

Optical Activity and Absolute Configuration of Chiral Allenes

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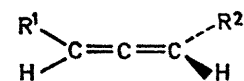
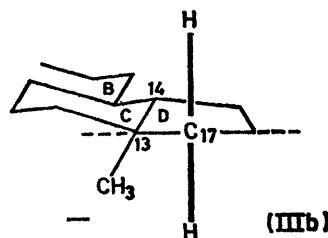
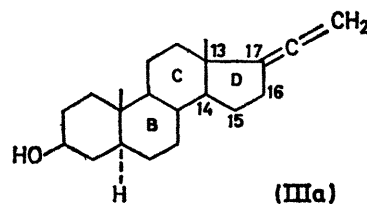
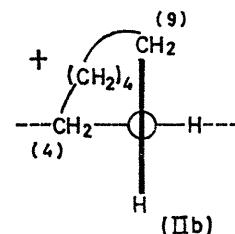
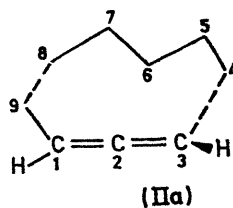
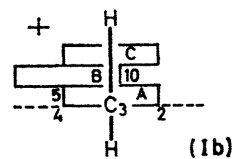
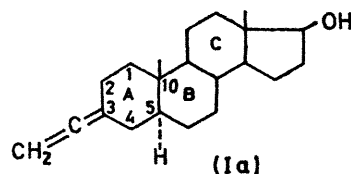
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Summary A sector rule for chiral allenenes is derived, relating the position of a substituent to the sign of the lowest-energy Cotton effect, and a physical basis is proposed for the Lowe-Brewster rule which connects the configuration of a chiral allene with the sign of its D-line rotation.

THE absolute configuration of a chiral allene is related to the sign of its optical rotation at the sodium D-line by the rule proposed by Lowe¹ and developed by Brewster.² The rule states¹ that if the most polarisable substituent (R^1) of a chiral allene is aligned uppermost along a vertical axis, and the more polarisable (R^2) of the two rear substituents in the horizontal plane is disposed on the right-hand side, a clockwise screw pattern of polarisability obtains, and the isomer is dextrorotatory (Figure 1a). Conversely, if the more polarisable of the two rear substituents in the horizontal plane is disposed to the left, the allene is laevorotatory. From the c.d. spectra of chiral allenenes with an established configuration, (Ia),³ (IIa),⁴ (IIIa),³ (IV)⁵ (Figure 2, Table) and the static⁶ and the dynamic⁷ coupling theory of optical activity we report a quasi-quadrant rule relating the stereochemical configuration of an allene to the sign of the Cotton effect associated with the lowest-energy absorption band of the allene chromophore (220–250 nm) and propose an electronic basis for the rule of Lowe¹ and Brewster.²

The allene chromophore has four singly-excited $\pi\pi^*$ configurations, resulting from the one-electron promotions, $\pi x \rightarrow \pi y^*$, $\pi y \rightarrow \pi x^*$, $\pi x \rightarrow \pi x^*$, and $\pi y \rightarrow \pi y^*$, where the xz and yz planes are, respectively, those of the set of bonds to the 1- and to the 3-carbon atom. The antisymmetric combination of the first two configurations gives an excited state to which an electronic transition from the ground state is magnetic-dipole allowed with z -polarisation, $A_1 \rightarrow A_2$ in the group D_{2d} of the allene chromophore. The analogous combination of the latter two configurations give an excited state to which a transition from the ground state,



- (IV) $R^1 = R^2 = \text{Me}$
 (V) $R^1 = R^2 = \text{Et}$
 (VI) $R^1 = R^2 = \text{Bu}^t$
 (VII) $R^1 = \text{CH}_3[\text{CH}_2]_{10}$
 $R^2 = [\text{CH}_2]_3 \text{CO}_2\text{H}$

