Role of Torsion in the Chirality of Twisted Olefins

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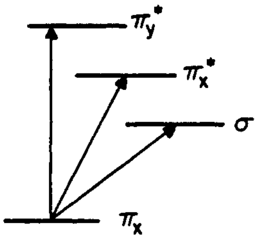
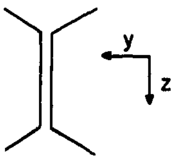
Abstract: Calculations of the rotatory strength of *trans*-cyclooctene and model chiral geometries of other substituted ethylenes show the presence of two effects in determining the sign of the Cotton effect. The dominant contribution is that of torsion in the olefin chromophore. The second effect, apparently of opposite sign, is due to the perturbation of chiral substituents.

The chiral olefin *trans*-cyclooctene has received more than passing attention in recent years owing to interest in the source of its optical activity.[1] Prior to its resolution by Cope and Mehta[2] in 1964, the chiroptical properties of this highly strained cycloolefin were investigated theoretically by Moscowitz and Mislow[1a] using an inherently dissymmetric twisted ethylene chromophore as a model. On the basis of this model they predicted the sign of the Cotton effect for the $\pi \rightarrow \pi^*$ transition, a prediction which subsequently proved incorrect. Later calculations by Moscowitz, *et al.*,[1c] using the same model successfully accounted for the sign of the rotatory strength by including a dominant contribution from a higher lying transition of opposite sign. Independently, Robin and coworkers[1b] reproduced the sign of the Cotton effect using only the $\pi \rightarrow \pi^*$ transition. Their *ab initio* calculations, which included configuration interaction, were also based on a twisted ethylene prototype.

The electronic absorption spectrum of ethylene and its alkyl-substituted derivatives has been extensively reviewed.[1c,3,4b] There is general agreement on the assignment of the three lowest singlet transitions in ethylene, and these are indicated schematically below.

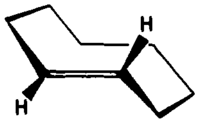




At longest wavelength is a weak intensity $\pi_x \rightarrow \sigma^*$ Rydberg-like transition, appearing as a shoulder on the tail of the much more intense $\pi_x \rightarrow \pi_x^*$ transition which follows at shorter wavelength. Still further blue shifted is the electric dipole forbidden, but magnetic dipole and electric quadrupole allowed, $\pi_x \rightarrow \pi_y^*$ transition. The $\pi_x \rightarrow \sigma^*$ transition has been shown[1c] to contribute negligibly to the rotatory strength of chiral olefins.

Recently Scott and Wrixon[1d,4a-d] have proposed an olefin octant rule which successfully correlates the rotatory strengths of nearly a hundred chiral olefins including *trans*-cyclooctene and twistene.[5] Theoretically, rules such as this one follow from the symmetry properties of an electrostatic potential which perturbs an inherently symmetric chromophore. The perturbing potential is produced by the neighboring chiral substituents. The nature of the symmetry rule depends critically on the transition and the local symmetry of the absorbing chromophore. The ketone octant rule, for example, is based on the carbonyl $n \rightarrow \pi^*$ transition; the olefin octant rule (with octant contributions of opposite sign to those in the ketone case) is based on the $\pi_x \rightarrow \pi_x^*$ transition.

We have calculated rotatory strengths for *trans*-cyclooctene and a number of simpler prototypes using both extended Hückel (EH)[6] and CNDO/2[7] wave functions. Two *trans*-cyclooctene conformations, **1** and **2**, were considered. The geometrical parameters for **1** were taken from the work of Buemi, Favini, and Zuccarello,[8] who obtained them by minimizing the total energy about this conformation in a classical Westheimer–Wiberg–Hendrickson-type force field calculation. A 17° torsion in the double bond was required to reach the energy minimum. While no final experimental structure determination of *trans*-cyclooctene is available,[9] the crystal structures of a copper complex of the olefin indicate significant torsion.[10] The geometry used for **2** was somewhat arbitrary as no attempt was



