V are optically active by virtue of an inherently dissymmetric chromophoric unit, $>C=C=C<$. Structures III and IV are optically active due to a dissymmetric arrangement of symmetric ligands attached to the allenic chromophoric unit. Structures VI-XII acquire optical activity from the presence of an optically active ligand at one end of the allenic chromophore. The cyclopentyl ring in each of the structures, VI-XI, possesses a dissymmetric conformational structure. In structures VII-XI, the cyclopentyl ring is conformationally dissymmetric *and* one or two carbon atoms within this ring are asymmetrically substituted. In each of the structures, VI-XI, the cyclopentyl ring was assumed to have C_2 symmetry and the dihedral twist angle within the carbon atom framework of the ring was set at 23°.

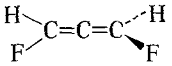


I.

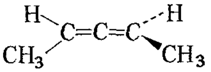


II. (ϕ = 6°).

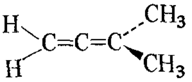




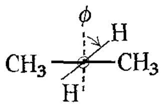
III.

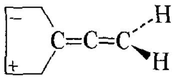


IV.

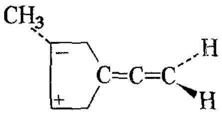


V (ϕ = 6°).

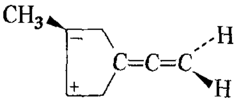




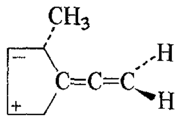
VI.



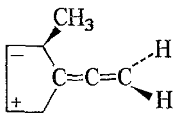
VII.



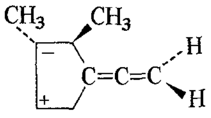
VIII.



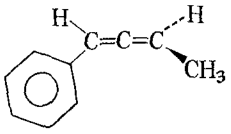
IX.



X.



XI.



XII.

Fig. 1. Drawings of the twelve allene structures examined. + and – denote, respectively, displacements of cyclopentyl ring atoms above and below the plane of the figure.

3. Methods of Calculation

SCF-MO calculations were carried out on structures I-XII in both the INDO and CNDO/S approximations. The INDO-MO calculations were carried out using the "standard" parameters of Pople and Beveridge [15]. The CNDO/S-MO calculations were carried out using the "modified" parameters of Jaffé and coworkers [16]. The molecular orbitals obtained from the SCF-MO calculations were renormalized ("deorthogonalized") by subjecting the eigenvector matrix, $\tilde{C}_\lambda$, obtained from the SCF-MO output to the transformation,

$$\tilde{C}_\chi = \tilde{S}_\chi^{-1/2}\tilde{C}_\lambda \qquad (1)$$

where χ denotes Slater orbitals, λ denotes the INDO or CNDO basis functions, $\tilde{S}_\chi$ is the overlap matrix over Slater orbitals. The renormalized moelcular orbitals, $\tilde{\phi}$, are then expressed as linear combinations of Slater orbitals,

$$\tilde{\phi} = \tilde{C}_\lambda \tilde{\lambda} = \tilde{C}_\chi \tilde{\chi}. \tag{2}$$

In this procedure the basis set $\tilde{\lambda}$ is considered to be derived from the usual Slater one $\tilde{\chi}$ by means of the Löwdin transformation,

$$\tilde{\lambda} = \tilde{\chi}\tilde{S}^{-1/2}. \tag{3}$$

Excited state wave functions were constructed in the virtual orbital-configuration interaction (CI) approximation. Electric dipole transition integrals were calculated using the dipole velocity formalism, and all one-, two-, and three-center terms were included in the calculations of both electric and magnetic dipole transition moments. Ground state dipole moments were calculated according to the procedures outlined by Pople and coworkers [15]. The optical properties calculated in this work were:

a) reduced rotatory strength,

$$[R_{ij}] = (100/\mathscr{D}\beta)\mathrm{Im}\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle\cdot\langle\psi_j|\hat{\boldsymbol{m}}|\psi_i\rangle \tag{4}$$

