

Optically Active (*E,Z*)-1,3-Cyclooctadiene: First Enantioselective Synthesis through Asymmetric Photosensitization and Chiroptical Property

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Abstract: Enantiodifferentiating photoisomerizations of (*Z,Z*)-1,3-cyclooctadiene (**1ZZ**) to the chiral *E,Z*-isomer **1EZ** were performed at varying temperatures in the presence of some benzenepoly-, naphthalene(di)-, and anthracene-carboxylates. Of these chiral sensitizers, (–)-menthyl benzenhexacarboxylate afforded the highest enantiomeric excesses (ee's) up to 10% and 18% in pentane at 25 and –40 °C, respectively. In contrast, the use of polar solvents greatly diminished the product's ee, suggesting intervention of a radical ionic rather than exciplex intermediate in these solvents. Optically pure **1EZ** is shown to possess anomalously high specific rotation and circular dichroism as a simple diene chromophore: $[\alpha]_D^{25}$ 1380° (CH₂Cl₂), $\Delta\epsilon$ 12.8 M⁻¹ cm⁻¹ (λ_{ext} 228 nm, cyclohexane). The chiroptical properties observed not only correct the previous data but also present the conclusive evidence for the recent theoretical predictions.

Introduction

E-Isomers of medium-sized cycloalkenes have long aroused much theoretical, spectroscopic, synthetic, and physicochemical interests because of their constrained, chiral molecular structures as well as enhanced thermal and photochemical reactivities,^{1–19} arising from the distorted π orbital and the hindered rope-jumping motion of the methylene chain bridging the double bond. However, only eight-membered cyclic *E*-isomers have been demonstrated unequivocally to be chiral with moderate thermal stability at ambient temperatures, and their chiroptical properties have been well documented.^{8–10,12,16} On the other hand, smaller-sized (*E*)-cycloalkenes, which should be chiral, are merely known as unstable transient species,¹⁵ while the larger

ones have been revealed to racemize spontaneously at room temperature.¹¹ In this context, (*E,Z*)-cyclooctadienes are intriguing as borderline cases. The *E,Z*-isomer of nonconjugated 1,5-cyclooctadiene is thermally as stable as the parent (*E*)-cyclooctene,¹³ whereas conjugated (*E,Z*)-1,3-cyclooctadiene (**1EZ**) is relatively stable only up to 60 °C but cyclizes to bicyclo[4.2.0]oct-7-ene at 90 °C with a lifetime of 50 min.^{14b}

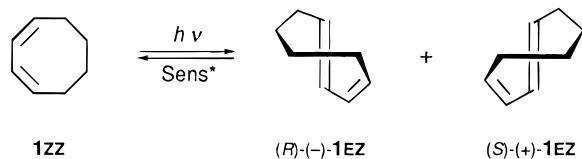
In spite of the thermal and photochemical syntheses of **1EZ** reported by Cope et al.¹⁷ and Liu,¹⁸ its chiroptical properties have not been investigated experimentally⁸ or theoretically¹⁹ until recently, probably due to the thermal instability and the lack of convenient enantioselective synthetic methods. Isaksson et al.⁸ reported that racemic **1EZ** can be resolved optically by chiral HPLC over triacetylcellulose to give optically active **1EZ** of >90% enantiomeric excess (ee). This sample was reported to show large specific rotation and circular dichroism: $[\alpha]_D^{20}$ –649° (*c* 0.017, ethanol), $\Delta\epsilon$ –8.83 M⁻¹ cm⁻¹ (λ_{ext} 230.5 nm, ethanol).⁸ Since the two CD peaks at 230 and <190 nm gave the same (negative) sign inconsistent with the prediction of the diene helical rule,²⁰ they attempted to determine the absolute configuration of **1EZ** by CNDO/S-CI calculation and tentatively assigned the (–)-form as possessing the *P* helicity or *R* configuration.⁸ This assignment was recently confirmed by Bouman and Hansen through more accurate *ab initio* RPA calculation.¹⁹

Besides the chromatographic optical resolution mentioned above, no chemical or photochemical synthetic approaches to the enantiomeric **1EZ** have been reported so far. In this aspect, the enantiodifferentiating photoisomerization of (*Z,Z*)-1,3-cyclooctadiene (**1ZZ**) sensitized by a chiral sensitizer provides us with a convenient synthetic access to optically active **1EZ**, since the photosensitization of (*Z*)-cyclooctene with chiral aromatic esters has been shown to afford its *E*-isomer in good optical yields up to 64%.^{21,22}

