

Chirality Rule for Substituted Oxiranes

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The circular dichroism sign of the 3s Rydberg transition of oxiranes is correlated with the absolute configuration of the molecule.

Correlations between the absolute configuration and the circular dichroism (c.d.) sign of certain electronic transitions have been established for many chromophores.¹⁻³ Various sector rules have also been formulated depending on the symmetry of the chromophore and the nature of the electronic transition. In parallel, extensive theoretical work⁴⁻⁷ was carried out to substantiate and explain these empirical rules. The extension of circular dichroism measurements into the vacuum-u.v. region enables one to probe excited electronic states and chromophores which have not been studied so far. In a recent study we reported the vacuum-u.v. optical absorption and c.d. of (-)-(*S*)-methyloxirane.⁸ The spectra were interpreted and assigned on the basis of *ab initio* self-consistent field calculations. The results⁸ show that the first electronic transition of the oxirane moiety is the $n(\text{O}) \rightarrow 3s$ Rydberg transition, where $n(\text{O})$ represents a non-bonding orbital centred on the oxygen atom. The anisotropy factor $g = \Delta\epsilon/\epsilon$ for this transition was the largest observed for both (-)-*S*-methyloxirane and (-)-(2*S*,3*S*)-2,3-dimethyloxirane.⁸ Basch *et al.*⁹ have shown that the absorption

spectrum of oxirane down to *ca.* 1400 Å is dominated by Rydberg transitions.¹⁰ Since the 3s Rydberg band centred at *ca.* 1730 Å is well separated from higher electronic transitions and is well identified it can serve as a probe for the absolute configuration of chiral oxiranes. In this communication we report c.d. and absorption studies of five monosubstituted oxiranes. Their absolute configuration and enantiomeric purities were determined by gas chromatographic methods which were reported elsewhere.¹¹

The c.d. and absorption measurements were carried out in the gas phase on a vacuum-u.v.-c.d. instrument which has been described previously.^{12,8} Figure 1 presents the c.d. and absorption spectra of (*R*)-[(*S*)-1-methylpropyl]oxirane. Similar spectra were observed for the other molecules studied. The spectra are assigned as consisting of 3s, 3p, and 3d Rydberg transitions. The strong negative c.d. band centred at

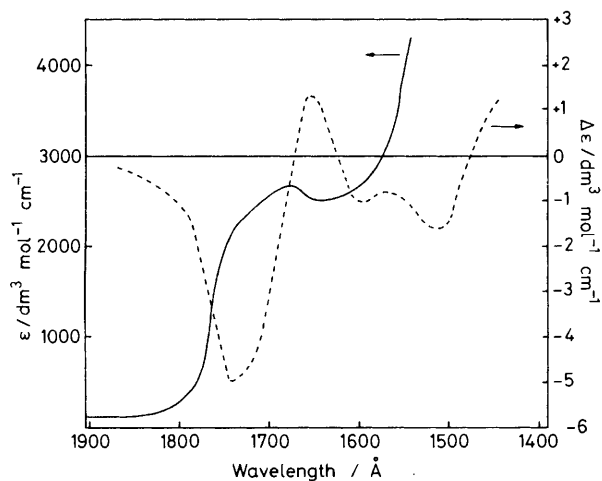


Figure 1. Absorption (—) and c.d. (---) spectra of (*R*)-[(*S*)-1-methylpropyl]oxirane. Spectral resolution 16 Å.

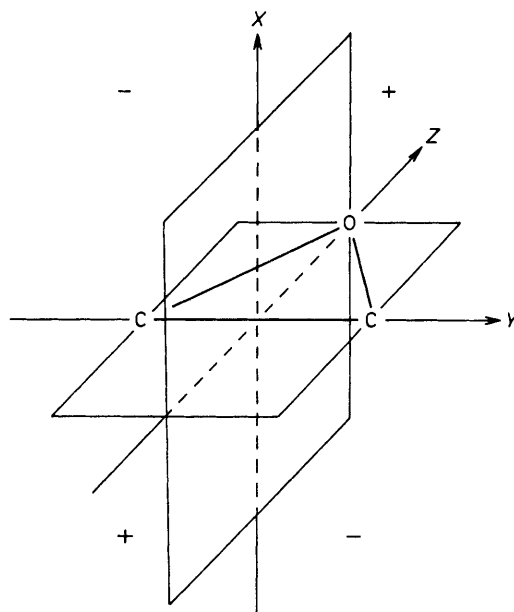


Figure 2. The planes of symmetry forming the quadrants.

