Dynamic-coupling Approach to the Optical Activity of the 260 nm Transition of Chiral Thiirans

By GIOVANNI GOTTARELLI and BRUNO SAMORÌ
(*Istituto di Chimica degli Intermedi, Viale Risorgimento, 4 Bologna, Italy*)
and GIOVANNI TORRE
(*Istituto di Chimica Organica, Via Campi 135, Modena, Italy*)

Summary The 260 nm optically active transition of chiral thiirans (episulphides) is rationalized in terms of the dynamic coupling mechanism; the transition charge distribution on the carbon atoms, derived mainly from two-centre overlap integrals between sulphur and carbon, plays an important role.

WE report a simple interpretation of the optical activity of the 260 nm $n \rightarrow \sigma^*$ transition of chiral thiirans (episulphides) in terms of the dynamic coupling theory.[1a,b]

The $n \rightarrow \sigma^*$ transition (where n is the $3p_x$ sulphur non-bonding orbital and σ^* an antibonding orbital involving carbon $2s$ and $2p_z$, and sulphur $3p_z$ and $3d_{yz}$ AOs) in the parent thiiran, $CH_2\cdot CH_2\cdot S$, is associated with a magnetic moment directed along the two-fold symmetry axis [2a,b] (see Figure). We have performed MO calculations on the multipolar charge distribution [1a] for this transition.

Table

	Rotational strengths	
	$R \times 10^{40}$ (exp.) (c.s.g. units)	$R \times 10^{40}$ (calc.[d]) (c.g.s. units)
(+)-*R*-Methylthiiran ..	−1[a]	−1·27
(+)-*R*-t-Butylthiiran ..	+0·6[b]	+0·15
(−)-*R*-Phenylthiiran ..	−4[c]	−0·95

[a] Ref. 2a. [b] Cyclohexane solvent. [c] Ref. 5. [d] Using a charge–dipole interaction potential and a magnetic moment $m_z = -0{\cdot}517$ a.u.[2b] The electric dipole transition moments were taken from polarizability data for the alkyl groups,[6] and from experimental spectra for the phenyl group.[7]

As expected, the charge of the monopoles located near the sulphur atom ($\pm 0{\cdot}658 \times 10^{-10}$ e.s.u.), 'front monopoles' (arising mainly from one-centre integrals), are larger than those of the monopoles lying near the carbon atoms, 'rear monopoles,' ($\pm 0{\cdot}081 \times 10^{-10}$ e.s.u.) (arising mainly from two-centre integrals), which are by no means negligible, however. The monopoles derived from the overlap of the $3p_z$ orbital of the sulphur with the rear lobe of the *sp* hybrid of the carbons were extremely small and were neglected. The transition monopoles induce in a polarizable group, dissymmetrically positioned, a dipole in a sense that is 'attractive.' Such a dipole provides components along the *z* direction which are parallel or antiparallel to the magnetic moment of the $n \rightarrow \sigma^*$ transition, giving a non-vanishing scalar product and hence optical activity.[3]

The transition charge distribution in the Figure gives the following approximate picture:

In the first region at the back of plane *a* where the contributions to the optical activity from the back set of monopoles is dominant, the perturbing group is polarized in such a way as to give an antiparallel component to the electric dipole moment. The signs of the optical activity expected are those of (I); this holds at least for groups very near to the thiiran ring. The front monopoles give opposite polarization, and hence opposite contributions to the optical activity, but, owing to their larger distance, their contribution is smaller than that from the rear ones. The optical activity is expected to be small as it is a sum of terms of opposite signs.

In the second region, between planes *a* and *b*, where a perturber is polarized in the same direction by both the front and the rear monopoles, the perturber gives a parallel component to the electric dipole moment; the front and the rear monopoles give contributions of the same sign. The optical activity observed should have the signs in (II). The effect of groups in this region should be higher than in region (I).

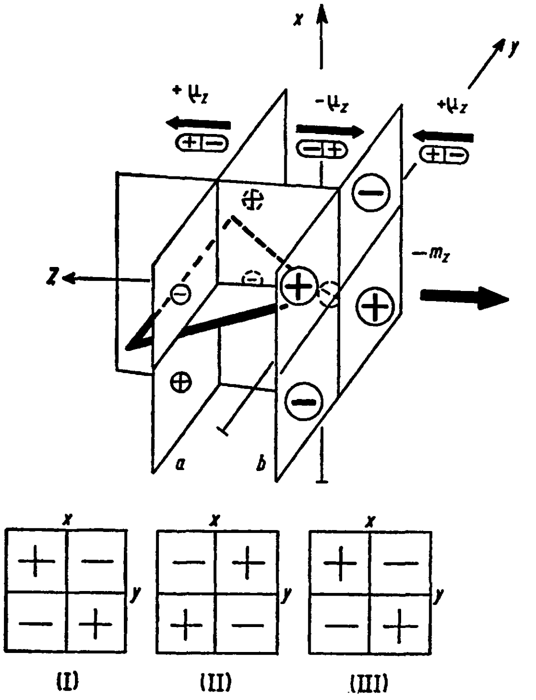

Figure. The interaction of the multipolar transition charge distribution of the $n \rightarrow \sigma^*$ transition with the dipole μ_z induced in a polarizable perturber, and the expected contributions to the optical activity.

Finally, in the third region limited by plane *b* a perturber feels mainly the effect of the front monopoles; the optical activity observed should have the signs in (III).

Experimental data for steroidal episulphides reported by Kuriyama *et al.*[4] fit our qualitative predictions well. These examples refer only to regions (I) and (II), and we have no examples of thiirans having perturbing groups in region (III).

The signs of the rotational strengths are different in (+)-*R*-methylthiiran and (+)-*R*-t-butylthiiran (see Table). Our calculations[1a,b] show that the reversal of sign in the t-butyl compound is due mainly to the contribution from the methyl group in region (II) in the staggered conformation. The optical activity of (−)-*R*-phenylthiiran[5] is also satisfactorily calculated.

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