On the Optical Activity of *trans*-Cyclo-octene

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Summary A critical estimate of the twisted *trans*-cyclo-octene model for optical activity has been made: it is suggested that a dissymmetrically-perturbed symmetric chromophore may provide a more satisfactory basis for calculation.

SEVERAL recent discussions[1–3] of the assignment of the lowest energy singlet–singlet transitions of chiral olefins have used the twisted ethylene chromophore as a basis for calculation of sign and magnitude of rotational strengths and for the allocation of transition energies. We suggest that there exists sufficient evidence to provide an alternative model for these assignments and calculations.

TABLE 1. *Calculated and observed singlet–singlet transition energies* (ev) *for ethylene and* trans-*cyclo-octene*[a]

	Ethylene		*trans*-Cyclo-octene		
Transition	Calculated	Experimental	Calculated $\delta^b = 0°$	 $\delta^b = +15°$	Experimental
$\pi_x \rightarrow \sigma^*$	7·55	7·1—7·6	—	—	5·95 (?)
$\pi_x \rightarrow \pi_x^*$	7·81	7·6	6·31	5·84	6·32
$\pi_x \rightarrow \pi_y^*$	8·31	*ca.* 7·5 (?)	6·51	6·65	5·95 (?)

[a] See ref. 1.
[b] δ defined as in ref. 1.

TABLE 2. *Computed singlet excitation energies and rotational strengths from twisted* trans-*cyclo-octene* ($\delta^b = +10°$)

Transition	E_{calc}(ev)	E_{obs} (ev)	R_{calc}(10^{-40} cm.g.sec.)	R_{obs}(10^{-40} cm.g.sec.)
$\pi_x \rightarrow \sigma^*$	—	5·95 (?)	$+ 0·297 \rightarrow + 4·33$	Not observed
$\pi_x \rightarrow \pi_x^*$	6·06 (8·92)[a]	6·32	+71·39 (−262·868)	−130 (at 6·32 ev)
$\pi_x \rightarrow \pi_y^*$	6·62	5·95 (?)	−131·39	
$\sigma \rightarrow \pi_x^*$	(9·89)[a]	—	(+328·496)	

[a] Values from ref. 2 are in parenthesis; all other data are from ref. 1.
[b] defined as in ref. 1.

The three principal singlet–singlet transitions† of planar ethylene whose calculated energies[1–3] lie in the order $\pi_x \rightarrow \pi_y^* > \pi_x \rightarrow \pi_x^* > \pi_x \rightarrow \sigma^*$ are as shown in Table 1.‡ However, while there is uniform agreement on the allocation of the $\pi_x \rightarrow \pi_x^*$ transition to the intense absorption of ethylene at 7·6 ev (shifted to *ca.* 6·32 ev in substituted alkenes: ϵ *ca.* 5000—10,000) and substantial agreement on the allocation of the lowest energy $\pi_x \rightarrow \sigma^*$ transition to the moderately intense absorption ($\epsilon < 1000$) at 7·1—7·6 ev in ethylene (5·95 ev in *trans*-cyclo-octene), the most recent calculations[1] predict a higher energy (8·31 ev for ethylene; 6·5—6·6 ev for *trans*-cyclo-octene) for the $\pi_x \rightarrow \pi_y^*$ absorption than is observed (7·5 and 5·95 ev respectively). Since the calculations on the rotational strength of (*R*)-*trans*-cyclo-octene are based on contributions from the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transitions it is surprising to find (Table 2) that the $\pi_x \rightarrow \pi_y^*$ absorption which carries 65% of the (negative) rotational strength ($R_{calc} = -131·39 \times 10^{-40}$ cm.g.sec. units) should appear as a shoulder at 5·95 ev (calc. 6·6 ev) whereas the $\pi_x \rightarrow \pi_x^*$ band is assigned $R + 71·39 \times 10^{-40}$ cm.g.sec. at 6·325 ev (calc. 6·32 ev for the planar olefins). Inspection of the c.d. curves of many other chiral olefins show that their maximal absorption appears near 6·3 ev.[4] The calculated difference between the $\pi_x \rightarrow \pi_x^*$ and $\pi_x \rightarrow \pi_y^*$ transition (10—12 nm) suggests that such a sign inversion could be measured. In fact quite a smooth Gaussian c.d. curve is observed[4a] for *trans*-cyclo-octene and many other chiral olefins.[4b]