where β is the Bohr magneton, $\mathscr{D}$ is the Debye unit, $\hat{\boldsymbol{\mu}}$ is the electric dipole operator, and $\hat{\boldsymbol{m}}$ is the magnetic dipole operator;

b) dipole strength,

$$D_{ij} = |\langle\psi_i|\hat{\boldsymbol{\mu}}|\psi_j\rangle|^2; \tag{5}$$

c) oscillator strength,

$$f_{ij} = (4\pi m\nu_{ij}/3he^2)D_{ij}, \tag{6}$$

where m = electron mass and $\nu_{ij} = (E_j - E_i)/h$;

d) dissymmetry factor,

$$g_{ij} = 4R_{ij}/D_{ij}. \tag{7}$$

4. Results

The dipole moments and first two ionization potentials calculated in the CNDO/S approximation for structures I-XIII are listed in Table 1. The ionization potentials are "vertical" ionization potentials calculated according to Koopmans' theorem [17]. The optical properties calculated in the CNDO/S approximation for the three lowest energy singlet-singlet transitions in structures II-XII are listed in Table 2. With the exception of structure XII (which includes a phenyl ligand on the allene group), these three lowest energy transitions are $\pi \to \pi^*$ excitations localized primarily on the allenic chromophoric unit. In structure XII the orbitals (π) involved in these three lowest energy transitions are delocalized to some extent over the phenyl and allenic groups.

The experimental ionization potential of the allene (unsubstituted) ground state has been found to be 10.19 ± 0.01 eV from the convergence limit of the allene Rydberg series [18], and 10.16 eV by electron impact studies [19]. The photoelectron spectrum of allene shows a double-humped π-band with maxima at 10.07 eV and 10.64 eV [9]. This double-humped

Table 1. Dipole moments and first two ionization potentials[a] calculated for structures I–XII (CNDO/S)

Structure	Dipole Moment (Debye units)	IP_1 (eV)	IP_2 (eV)
I	0	10.410	10.410
II	0	10.194	10.629
III	2.23	10.666	10.677
IV	0.29	9.529	9.538
V	1.30	9.216	9.947
VI	1.29	9.351	9.991
VII	1.36	9.346	9.862
VIII	1.28	9.342	9.890
IX	1.44	9.212	9.846
X	1.42	9.214	9.838
XI	1.58	9.341	9.872
XII	1.00	8.572	9.656

[a] Calculated according to Koopmans' theorem.

feature has been attributed to a Jahn-Teller effect due to the degeneracy of the two highest occupied π orbitals in allene [9]. The photoelectron spectrum of 1,3-dimethylallene (our structure IV) also exhibits a double-humped π-band with maxima at 9.13 eV and 9.65 eV [9]. The 1,3-dimethylallene molecule has D_2 symmetry and its two highest filled π orbitals are not strictly degenerate; however, these two orbitals are expected to be nearly isoenergetic and subject to pseudo Jahn-Teller distortion [9]. Our calculated values of the ionization potentials for unsubstituted allene and for 1,3-dimethylallene using the CNDO/S approximation (see Table 1) appear to be in excellent agreement with experiment. Buenker's *ab initio* SCF-MO calculations on allene lead to a predicted ionization potential of 11.45 eV, and our INDO-SCF-MO calculations produced the values, IP_1 = 13.075 eV and IP_2 = 13.747 eV, for unsubstituted allene and IP_1 = 12.202 eV and IP_2 = 12.213 eV for 1,3-dimethylallene.

In our CNDO/S-MO-CI calculations on unsubstituted allene, the six lowest energy singlet-singlet transitions were identified as:

Transition	ΔE (eV)	Assignment	Symmetry (in D_{2d})
1	4.58	$\pi \rightarrow \pi^*$	$^1A_2$
2	4.58	$\pi \rightarrow \pi^*$	$^1B_1$
3	6.20	$\pi \rightarrow \pi^*$	$^1B_2$
4	7.16	$\pi \rightarrow \sigma^*$	^1E
5	7.16	$\pi \rightarrow \sigma^*$	^1E
6	8.40	$\pi \rightarrow \pi^*$	$^1A_1$