Table 1. C.d. and absorption data of oxiranes.

Oxirane	e.e. (%)	ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$\Delta\epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	$\lambda(\Delta\epsilon_{\text{max}})$ (Å)	$\Delta\epsilon/\epsilon$
(<i>S</i>)-Methyloxirane (ref. 11a)	96.4	2000	+ 15	1730	7.5×10^{-3}
(<i>S</i>)-Ethyloxirane (ref. 11b)	> 99.5	^a	+	1745	
(<i>R</i>)-Butyloxirane (ref. 11c)	> 99.5	1000	- 2.7	1725	2.7×10^{-3}
(<i>R</i>)-Isopropyloxirane (ref. 11d)	97.2	1960	- 4.8	1725	2.4×10^{-3}
(<i>R</i>)-[(<i>S</i>)-1-Methylpropyl]-oxirane	> 99.5	2300	- 5	1745	2.2×10^{-3}
(<i>R</i>)-Isobutyloxirane (ref. 11e)		1300	- 5.5	1737	4.2×10^{-3}

^a The (*S*)-ethyloxirane was contaminated by triethylamine leading to the deterioration of the sample and therefore exact results were not obtained, however, a positive c.d. band was observed at 1745 Å.

ca. 1745 Å is assigned as the $n(\text{O}) \rightarrow 3s$ Rydberg transition. It shows the largest anisotropy factor which supports its assignment. The negative c.d. sign is related to the R configuration of the oxirane, and as will be explained later we expect an R enantiomer to yield a negative c.d. signal for the $3s$ transition, but the S enantiomer to show a positive band. In Table 1 we summarize the results observed for the sign of the $n(\text{O}) \rightarrow 3s$ Rydberg transitions in the molecules studied. These results lead to the quadrant rule presented in Figure 2. The proposed rule also holds for *trans*-2,3-disubstituted oxiranes. The measurements for (-)-(2*S*,3*S*)-2,3-dimethyloxirane have been reported⁸ and revealed a positive signal for the $3s$ Rydberg peak at ca. 1750 Å. A similar result was obtained for (-)-(2*S*,3*S*)-2-ethyl-3-methyloxirane where a positive c.d. signal with a large anisotropy factor was found at 1750 Å. A similar quadrant rule for chiral enantiomers was proposed by Schurig *et al.* based on complexation gas chromatography.^{11a}

Applying the static field mechanism⁴ to the oxirane chromophore would indeed yield a quadrant rule. This method requires a static perturbation of the zero-order electronic states of the oxirane chromophore. This perturbation is caused by the ground-state charge distribution of the substituent. In the oxirane chromophore the $n(\text{O}) \rightarrow 3s$ is an electric dipole allowed transition polarized out of plane (y axis according to ref. 8). This excited Rydberg state will have a B_2 symmetry. The state contributing the magnetic moment will therefore have a B_1 symmetry. Using Schellman's formalism for 'electrically allowed rotational strength,' the matrix element of the perturbation is $\langle n(\text{O}) \rightarrow 3s (B_2) | V | n(\text{O}) \rightarrow 3d (B_1) \rangle$. This connects the two zero-order excitations of the oxirane chromophore. The external perturbation represented by V must transform like the A_2 representation in the C_{2v} symmetry group. The simplest function for the A_2 representation is ZX which determines the quadrant rule for the oxirane chromophore. This corresponds to XY for the co-ordinate system used in our previous work and also in Figure 2. If a

positive charge (common organic substituents bear an effective positive charge) is placed in a $+XY$ region (S -enantiomer), a positive c.d. signal is predicted for the $n(\text{O}) \rightarrow 3s$ transition, whereas if a positive charge is placed in a $-XY$ region (R -enantiomer), a negative sign will result. Since many other organic substituents absorb in this energy region the rule is applied to alkyl substituents only.

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