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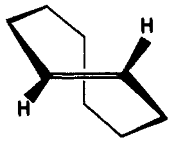
chair form



2

twist form

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[1] (a) A. Moscowitz and K. Mislow, *J. Amer. Chem. Soc.*, **84**, 4605 (1962); (b) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968); (c) M. Yaris, A. Moscowitz, and R. S. Berry, *ibid.*, **49**, 3150 (1968); (d) A. I. Scott and A. D. Wrixon, *J. Chem. Soc. D*, 43 (1970); (e) R. D. Bach, *J. Chem. Phys.*, **52**, 6423 (1970); (f) O. Schnepp, E. F. Pearson, and E. Sharman, *ibid.*, **52**, 6424 (1970).

[2] A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964).

[3] A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969), and references therein.

[4] (a) A. I. Scott and A. D. Wrixon, *J. Chem. Soc. D*, 1182 (1969); (b) *Tetrahedron*, **26**, 3695 (1970); (c) M. Fétizon and I. Hanna, *J. Chem. Soc. D*, 462 (1970); (d) M. Fétizon, I. Hanna, A. I. Scott, A. D. Wrixon, and T. K. Devon, *ibid.*, 545 (1971).

[5] M. Tichý and J. Sicher, *Tetrahedron Lett.*, 4609 (1969).

[6] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963), and subsequent papers.

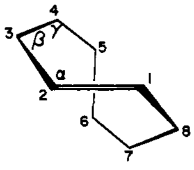
[7] J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965), and subsequent papers. The CNDO/2 wave functions were renormalized including overlap, and rotatory strengths were calculated with two-center terms included.

[8] G. Buemi, G. Favini, and F. Zuccarello, *J. Mol. Struct.*, **5**, 101 (1970).

[9] An electron diffraction study of *trans*-cyclooctene is in progress by G. M. Gavin, Haverford.

[10] P. Ganis, U. Lepore, and E. Martuscelli, *J. Phys. Chem.*, **74**, 2439 (1970).

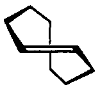
Table I. Geometry of Twist Form of *trans*-Cyclooctene



Bond lengths, Å	Bond angles, deg	Torsional angles, deg
C_1–C_2, 1.34	α, 120	ω_{12}, 209
C–C[a], 1.54	β, 108	ω_{23}, 60
C–H, 1.10	γ, 112	ω_{34}, 0

[a] All saturated C–C bonds. [b] Torsional angle ω_{ij} about bond *i*–*j* is defined as the angle of clockwise rotation of bond *j*–(*j* + 1) necessary to make it eclipse bond *i*–(*i* − 1) as one looks down the *i*–*j* bond from *j* to *i*.

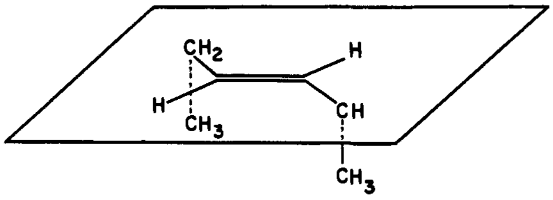
Table II. Calculated Rotatory Strengths

	Compound	Torsion angle, deg	Sign by octant rule[a]	Calculated rotatory strength[b] EH	CNDO
	(*R*)-*trans*-Cyclooctene	29	−	−0.035	−0.025
	(*R*)-*trans*-Hexene-3[c]	29	−	−0.039	−0.046
		20	−	−0.028	−0.048
		10	−	−0.001	−0.027
		0	−	+0.027	+0.009
	(*R*)-*trans*-Cyclooctene[d]	17	−	−0.014	−0.040
	(*R*)-*trans*-Hexene-3[e]	17	−	−0.007	−0.021
		0	−	+0.033	+0.020
	(*R*)-*trans*-Cyclononene[f]	18.5	−	−0.037	
	(*R*)-*trans*-Butene-2[g,h]	10		−0.041	−0.057
	(*R*)-*cis*-Butene-2[g,h]	10		−0.041	−0.062
	(*R*)-Ethylene[g]	29		−0.027	−0.042
		20		−0.041	−0.038
		10		−0.065	−0.024