The first two transitions are accidentally degenerate and are rigorously forbidden in electric-dipole radiation. The third transition is electric-dipole allowed with a computed oscillator strength of 0.1718 (computed in the dipole velocity representation). The fourth and fifth transitions involve excitations out of the highest occupied degenerate pair of allenic π orbitals into carbon $2s$ and hydrogen $1s$ atomic orbitals which form antibonding combinations within the allene framework. These degenerate transitions are symmetry allowed in electric-dipole radiation but their computed oscillator strengths are $<$ 0.0001. The sixth transition is a $\pi \rightarrow \pi^*$ excitation which is configurationally related to the first three $\pi \rightarrow \pi^*$ transitions. The sixth transition is symmetry forbidden in both electric-dipole and magnetic-dipole radiation.

Table 2. Computed optical properties for the three lowest energy ($\pi \rightarrow \pi^*$) transitions in structures II-XII (CNDO/S)

Structure	Transition	ΔE (eV)	f	D (Debye)	[R]	|g|
II	1	4.53	–		–	–
	2	4.55	0.0002	0.01	6.85	0.2740
	3	6.19	0.1709	7.28	–9.96	0.0005
III	1	4.19	0.0003	0.02	–0.69	0.0138
	2	4.19	0.0045	0.29	8.14	0.0112
	3	5.66	0.1949	9.08	–5.31	0.0002
IV	1	4.05	0.0002	0.02	–0.84	0.0168
	2	4.06	–	–	0.02	0.0060
	3	5.89	0.2546	11.39	3.58	0.0002
V	1	3.76	–	–	0.11	7.4674
	2	4.39	0.0003	0.02	5.48	0.1096
	3	5.97	0.2672	11.81	–9.75	0.0003
VI	1	3.88	0.0002	0.01	0.90	0.0360
	2	4.54	0.0002	0.01	–0.55	0.0220
	3	6.30	0.3568	14.93	0.84	–
VII	1	3.87	0.0002	0.01	0.93	0.0372
	2	4.54	0.0002	0.01	–0.88	0.0352
	3	6.17	0.3253	13.91	1.14	0.0001
VIII	1	3.86	0.0002	0.01	0.61	0.0244
	2	4.54	0.0002	0.01	–0.19	0.0076
	3	6.30	0.3593	15.05	1.80	0.0001
IX	1	3.78	0.0003	0.02	1.64	0.0328
	2	4.55	0.0002	0.01	–5.48	0.2192
	3	6.09	0.3151	13.64	2.10	0.0001
X	1	3.78	0.0003	0.02	–0.64	0.0128
	2	4.54	0.0002	0.01	3.92	0.1568
	3	6.12	0.3254	14.09	–1.87	0.0001
XI	1	3.80	0.0003	0.02	–0.24	0.0048
	2	4.52	0.0003	0.02	2.47	0.0494
	3	6.19	0.3319	14.44	–1.76	0.0001
XII	1	3.62	0.0008	0.06	–1.65	0.0110
	2	3.88	0.0002	0.02	–0.48	0.0096
	3	4.36	0.0369	2.23	3.11	0.0006

In our CNDO/S-MO-CI calculations on 1,3-dimethylallene (IV), the six lowest energy singlet-singlet transitions were identified as:

Transition	ΔE (eV)	Assignment	Symmetry (in D_{2d})
1	4.05	$\pi \rightarrow \pi^*$	^1B
2	4.06	$\pi \rightarrow \pi^*$	^1A
3	4.89	$\pi \rightarrow \pi^*$	^1B
4	6.76	$\pi \rightarrow \sigma^*$	^1B
5	6.76	$\pi \rightarrow \sigma^*$	^1A
6	7.85	$\pi \rightarrow \pi^*$	^1A

The assignments of the transitions in 1,3-dimethylallene parallel those described above for unsubstituted allene. The σ^* orbitals again denote molecular orbitals comprised almost entirely of carbon (including the methyl carbons) 2*s* and hydrogen 1*s* atomic orbitals. In this case all of the transitions are symmetry allowed in electric-dipole radiation, but only the third transition is computed to have a significant oscillator strength (0.2546). The first transition, $^1A \rightarrow {^1B}$ ($\pi \rightarrow \pi^*$), is calculated to have the largest magnetic dipole transition moment: $|\langle m \rangle| = 0.66$ Bohr mageton, oriented along the C=C=C bond axis. The substantial electric dipole transition moment associated with the third transition ($^1A \rightarrow {^1B}$, $\pi \rightarrow \pi^*$) is also oriented along the C=C=C bond axis. According to our CNDO/S-MO calculations the two highest filled molecular orbitals (π) in 1,3-dimethylallene are split by 0.009 eV.