- [⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.
- (1) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.
 - (2) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.
 - (3) Johnson, R. P.; DiRico, K. J. *J. Org. Chem.* **1995**, *60*, 1074.
 - (4) Yaris, M.; Moscowitz, A.; Berry, R. S. *J. Chem. Phys.* **1968**, *49*, 3150.
 - (5) Bach, R. D. *J. Chem. Phys.* **1970**, *52*, 6423.
 - (6) Robin, M. B.; Taylor, G. N.; Kuebler, N. A.; Bach, R. D. *J. Org. Chem.* **1973**, *38*, 1049.
 - (7) Mason, M. G.; Schnepf, O. *J. Chem. Phys.* **1973**, *59*, 1092.
 - (8) Isaksson, R.; Roschester, J.; Sandström, J.; Wistrand, L. *J. Am. Chem. Soc.* **1985**, *107*, 4074.
 - (9) Cope, A. C.; Ganellin, C. R.; Johnson, H. W., Jr.; Van Auken, T. V.; Winkler, J. S. *J. Am. Chem. Soc.* **1963**, *85*, 3276.
 - (10) Cope, A. C.; Mehta, A. S. *J. Am. Chem. Soc.* **1964**, *86*, 5626.
 - (11) Cope, A. C.; Banholzer, K.; Keller, H.; Pawson, B. A.; Whang, J. J.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1965**, *87*, 3644.
 - (12) Cope, A. C.; Pawson, B. A. *J. Am. Chem. Soc.* **1965**, *87*, 3649.
 - (13) Cope, A. C.; Hecht, J. K.; Johnson, H. W., Jr.; Keller, H.; Winkler, H. J. S. *J. Am. Chem. Soc.* **1966**, *88*, 761.
 - (14) (a) Shumate, K. M.; Neuman, P. N.; Fonken, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 3996. (b) Bromfield, J. J.; MaConaghy, J. S., Jr. *Tetrahedron Lett.* **1969**, 3723.
 - (15) Inoue, Y.; Ueoka, T.; Kuroda, T.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1981**, 1031. Inoue, Y.; Hagiwara, S.; Daino, Y.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1307.
 - (16) Tsuneishi, H.; Hakushi, T.; Tai, A.; Inoue, Y. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2057.
 - (17) Cope, A. C.; Bumgardner, C. L. *J. Am. Chem. Soc.* **1956**, *78*, 2812.
 - (18) Liu, R. S. H. *J. Am. Chem. Soc.* **1967**, *89*, 112.
 - (19) Bouman, T. D.; Hansen, A. E. *Croatia Chem. Acta* **1989**, *62*, 227.

- (20) Moscowitz, A.; Charney, E.; Weiss, U.; Zeffer, H. *J. Am. Chem. Soc.* **1961**, *83*, 4661. Lighter, D. A.; Bouman, T. D.; Gawronski, J. K.; Gawronska, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*.

Scheme 1



In this study, we performed the enantiodifferentiating geometrical photoisomerization of **1ZZ** sensitized by a variety of optically active benzenepoly-, naphthalene(di)-, and anthracene-carboxylates in order to reveal the (chir)optical properties of the optically active **1EZ** obtained and also to elucidate the electronic and steric effects of the conjugating double bond upon the enantiodifferentiation process in the excited state.

Experimental Section

General. Melting points were measured with a YANACO MP-21 apparatus and are uncorrected. ^1H NMR spectra were obtained on a JEOL GX-400 spectrometer in chloroform-*d*. Infrared spectra were obtained on a JASCO IR-810 instrument. Electronic absorption and fluorescence spectra were recorded on JASCO Ubest-50 and FP-777 instruments, respectively; fluorescence spectra are not corrected for the instrument response function. Optical rotations were determined at 589 nm in a thermostated conventional 10-cm cell, using a Perkin-Elmer polarimeter model 243B. Circular dichroism spectra were recorded in the vapor and solution phases on a JASCO J-720 spectrometer.

Fluorescence lifetimes were measured with 0.1–0.01 mM solutions of **3** or **6** in aerated pentane and/or acetonitrile by means of the time-correlated single-photon-counting method on a Horiba NAES-550 instrument equipped with a pulsed H_2 light source. The radiation from the lamp was made monochromatic by a 10-cm monochromator, and the emission from sample solution was detected through an appropriate filter (UV-33, -35, or -39).

Gas chromatographic analyses of the geometrical isomers **1ZZ** and **1EZ** in photolyzed solutions were performed on a 1-m packed column of 40% β,β' -oxydipropionitrile at 65 °C with a Shimadzu 6A instrument. Enantiomeric excesses of **1EZ** isolated through the selective extraction with aqueous silver nitrate were determined by gas chromatography over a 30-m chiral capillary column (SUPELCO β -DEX 120) at 45 °C, using a Shimadzu GC-14B instrument. It may be interesting to note that, in order to attain good enantiomeric separation and high reproducibility in the chiral GC analysis, the amount of injected sample should be kept in a certain range. In our case using a Shimadzu integrator C-R6A, the best reproducibility (within an error of $\pm 0.5\%$ ee) was obtained when the integrated area of the enantiomer peak was kept in the range 30 000–100 000.

Materials. Solvent pentane was stirred over concentrated sulfuric acid until the acid layer no longer turned yellow, washed with water, neutralized with aqueous sodium bicarbonate, dried over magnesium sulfate, and then distilled fractionally. Methanol and acetonitrile were fractionally distilled from magnesium turnings and diphosphorus pentoxide, respectively.