[a] Sign predicted by olefin octant rule of ref 1d. [b] Atomic units. [c] Bond and dihedral angles of carbon atoms same as those in twist form of (*R*)-*trans*-cyclooctene. [d] Chair geometry of ref 8. [e] Bond and dihedral angles of carbon atoms same as those in chair form of (*R*)-*trans*-cyclooctene. [f] Chair–chair geometry of ref 8. [g] *R* here is operationally defined to be that sense of twist present in (*R*)-*trans*-cyclooctene. [h] Conformation of both methyl groups is that with one C–H bond eclipsing C_2–C_3.

made to minimize the total energy.[11] The geometrical parameters are summarized in Table I; the double bond torsion is 29°. The details of the rotatory strength calculations have been reported previously.[12] The results, presented in Table II, are for the $\pi_x \rightarrow \pi_x^*$ transition, the absorption of lowest energy in each method. The calculated rotatory strengths for (−)-(*R*)-*trans*-cyclooctene agree in sign with the experimentally observed Cotton effect. The absolute magnitudes are not considered reliable.

A priori, several sources of optical activity can be imagined. The chirally disposed allylic substituents, the transannular portion of the methylene chain in particular, and the double bond torsion are three immediate possibilities. To focus on the origin of the optical activity, the following numerical experiments were performed. Normally achiral *trans*-hexene was held fixed in the optically active conformation **3** to simulate the twist form of *trans*-cyclooctene. Another *trans*-hexene was fixed in a conformation with bond and torsional angles corresponding to those of the chair form. Rotatory strengths were then computed with and without torsion in the double bond; the results appear in Table II.[12a]



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In the twist conformation series, the rotatory strength for the *trans*-hexene with 29° torsion is quite close to that for a *trans*-cyclooctene with the same amount of twist, suggesting that the transannular portion of the methylene chain is only a minor perturber. As the angle of twist is decreased the magnitude of the rotatory strength is attenuated and at 0° (planar *trans*-hexene-3) it has changed sign.[13] The remaining entries in Table II serve to demonstrate that the situation is unique neither to the olefin nor to the method of calculation. Note, however, that in the chair conformation series the change in rotatory strength on going from cycloolefin to acyclic alkene with the same torsion is relatively larger, indicating that the transannular methylene contribution is more important here.

The computed rotatory strengths are seen to be a superposition of two major terms: a substituent effect and a contribution from double bond torsion. The substituent term is opposite in sign to the *trans*-cyclooctene Cotton effect whereas the torsional term is of the same sign and starts to dominate at torsional angles approaching 10°. According to the calculations the optical activity in twisted chiral olefins is dominated by double bond torsion with substituent effects relegated to secondary importance. The relative importance of the

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(11) In comparing **1** and **2** it is important to note that interconversion of conformations by rotating the double bond about bonds to the allylic carbons converts **2** (*R*) into **1** (*S*). We have, of course, compared **1** and **2** with the same *R* configuration so that they are not interconvertible conformers.

(12) R. R. Gould and R. Hoffmann, *J. Amer. Chem. Soc.*, **92**, 1813 (1970).

(12a) Note Added in Proof. The quantities presented in Table II and Figure 1 are, strictly speaking, rotatory strengths multiplied by Δ*E*, where Δ*E* is the π_x–π_x^* transition energy expressed in atomic units. We have chosen to leave Δ*E* unspecified since: (a) it does not affect the sign of the tabulated values, and (b) we do not consider the EH or CNDO/2 transition energies reliable.

(13) We have not tried to calculate a rotatory strength for planar *trans*-cyclooctene as the geometry necessary would introduce so much strain and perturb the wave functions so extremely that computed observables might not be meaningful.