In our CNDO/S-MO-CI calculations on twisted unsubstituted allene (structure II), the six lowest energy singlet-singlet transitions were identified as:

Transition	ΔE (eV)	Assignment	Symmetry (in D_{2d})
1	4.53	$\pi \rightarrow \pi^*$	^1A
2	4.55	$\pi \rightarrow \pi^*$	$^1B_1$
3	6.19	$\pi \rightarrow \pi^*$	$^1B_1$
4	7.02	$\pi \rightarrow \sigma^*$	$^1B_2$
5	7.27	$\pi \rightarrow \sigma^*$	$^1B_3$
6	8.41	$\pi \rightarrow \pi^*$	^1A

Twisting the allene structure by 6° about the C=C=C bond axis lifts the degeneracy (accidental) of the two highest filled π orbitals by 0.435 eV. The excited states involved in the first, second, third, and sixth transitions all derive from singly excited configurations formed from excitations between the two highest occupied π orbitals and the two lowest unoccupied π^* orbitals localized on the allenic chromophore. The third transition is again highly allowed in electric dipole radiation (with a transition dipole directed along the C=C=C bond axis), and the second transition has a magnetic dipole transition moment of 0.673 Bohr magneton directed along the C=C=C bond axis.

The identification and assignment of states in the cyclopentyl substituted structure (VI) follow roughly the same pattern as was discussed above for the dimethyl substituted and unsubstituted allene structures. However, the detailed distrubitions of electron density in structure VI are, as one might expect, somewhat different. The three lowest energy $^1\pi\pi^*$ states of VI are calculated to have *A* symmetry in the C_2 point group of the molecule. The first two transitions each have a magnetic dipole transition moment of ~0.5 Bohr magneton (directed along the C=C=C bond axis), and the third transition has significant electric dipole strength with a transition dipole moment pointed along the C=C=C bond axis. The two highest occupied orbitals in VI are split by 0.640 eV, and the two lowest energy $\pi \rightarrow \pi^*$ (singlet-singlet) transitions are split by 0.66 eV. The general characteristics of the six lowest energy transitions in the other cyclopentyl substituted structures (VII–XI) are similar to those calculated for structure VI in the CNDO/S-MO-CI approximation. Likewise, the general characteristics of the six lowest energy transitions in twisted 1,1-dimethylallene (structure V) were found to be similar to those calculated for structure VI.

To assess the extent of rearrangement of electron density within the C=C=C moiety for the three lowest energy $\pi \rightarrow \pi^*$ transitions, we show in Table 3 the values of electron density changes computed for several of the simpler structures.

Table 3. Electron density differences between ground state and excited states in three lowest energy singlet–singlet transitions (CNDO/S-MO-CI)

Structure	Transition	Atom[a] 1	2	3
I	1	−0.199	0.199	0.027
	2	0.041	0.201	−0.211
	3	−0.081	0.188	−0.077
II	1	−0.088	0.202	−0.088
	2	−0.086	0.196	−0.086
	3	0.188	0.188	−0.079
III	1	−0.018	0.111	−0.018
	2	−0.018	0.111	−0.018
	3	−0.012	0.104	−0.012
IV	1	0.040	0.174	−0.040
	2	−0.040	0.173	−0.040
	3	−0.036	0.166	−0.036
V[b]	1	−0.357	0.178	0.313
	2	0.340	0.151	−0.469
	3	0.055	0.137	−0.108

[a] Atomic numbering system: $C_3{=}C_2{=}C_1$.
[b] 1,1-Dimethylallene.