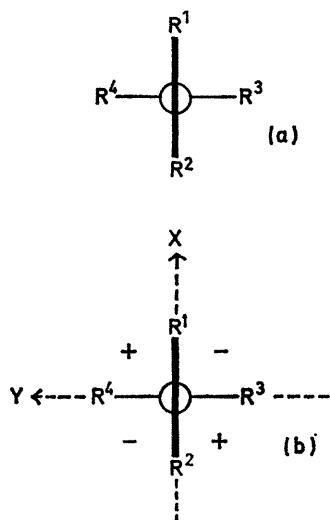


FIGURE 1. (a) The rule of Lowe¹ and Brewster.² Dextrorotation at the sodium D-line is associated with a clockwise screw pattern of polarisability, given by the group polarisability-order, $R^1 > R^2$ and $R^3 > R^4$ and laevorotation with the order $R^1 > R^2$ but $R^3 < R^4$. (b) The XY quadrant rule for chiral allenes connecting the position of a substituent with the sign of the lowest-energy Cotton effect.

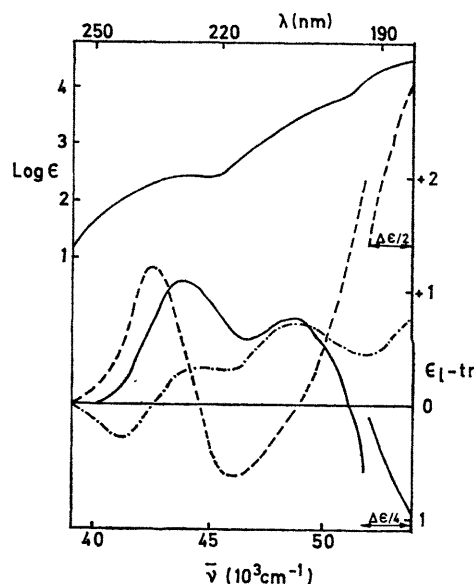


FIGURE 2. The absorption spectrum (upper curve) and c.d. spectra (lower curves) of (I) (—), (II) (---), and (III) (-·-·-·-·-·).

$A_1 \rightarrow B_2$, is electric-dipole allowed with z -polarisation. A transition to the state formed by the symmetric combination of the former two configurations, B_1 , or of the latter two, A_1 , has only an electric quadrupole moment.

Theoretical treatments of the electronic spectrum of allene⁸⁻¹⁴ generally place the excited $\pi\pi^*$ states in the energy-order, $B_2 > B_1 > A_2$, the position of the A_1 state being variable. The lowest-energy transition is expected to be magnetic-dipole allowed, $A_1 \rightarrow A_2$, in accord¹⁵ with the observation (Figure 2) that the lowest-energy c.d. band of chiral allenes (220–250 nm) has a dissymmetry factor, $g = \Delta\epsilon/\epsilon$, which is relatively large (g ca. 0.01). The high intensity of the absorption of alkyl-substituted allenes^{16,17} near 180 nm (Figure 2) suggests that the electric-dipole $A_1 \rightarrow B_2$ transition lies in this region.

(a) Sector rules. A regional rule connecting the position of substituents with the sign of the lowest-energy c.d. band of a chiral allene is provided by either a static⁶ or a dynamic⁷

coupling mechanism. If the static Coulombic field of a substituent mixes the magnetic-dipole $A_1 \rightarrow A_2$ transition with a z -polarised electric-dipole excitation of the allene chromophore, notably $A_1 \rightarrow B_2$, which is close in energy, to produce optical activity the field has a pseudoscalar component with XY symmetry.⁶ The resultant quadrant rule has the signs depicted (Figure 1b) for the c.d. due to the $A_1 \rightarrow A_2$ transition if the perturbing field arises from positive charges, e.g. the incompletely-screened nuclei of the substituent atoms.