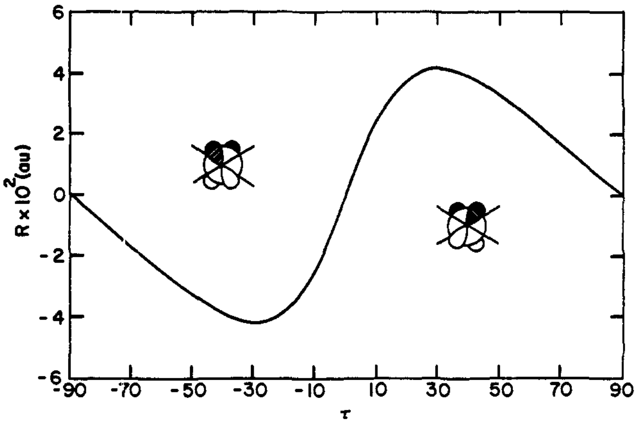

Figure 1. Calculated rotatory strength from extended Hückel wave functions for twisted ethylene. The sense of twist is defined in the inserted figures.

two terms will clearly be a sensitive function of the *degree* of twist.

The following considerations support the dominance of the torsional term. Equation 1 is the familiar expression

$$R_{ab} = \mathrm{Im}\langle a|\boldsymbol{\mu}|b\rangle\cdot\langle b|\mathbf{m}|a\rangle \qquad (1)$$

for the rotatory strength of a transition between two states, a and b; $\boldsymbol{\mu}$ and $\mathbf{m}$ are the electric and magnetic transition moment operators, respectively, and Im means "imaginary part of." Atomic units are assumed. $\boldsymbol{\mu}$ and $\mathbf{m}$ as well as their associated matrix elements are vector quantities. To have a finite rotatory strength there must be nonzero components of the electric and magnetic transition moments along the same axis of the reference frame. In molecules with a plane, center, or alternating axis of symmetry, this requirement is never met. In the local D_{2h} symmetry of an olefin, for example, the $\pi \rightarrow \pi^*$ electric transition dipole is polarized along the internuclear axis, but the magnetic moment vanishes. In an optically active olefin the chirally disposed substituents perturb the local symmetry, mixing higher excited states (particularly those involving $\pi_x \rightarrow \pi_y^*$ excitation) having magnetic transition moments along the internuclear axis into $\pi_x \rightarrow \pi_x^*$. This approach leads naturally to an octant rule.[14]

Twisting the double bond out of planarity reduces the local symmetry of the olefin from D_{2h} to D_2. The electric moment of the $\pi_x \rightarrow \pi_x^*$ transition remains polarized along the C–C bond axis, but now there is a finite magnetic transition moment in this direction. From the standpoint of perturbation theory optical activity again arises from mixing of π_x^* and π_y^*. In D_2 these levels transform under the same (B_1) representation and therefore interact as the D_{2h} symmetry is destroyed. As a result of the mixing the $\pi_x \rightarrow \pi_x^*$ transition acquires magnetic dipole intensity from $\pi_x \rightarrow \pi_y^*$ and becomes optically active.

The practical distinction between the chirality due to substitution and that due to torsion is one of degree. Local D_{2h} symmetry is preserved in the first case, but not in the second. We would expect the second factor, one of inherent dissymmetry, to be dominant,[15] and so it is in our calculations. Figure 1 presents calculated rotatory strengths for the $\pi_x \rightarrow \pi_x^*$ transition in ethylene as a function of twist angle τ. Negative τ corresponds to the sense of twist in (−)-(R)-*trans*-cyclooctene. The computed negative rotatory strengths for τ less than zero agree with the sign of the *trans*-cyclooctene Cotton effect and also with that calculated by Robin.[1b]