We report here only those results obtained using the CNDO/S approximation for calculating the ground state molecular wave functions. The transition energies calculated using CNDO/S-MO-CI state functions are generally 5–20% lower than the estimated experimental values for structures which have been studied experimentally. In contrast, the transition energies calculated using INDO-MO-CI state functions were found to be about 30–40% too high. Furthermore, the oscillator strengths calculated in the CNDO/S-MO-CI approximation are generally within a factor of 2 of the experimentally observed values, whereas the oscillator strengths calculated using INDO-MO-CI state functions are 10–50 times too low. The signs and relative magnitudes of the rotatory strengths calculated using INDO versus CNDO/S wave functions follow the same general patterns, although there are significant quantitative (but not qualitative) differences.

Differences between the ground electronic state descriptions provided by the INDO versus CNDO/S models are reflected in the dipole moments computed for the various structures. Differences for several of the structures are summarized as follows:

	Computed Dipole Moment (in Debye units)	
Structure	INDO	CNDO/S
III	2.14	2.23
IV	0.07	0.29
V	0.49	1.30
VI	0.45	1.29
VII	0.63	1.36

5. Discussion

Previous theoretical treatments of the electronic spectrum of allene generally place the $^1\pi\pi^*$ excited states in the energy-order, $B_2 > B_1 > A_2$, the position of the A_1 state being variable [1-4, 20-22]. For unsubstituted allene we calculate the energy ordering to be $A_1 > B_2 > B_1 \approx A_2$. For the 1,3-disubstituted derivatives of allene (structures III and IV), the two lowest energy $^1\pi\pi^*$ states are closely related to the B_1 and A_2 allene states and remain nearly degenerate. The B_1 and A_2 allene parentage of the two lowest energy $^1\pi\pi^*$ states persists in the 1,1-dimethyl (V) and cyclopentyl (VI-XI) derivatives, but in these cases these states are significantly scrambled and the resultant states are split in energy by $\approx$ 0.60-0.80 eV. In each case studied here, the transition derived from the $^1A_1 \rightarrow {}^1B_2$ allene transition carries the largest electric dipole strength with a transition dipole oriented along the C=C=C bond axis.

From the data shown in Table 2 for structures II and V, it is seen that a very small chiral (twist) distortion about the C=C=C bond axis generates significant optical activity in the allenic $\pi \rightarrow \pi^*$ transitions. The allenic chromophoric unit is "inherently" dissymmetric in these structures (having a "chiral first sphere" in the parlance of F. Snatzke and G. Snatzke [23]). The helicity of each of these structures is M (left-handed screw sense about the C=C=C bond axis), and in a classical sense the chromophoric π electrons may be pictured as following a helical trajectory along (and about) the C=C=C bond axis when involved in $\pi \rightarrow \pi^*$ transitions in these structures.

Structure III (1,3-difluoroallene) and IV (1,3-dimethylallene) each possess R absolute configuration in the Cahn-Prelog convention. The *net* rotatory strength calculated for the lowest energy nearly degenerate pair of transitions in III is > 0, while the net rotatory strength calculated for the analogous pair of transitions in IV is < 0. The rotatory strength calculated for the third transition in III is < 0, while the rotatory strength calculated for the same transition in IV is > 0. This opposition in signs for the rotatory strengths calculated for chiral fluoro- versus chiral methyl-substituted chromophores is reminiscent of the "anti-octant" behavior observed for chiral fluoro-substituted carbonyl compounds.