Frequently the beginning of sign inversion corresponding to a higher energy transition (*ca.* 6·9 ev $\sigma \rightarrow \pi_x^*$?) can be detected. Tables 1 and 2 show that the calculated rotational strengths for twisted *trans*-cyclo-octene ($\delta = +10°$) not only require reassessment of the placing of the $\pi_x \rightarrow \pi_y^*$ transition but significantly that the 'planar' cyclo-octene model gives the best calculated fit for energy (calc. 6·31 ev; obs. 6·32 ev).

We therefore suggest that a dissymmetrically-perturbed planar ethylene model offers an attractive alternative for future calculations and that it is the $\pi_x \rightarrow \pi_x^*$ transition in such a model which reflects the absolute configuration in terms of the substituent or methylene population of octants formed by the intersecting *xy*, *yz*, and *xz* planes of ethylene. In support of this suggestion we summarize several pieces of evidence.

(1) The simpler SCF calculation of Robin *et al.*[2] (with or without CI) gives the correct sign of the Cotton Effect of *trans*-cyclo-octene using the $\pi_x \rightarrow \pi_x^*$ transition even though the energies are high.

(2) The Octant Rule[4,5] relates the chirality of some 40

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† The ethylene axes are defined as *z* for the C–C sigma axis, *y* in the plane of the C–H bonds perpendicular to *z*, and the *x* axis perpendicular to the *yz* plane passing through the centre of the double bond.

‡ *Added in proof:* An excellent review of this problem has recently appeared. A. J. Merer and R. S. Mulliken, *Chem. Rev.*, 1969, **69**, 639.

diverse olefins (including the *trans*-cycloalkenes) to their $\pi_x \rightarrow \pi_x^*$ c.d. maxima assuming that the 6·3 ev c.d. and u.v. maxima correspond to this principal transition.

(3) If the ground-state twist of *trans*-cyclo-octene were dominant in determining the chirality of this olefin why should *trans*-cyclononene[6] have a rotational strength of the same order of magnitude $[\alpha]_D - 147°$ ($t^0_{1/2} = 4$ min.)?

(4) *trans*-Cyclo-octene was originally selected for the twisted ground state model on the premise of its exceptionally high rotation at the D-line. However, the $[\phi]_D$ of this olefin is unexceptional and the literature[4] indicates similar $[\theta]$ and $[\phi]_D$ values for a random selection of chiral olefins. It was earlier stated[7] that the methylene-chain contribution would have to exceed $[\alpha]_D + 460°$ for the twisted model to be incorrect. Since it has more recently been shown by chemical[8] and spectroscopic methods[5,9] that this earliest calculation gave the incorrect absolute configuration we must conclude that the methylene-chain octant projection is the absolute configurational determinant for the olefinic chromophore and that *trans*-cyclo-octene should not be treated as a special case for either spectroscopic or rotational strength calculations.

(5) The principal evidence for allocation of the 10° twist to *trans*-cyclo-octene appears to come from the angle observed in the Dreiding model. However, Allinger[10] has pointed out that twisting alone is not sufficient to account for the observed dipole moment, and therefore some bending must occur. It appears from a comparison of the spectra of *trans*-cyclo-octene with those of some severely twisted olefins[11] that the ground-state twist has little effect upon the position of the u.v. maximum of the former in the $\pi_x \rightarrow \pi_x^*$ region (< 0·1 ev).

We feel that the data summarized above are sufficient to suggest that the alternative (dissymmetrically-perturbed chromophore) model be examined side by side with the twisted olefin calculations as a basis for chirality assignments and transition energy allocations for chiral olefins.

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[11] See for example H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, 1962.