In the dynamic case⁷ the magnetic moment of the $A_1 \rightarrow A_2$ allene transition couples with a transient electric dipole induced in the substituent by the radiation field to produce optical activity. The coupling is mediated by the Coulombic potential between the induced electric dipole of the substituent and the leading electric multipole of the $A_1 \rightarrow A_2$ allene transition, the latter being an xyz octupole. If the polarisability of the substituent is isotropic, or if the

TABLE

The specific rotation, $[\alpha]_D$ (degrees), the wavelength, λ (nm), and c.d. maxima, $\Delta\epsilon = (\epsilon_l - \epsilon_r)$, of chiral allenes in a paraffinic solvent. The $\Delta\epsilon$ values are not corrected for optical impurity.

Allene	$[\alpha]_D$	$A_1 \rightarrow A_2$		$A_1 \rightarrow B_1, A_1$		$A_1 \rightarrow B_2$	
		λ	$\Delta\epsilon$	λ	$\Delta\epsilon$	λ	$\Delta\epsilon$
(I) ^{a,b}	+16	229	+1.14	205	+0.79	<185	<-4
(II) ^{c,d}	+126.8	236	+1.22	218	-0.63	<185	>+6
(III) ^{a,b}	+32	243	-0.28	225	+0.33	<185	>+0.7
(IV) ^{c,e}	-24.2	223	+0.63	206	+0.74	<185	-ve
(V) ^{c,f}	-54.4	222	+0.73	192	+1.7	<185	-ve
(VI) ^{c,g}	-75.7	219	+1.01			<185	-ve

^a Iso-octane solution. ^b Optical purity 100%. ^c Pentane solution. ^d Optical purity 90.5%. ^e Optical purity 56% relative to the largest value, $[\alpha]_D - 43.8$, for (IV) reported,^{5b} or 12% relative to $[M]_D - 132$ (EtOH) for laballic acid²² (VII). ^f Optical purity 40% relative to $[M]_D - 132$ (EtOH) for (VII).²² ^g Optical purity 100% relative to the largest value, $[\alpha]_{578} - 72.8$, for (VI) reported,¹⁹ or 87% relative to $[M]_D - 132$ (EtOH) for (VII).²²

contribution of the mean polarisability is dominant, the regional rule is given by the geometric factor, $XY(7Z^2 - R^2)$ for the potential between the z -component of a dipole and the xyz -component of an octupole.

Both the simple XY quadrant rule (Figure 1b) and the bifurcated-quadrant rule, $XY(7Z^2 - R^2)$ (Figure 3), are

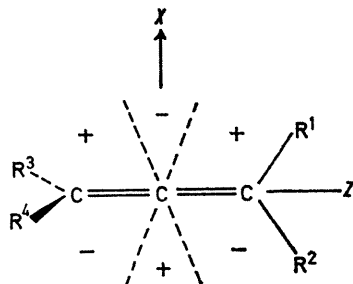


FIGURE 3. The bifurcated quadrant rule $XY(7Z^2 - R^2)$ for chiral allenes. The signs refer to the lowest-energy Cotton effect associated with groups substituted into the $+Y$ hemisphere. The signs are reversed for groups substituted into the $-Y$ hemisphere.

consistent with the c.d. data for chiral allenes in the 220–250 nm region (Table, Figure 2), e.g. (Ib), (IIb), and (IIIb). However, the dynamic mechanism appears the more probable on three grounds. Firstly, the c.d. band of the 3-steriodal allene³ (I) and of (*R*)-(+)-1,2-cyclononadiene⁴ (II) near 230 nm are comparable in magnitude (Figure 2, Table), whereas the XY rule (Figure 1b) suggests that (II) should have a substantially larger c.d. than (I) in this region. The comparability is consistent with the $XY(7Z^2 - R^2)$ rule (Figure 3) since the C(6)–C(7) bond of (II) lies in the region where $(7Z^2 - R^2)$ is negative and the C(4)–C(5) and C(8)–C(9) bonds in the region where that function is positive.