Experimental chiroptical data on 1,3-difluoroallene (III) has not yet been reported. However, the CD spectrum of 1,3-dimethylallene (IV) *has* been published [10d, 10h, 11] and the following data were reported [10h] for the R isomer (56% optical purity in pentane solvent at 300°K): $\Delta\epsilon = 0.63$ ($\lambda = 223$ nm), $\Delta\epsilon = 1.7$ ($\lambda = 192$ nm), $\Delta\epsilon < 0$ ($\lambda < 185$ nm), $[\alpha]_D = -24.2$ degrees. Mason [11] has also published the CD spectra of (S)-(+)-1,3-dimethylallene in the vapor phase and in iso-octane solvent at 300°K, and found: a) vapor phase, $\Delta\epsilon \sim -1.1$ ($\lambda = 220$ nm), $\Delta\epsilon \sim -0.75$ ($\lambda = 200$ nm); b) iso-octane solvent, $\Delta\epsilon \sim -0.6$ ($\lambda = 222$ nm), $\Delta\epsilon \sim -1.1$ ($\lambda = 192$ nm). (The optical purities of Mason's samples were not reported [11]). The assignments of absolute configuration to 1,3-dimethylallene have been based on work by Caserio [24] and by Moore *et al.* [10d] in which various optically active allenes were prepared by partial asymmetric hydroboration. In these studies, the R configuration was assigned to the (–) enantiomer of 1,3-dimethylallene. Application of Lowe's rule [10b, 10h] for assignments of absolute configuration to optically active allene systems also leads to the R configuration for the (–) enantiomer of 1,3-dimethylallene. Crabbe, *et al.* [10h] have derived a sector rule relating the position of a substituent on the allene chromophore to the sign of the lowest energy Cotton effect, and they have predicted a positive Cotton effect for the lowest energy transition in the R enantiomer of 1,3-dimethylallene. These workers assumed that the lowest energy transition has $^1A_1 \rightarrow {}^1A_2$ allene parentage (magnetic-dipole allowed) and based their proposed sector rule on the dynamical coupling model of molecular optical activity [25].

If previous assignments of R absolute configuration to the (–) enantiomer of 1,3-dimethylallene are correct, then the calculations performed in the present study are incorrect with respect to the signs predicted for the first two Cotton effects of structure IV. Given the near-degeneracy of the first two transitions, the results shown in Table 2 would predict two resolvable Cotton effects associated with the three lowest energy $\pi \rightarrow \pi^*$ transitions - a low energy weak negative one and a higher energy moderately intense positive one. The reduced rotatory strength calculated for the fourth $\pi \rightarrow \pi^*$ transition (of ${}^1A_1 \rightarrow {}^1A_1$ allene parentage) is 2.43 ($|g| = 0.1348, f = 0.0002$). Assuming that previous assignments of absolute configuration are correct our computed results for the chiroptical properties of the $\pi \rightarrow \pi^*$ transitions in 1,3-dimethylallene appear to be in complete disagreement with experiment. It is possible that vibronic interactions will lead to extensive couplings between the ${}^1\pi\pi^*$ excited states and that the CD features observed in the 240–185 nm region cannot be assigned to transitions with well-defined electronic orbital parentage. In this case, only the sign of the *net* $\pi \rightarrow \pi^*$ rotatory strength will be meaningful. The *net* rotatory strength calculated for the $\pi \rightarrow \pi^*$ transitions is positive as is the circular dichroism observed in the 190–240 nm region for (R)-(–)-1,3-dimethylallene (accepting the assigned absolute configuration). Based on the computed energy differences between the four $\pi \rightarrow \pi^*$ transitions, it seems unlikely that vibronic interactions of the pseudo Jahn-Teller or Herzberg-Teller type could be so strong that observation of negative CD in the 190–240 nm region is precluded. Although only results obtained from the CNDO/S variant of our molecular orbital model have been presented in Table 2 for structure IV, results obtained from INDO-MO-CI calculations of the $\pi \rightarrow \pi^*$ rotatory strengths are qualitatively similar. That is, the *net* $\pi \rightarrow \pi^*$ rotatory strength is computed to be > 0, but the lowest energy Cotton effect is computed to be negative. Additionally, variations in CI (configuration interaction) basis size from 20 to 35 did not alter the qualitative nature of these results (either in the CNDO/S or the INDO approximations).