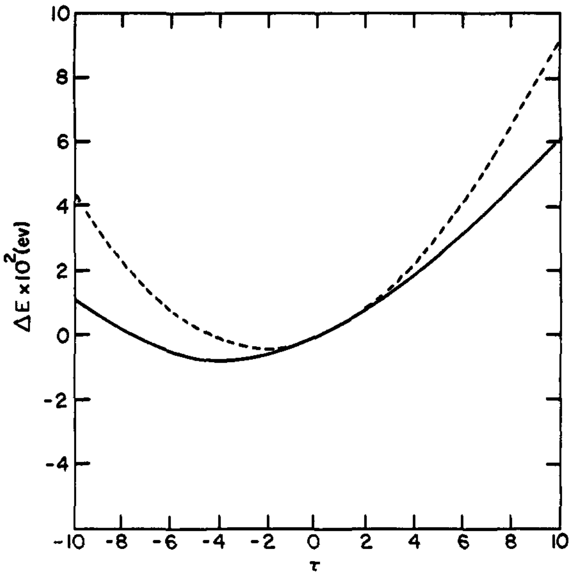

Figure 2. EH (solid line) and CNDO/2 (dashed) energies for *cis*-pentene-2 as a function of torsional angle τ. Convention for τ is given in the text. The energy scale for both calculations is relative to the planar olefin.

Let us allow for the moment that double bond torsion is the principal contributor to the negative $\pi_x \rightarrow \pi_x^*$ rotatory strength in (−)-(R)-*trans*-cyclooctene. Why then would a symmetry rule based on a planar olefin correctly predict the sign of the rotatory strength in *trans*-cyclooctene or the equally strained twistene? A trivial answer is, of course, that the agreement is fortuitous. A more realistic possibility is that the chiral disposition of substituents around the double bond uniquely defines its sense of twist. Charney and coworkers,[16] for example, have found this to be so for a number of steroidal dienes. The diene chromophore skews out of planarity making it inherently dissymmetric, and the sense of skewing is fixed by the absolute configuration at the neighboring chiral centers. Time-averaged nonplanarity of substituted olefins has also been suggested by Bauer.[17]

Our speculation leads to an interesting question. On a time-average basis are all chiral olefins nonplanar? As we know, an optically active olefin can have no symmetry planes. Each sense of out-of-plane twist is therefore unique, so that the torsional potential of the double bond must, to some degree, be asymmetric. Consider, for example, *cis*-pentene-2 fixed in the optically active conformation **4**. The two senses of twist are defined in **5** and **6**, and we now follow motion along these degrees of freedom.

The curves in Figure 2 plot extended Hückel and CNDO/2 total energies for 10° excursions away from planarity along each path. Positive τ corresponds to

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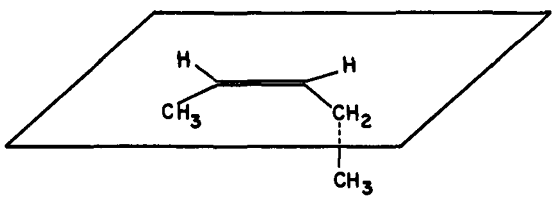
(14) J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966).

(15) A. Moscowitz, *Proc. Roy. Soc.*, **297**, 16 (1967).

(16) (a) E. Charney, H. Ziffer, and U. Weiss, *Tetrahedron*, **21**, 3121 (1965); (b) U. Weiss, H. Ziffer, and E. Charney, *ibid.*, **21**, 3105 (1965); see also (c) A. W. Burgstahler and R. C. Barkhurst, *J. Amer. Chem. Soc.*, **92**, 7601 (1970).

(17) S. H. Bauer, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971.