Secondly, the static coupling mechanism⁶ provides no explanation for the observed optical activity in the 220–250 nm $A_1 \rightarrow A_2$ region of allenes with cylindrically symmetrical 1- and 3-substituents, e.g. (IV) (Table). According to the dynamic mechanism⁷ this optical activity originates from the anisotropy of the polarisability of the methyl substituents in (IV). Finally, the static mechanism⁶ requires that the mixed transitions, $A_1 \rightarrow A_2$ and $A_1 \rightarrow B_2$, have rotational strengths of opposite sign and equal magnitude, whereas the dynamic mechanism⁷ implies no such necessary connection. The c.d. bands due to these two transitions are of opposite sign for the allenes (I), (III), (IV), (V), and (VI), but they have the same sign in the case of (II) (Table, Figure 2).

(b) The Lowe–Brewster rule. Although accessible only to 185 nm the c.d. due to the $A_1 \rightarrow B_2$ allene transition is large (Figure 2, Table) and Drude plots of the o.r.d. indicate that generally it makes the major contribution to the optical rotation at the sodium D-line. The rotational strength of the $A_1 \rightarrow B_2$ allene transition, according to the dynamic coupling mechanism,⁷ depends upon the steric disposition of the substituents and the anisotropy of their polarisabilities, an isotropic group making no contribution.

Whilst the C–H bond has a virtually isotropic polarisability, that of the C–C bond is markedly anisotropic¹⁸ ($\alpha_{11} = 1.88$ and $\alpha_{12} = 0.02 \text{ \AA}^3$), so that the major component of a dipole induced in a C–C bond lies along the bond direction. For (*R*)-(-)-1,3-dimethylallene⁵ (IV), and other (*R*)-(-)-substituted allenes,^{5,19–23} the particular phase-relationship between the induced dipoles of the two C–C bonds from the 1- and 3-carbon atom of the allene chromophore, due to Coulombic interaction with the $A_1 \rightarrow B_2$ transition dipole (Figure 4a), gives that transition a negative rotational

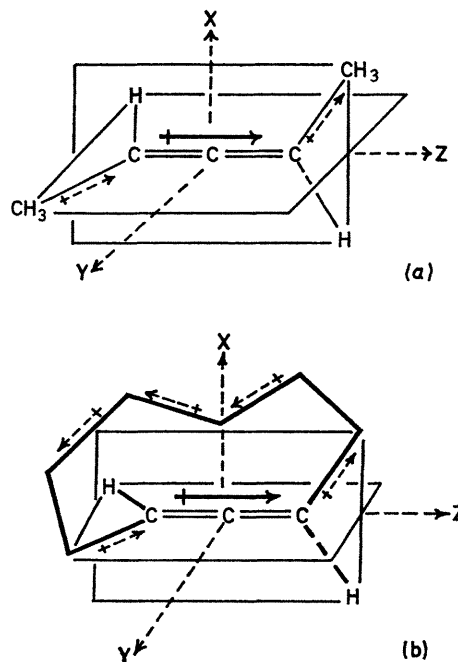


FIGURE 4. The phase-relationship between the electric dipole moment of the $A_1 \rightarrow B_2$ transition (full arrow) and the induced moments along the C–C bonds of (a) (*R*)-(-)-1,3-dimethylallene (IV) and (b) (*R*)-(+)-1,2-cyclononadiene (II).

strength. The D-line rotation is consequently negative, in accord with the rule of Lowe¹ and Brewster.²

(*R*)-(+)-1,2-Cyclononadiene⁴ (II) does not conform to the Lowe–Brewster rule because the phase-relationships between the induced dipoles along each C–C bond are now such that the $A_1 \rightarrow B_2$ allene transition has an overall positive rotational strength (Figure 4b). Whereas the induced dipoles along C(3)–C(4) and C(1)–C(9) of (II) couple to give a negative rotational strength, as in (IV), those along C(5)–C(6)–C(7)–C(8) couple with the $A_1 \rightarrow B_2$ transition dipole along C(1)–C(2)–C(3) to generate a substantially larger positive rotational strength (Figure 4b). A similar conclusion emerges from the coupling schemes for the induced C–C dipoles and the $A_1 \rightarrow B_2$ transition moment in conformations of (II) other than the one depicted (Figure 4b)

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