The source of optical activity in structure VI is a chiral distortion within the cyclopentyl ring. As might be expected, the $\pi \rightarrow \pi^*$ rotatory strengths are computed to be relatively small in this case since the "chiral center" is not attached directly to the allenic chromophore. The $\pi \rightarrow \pi^*$ rotatory strengths computed for structures VII and VIII are also relatively small. In these cases, the "chiral centers" are again one atom removed from the allenic chromophore. Structures IX–XI each have a chiral center attached directly to the allene group and the $\pi \rightarrow \pi^*$ rotatory strengths calculated for these structures are significantly larger than those computed for structures IV–VIII. The results given in Table 2 suggest that the three lowest energy $\pi \rightarrow \pi^*$ transitions in structure VI–VIII should give rise to three resolvable Cotton effects whose signs are (+) (lowest energy transition), (–) (second transition), and (+) (third transition). The *net* $\pi \rightarrow \pi^*$ rotatory strength calculated for each of these structures is > 0. The results obtained for structure IX suggest the appearance of three separate Cotton effects for the three lowest energy $\pi \rightarrow \pi^*$ transitions with signs (+) (lowest energy transition), (–) (second transition, and (+) (third transition). The *net* $\pi \rightarrow \pi^*$ rotatory strength in this case (structure IX) is calculated to be < 0.

Three separate Cotton effects are also predicted for the three lowest energy $\pi \rightarrow \pi^*$ transitions in structures X and XI, but in these cases the sign pattern is predicted to be (–) (lowest energy transition), (+) (second transition), and (–) (third transition). The *net* $\pi \rightarrow \pi^*$ rotatory strengths calculated for structures X and XI are > 0.

The rotatory strengths calculated for the lowest energy transition in structures VI–XI appear to follow a quadrant rule similar to that proposed by Crabbe *et al.* [10h, 26]. In structure VI the two β carbons of the cyclopentyl ring lie in positive sectors of Crabbe's quadrant rule diagram. In structure VII, the two β carbons of the cyclopentyl ring as well as the methyl substituent on the ring lie in positive sectors of the quadrant rule diagram. In structure VIII the methyl substituent lies very slightly in a positive sector (it is nearly on a nodal surface), and again the two β carbon atoms are in positive sectors. In structure IX, the methyl substituent (now on an α ring carbon) lies in a positive sector as do the two β carbon atoms of the cyclopentyl ring. According to the so-called allene quadrant rule, the lowest energy transition in each of the structures VI–IX should have a positive rotatory strength. This is what is calculated with the CNDO/S-MO-CI model employed in the present study (see Table 2).

In structure X, the β ring carbons lie in positive sectors but the α-methyl substituent penetrates a negative sector very close to the chromophoric group. From sector rule considerations, one might expect a negative rotatory strength for the lowest energy $\pi \rightarrow \pi^*$ transition. This is in agreement with our calculated results for structure X. In structure XI, the two β ring carbons and the β-methyl substituent lie in positive sectors, but again the α-methyl substituent is in a negative sector and lies very close to the chromophoric group. The rotatory strength of the lowest energy transition in XI is calculated to be negative.

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References

1. Pellegatti, A.: Theoret. Chim. Acta (Berl.) **8**, 128 (1967)
2. Tai, J. C., Allinger, N. L.: Theoret. Chim. Acta (Berl.) **12**, 261 (1968)
3. DelBene, J., Jaffe, H. H.: J. Chem. Phys. **50**, 1126 (1969)
4. Albinati, A., Maraschini, F., Zocchi, M.: J.C.S. Faraday II 798 (1973)
5. Dillon, P., Underwood, G. R.: J. Am. Chem. Soc. **96**, 779 (1974)
6. Buenker, R. J.; J. Chem. Phys. **48**, 1368 (1968)
7. Schaad, L. J., Burnelle, L. A., Dressler, K. P.: Theoret. Chim. Acta (Berl.) **15**, 91 (1969)