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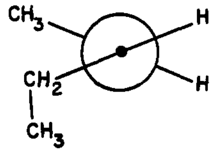

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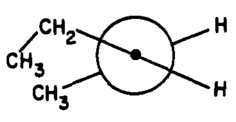

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bringing the methyl groups together, negative τ to moving them apart. Note that the potentials are quite soft, the maximum change in energy being about 0.06 and 0.09 eV for EH and CNDO/2, respectively. This is consistent with the low-energy infrared twisting frequency for olefins which is 1023 cm^{-1} for ethylene itself.[3]

The curves conform to our intuitive expectations: the methyl groups prefer to bend away rather than toward one another, thus favoring motion along path **5**. The asymmetry in the torsional potential means that the time-averaged value of τ will be negative instead of zero. Accordingly, the torsional contribution to the rotatory strength will be negative (see Figure 1). Application of the olefin octant rule[4a,b] to the hypothetically chiral *cis*-pentene-2 **4** also leads to this prediction. In the case at hand then, the olefin octant rule correctly assesses the sign of the torsional rotatory strength contribution. Attempts to extrapolate this sort of reasoning to the steroidal olefins correlated by the rule would not be very meaningful owing to the many degrees of freedom present in their multicyclic frameworks. Nevertheless the possibility that torsion is important in these compounds should not be overlooked.

Recapitulating, our calculations suggest that the sign of the Cotton effect in twisted olefins such as twistene and *trans*-cyclooctene is dominated by double bond torsion. For these olefins it appears that the success of the octant rule derives from its ability to correctly predict the sense of twist from the absolute configuration of the nearest substituents. A torsion contribution may also be important in less strained olefins, but this is hard to assess with the experimental data presently available.

Acknowledgment. The computer program utilized in this work was written by R. R. Gould and J. M. Howell. Our work was generously supported by Research Grant GM-13468 from the National Institutes of Health.

Mechanisms of Photochemical Reactions in Solution. LXVII.[1] Energy Wastage in Photosensitized Isomerizations of the Stilbenes[2]

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Abstract: Photosensitized isomerizations of the stilbenes using high energy sensitizers, capable of exothermic triplet energy transfer to either *cis*- or *trans*-stilbene, have been investigated in detail. Our present measurements differ slightly in some cases from those reported previously. Detailed scrutiny reveals that, with sensitizers having excitation energies in the range 62–74 kcal, there is a small, but significant, variation in the final photostationary states. The variation is a systematic function of excitation energy, and $(c/t)_{pss}$ varies from 1.3 at the high end of the energy scale to 2.0 at the low end. Careful study of energy balance in photosensitized stilbene isomerizations with acetophenone, benzophenone, and 9-fluorenone as sensitizers reveals that quenching of sensitizer triplets by stilbene does not always occur with energy transfer to stilbene. Our data indicate that about 5% of the time when acetophenone triplets are quenched by *trans*-stilbene the stilbene does not become electronically excited. Similarly 9-fluorenone triplets are quenched readily by both *trans*- and *cis*-stilbene. Triplet energy to trans is exothermic and occurs in about 95% of the quenching events; triplet energy transfer to cis is slightly endothermic and occurs in only about half of the quenching events. Various possible quenching mechanisms are discussed.

Quenching of sensitizer triplets by other substrates may in the general case involve one or more of processes 1–3, where S is the sensitizer, A is the substrate, and subscripts T_1 and S_0 refer respectively to lowest triplet and ground singlet states.

Where A is an olefin, cis–trans isomerization may follow reaction 1, providing a basis for monitoring the occurrence of reactions 1 and 3. When reaction 1 provides the only path leading to olefin isomerization, then

Triplet energy transfer

$$S_{T_1} + A_{S_0} \longrightarrow S_{S_0} + A_{T_1} \tag{1}$$

Quenching *via* net chemical reaction

$$S_{T_1} + A_{S_0} \longrightarrow \text{products} \tag{2}$$

Quenching without energy transfer or net chemical reaction

$$S_{T_1} + A_{S_0} \longrightarrow S_{S_0} + A_{S_0} + \text{heat} \tag{3}$$

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(1) Part LXVI: L. J. Sharp IV and G. S. Hammond, *Mol. Photochem.*, 2, 225 (1970).

(2) Taken in part from the Ph.D. Thesis of D. Valentine, Jr., California Institute of Technology, Pasadena, Calif., 1966.

(3) Author to whom correspondence should be addressed.