8a. Iverson, A. A., Russell, B. R.: Spectrochim. Acta **28A**, 447 (1972);
8b. Scott, J. D., Russell, B. R.: J. Am. Chem. Soc. **95**, 1429 (1973)
9. Brogli, F., Crandall, J. K., Heilbronner, E., Kloster-Jensen, E., Sojka, S. A.: Electron Spectry. **2**, 455 (1973)
10a. Wynberg, H., Houbiers, J. P. M.: J. Org. Chem. **36**, 834 (1971);
10b. Lowe, G.: Chem. Commun. 411 (1965);
10c. Mason, S. F., Vane, G. W.: Tetrahedron Letters 1593 (1965);
10d. Moore, W. R., Anderson, H. W., Clark, S. D.: J. Am. Chem. Soc. **95**, 835 (1973);
10e. Moore, W. R., Anderson, H. W., Clark, S. D., Ozretich, T. M.: J. Am. Chem. Soc. **93**, 4932 (1971);
10f. Brewster, J. H.: J. Am. Chem. Soc. **81**, 5475 (1959);
10g. Brewster, J. H.: Topics Stereochem. **2**, 33 (1967);
10h. Crabbe, P., Verlarde, E., Anderson, H. W., Clark, S. D., Moore, W. R., Drake, A. F., Mason, S. F.: Chem. Commun. 1261 (1971);
10i. Waddell, W. H., Yudd, A. P., Nakanishi, K.: J. Am. Chem. Soc. **98**, 236 (1976)
11. Mason, S. F. in: Fundamental aspects and recent developments in optical rotatory dispersion and circular dichroism, Ciardelli, F., Salvadori, P., Eds., chapt. 2.1. London: Heyden and Son Ltd. 1973
12. Ruch, E.: Accounts Chem. Res. **5**, 49 (1972)

13a. Richardson, F. S., Caliga, D.: Theoret. Chim. Acta (Berl.) **36**, 49 (1974);
13b. Richardson, F. S., Pitts, W.: Biopolymers **13**, 703 (1974);
13c. Richardosn, F. S., Shillady, D., Bloor, J.: J. Phys. Chem. **75**, 2466 (1971);
13d. Richardson, F. S., Cox, N.: J.C.S. Perkin II 1240 (1975);
13e. Richardson, F. S., Pitts, W.: J.C.S. Perkin II 1276 (1975)
14a. Pao, Y., Santry, D. P.: J. Am. Chem. Soc. **88**, 4157 (1966);
14b. Hug, W., Wagnière, G.: Theoret. Chim. Acta (Berl.) **18**, 57 (1970);
14c. Gould, R., Hoffmann, R.: J. Am. Chem. Soc. **92**, 1813 (1970);
14d. Levin, C. C., Hoffmann, R.: J. Am. Chem. Soc. **94**, 4797 (1972);
14e. Linderberg, J., Michl, J.: J. Am. Chem. Soc. **92**, 2619 (1970);
14f. Rosenfeld, J., Moscowitz, A.: J. Am. Chem. Soc. **94**, 4797 (1972)
15. Pople, J. A., Beveridge, D.: Approximate molecular orbital theory. New York: McGraw-Hill 1970
16. Ellis, R. L., Kuehnlenz, G., Jaffé, H. H.: Theoret. Chim. Acta (Berl.) **26**, 131 (1972)
17. Koopmans, T.: Physica **1**, 104 (1934)
18. Sutcliff, L. H., Walsh, A. D.: J. Chem. Phys. **19**, 1210 (1951); J. Chem. Soc. 899 (1952)
19. Collen, J., Lossing, F. P.: J. Am. Chem. Soc. **79**, 5848 (1957)
20. Parr, R. G., Taylor, R.: J. Chem. Phys. **19**, 497 (1951)
21. Serre, J.: J. Chim. Phys. **53**, 284 (1956)
22. Borden, W. T.: J. Chem. Phys. **45**, 2512 (1966)
23. Snatzke, G., Snatzke, F. in: Fundamental aspects and recent developments in optical rotatory dispersion and circular dichroism, Ciardellie, F., Salvadori, P., Eds., chapt. 3.5. London: Heyden and Son Ltd. 1973
24a. Waters, W. L., Caserio, M. C.: Tetrahedron Letters 5233 (1968);
24b. Waters, W. L., Linn, W. S., Caserio, M. C.: J. Am. Chem. Soc. **90**, 6741 (1968)
25. Höhn, E. G., Weigang, Jr., O. E.: J. Chem. Phys. **48**, 1127 (1968)
26. Crabbe, P.: ORD and CD in chemistry and biochemistry, chapt. II-5. New York: Academic Press 1972

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