(-)-Menthyl, (-)-bornyl, and/or (-)-1-methylheptyl arenecarboxylates employed as chiral sensitizers were synthesized in pyridine from the corresponding alcohols and acid chlorides and purified by repeated recrystallization from methanol or ethanol, according to the procedures reported previously.^{21–25} (-)-Dimethyl 1,4-naphthalenedicarboxylate (**6a**): mp 93.5–94.5 °C; $[\alpha]_D^{25} -88.1^\circ$ (*c* 1.51, CHCl_3); IR (KBr) ν 2950, 2870, 1720, 1590, 1520, 1460, 1380, 1250, 1190, 1140, 1100, 1030, 990, 960, 920, 840, 780, 660 cm^{-1} ; UV (pentane) λ_{max} (ϵ) 212.6

(21) Inoue, Y.; Yamasaki, N.; Yokoyama, T.; Tai, A. *J. Am. Chem. Soc.* **1989**, *111*, 6480; *J. Org. Chem.* **1992**, *57*, 1332.

(22) Inoue, Y.; Yamasaki, N.; Yokoyama, T.; Tai, A. *J. Org. Chem.* **1993**, *58*, 1011.

(23) Yamasaki, N.; Inoue, Y.; Yokoyama, T.; Tai, A.; Ishida, A.; Takamuku, S. *J. Am. Chem. Soc.* **1991**, *113*, 1933.

(24) Inoue, Y.; Okano, T.; Yamasaki, N.; Tai, A. *J. Photochem. Photobiol. A* **1992**, *66*, 61.

(25) Inoue, Y.; Yamasaki, N.; Shimoyama, H.; Tai, A. *J. Org. Chem.* **1993**, *58*, 1785.

(33 400), 241.8 (21 300), 315.2 nm (6480 $\text{M}^{-1} \text{cm}^{-1}$); ^1H NMR (CDCl_3) δ 0.85 (d, *J* = 6.8 Hz, 6H), 0.93 (d, *J* = 6.8 Hz, 6H), 0.97 (d, *J* = 6.6 Hz, 6H), 0.92–1.00 (m, 2H), 1.12–1.24 (m, 4H), 1.54–1.63 (m, 4H), 1.87 (m, 4H), 2.01 (m, 2H), 2.24 (m, 2H), 5.07 (d–t, *J* = 4.4, 11.0 Hz, 2H), 7.64 (d–d, *J* = 3.4, 6.6 Hz, 2H), 8.04 (s, 2H), 8.80 (d–d, *J* = 3.4, 6.6 Hz, 2H). (-)-Dimethyl 1,8-naphthalenedicarboxylate (**9a**): mp 161.5–162.5 °C; $[\alpha]_D^{25} -20.9^\circ$ (*c* 0.97, CHCl_3); UV (pentane) λ_{max} (ϵ) 219.8 (31 500), 293.2 nm (6900 $\text{M}^{-1} \text{cm}^{-1}$); IR (KBr) ν 2950, 2850, 1070, 1510, 1460, 1380, 1280, 1200, 1140, 1080, 990, 770 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.86 (d, *J* = 6.8 Hz, 6H), 0.97 (m, 2H), 0.99 (d, *J* = 6.3 Hz, 6H), 0.99 (d, *J* = 7.1 Hz, 6H), 1.14 (m, 2H), 1.24 (m, 2H), 1.54 (m, 2H), 1.65 (m, 2H), 1.76 (m, 4H), 2.25 (m, 2H), 2.34 (m, 2H), 4.90 (d–t, *J* = 11.0, 4.4 Hz, 2H), 7.51 (m, 2H), 7.94 (m, 4H).

Photolysis. All irradiations were carried out in a temperature-controlled water (25 °C) or methanol (–40 to –74 °C) bath. The light sources employed were a conventional 300-W high-pressure mercury lamp for irradiations at 25 °C and an equivalent lamp fitted with a transparent Pyrex vacuum sleeve designed for the low-temperature irradiation (Eikosha). A solution (3 or 300 mL), containing **1ZZ** (0.2 M), optically active sensitizer **2–10** (10 mM), and cyclooctane (10 mM) added as an internal standard, was irradiated at >300 nm under an argon atmosphere in a Pyrex tube (1-cm i.d.) placed near the lamp surface or in an annular Pyrex vessel surrounding the lamp, the whole system being immersed in a cooling bath. In most cases, irradiations were continued until the apparent photostationary states were reached, frequently monitoring the isomer composition of irradiated solution on GC.

Product Isolation. In preparative runs using an annular vessel (300 mL), **1EZ** produced was selectively extracted from the photolysate with three 30-mL portions of 20% aqueous silver nitrate at <5 °C. The combined aqueous extract was washed with two 25-mL portions of pentane and then added dropwise with vigorous stirring into a concentrated aqueous ammonia solution at 0 °C. The resulting mixture was extracted with three 25-mL portions of pentane. The combined pentane extract was dried over sodium sulfate and concentrated at a reduced pressure (50–100 Torr), and then the residue obtained was subjected to bulb-to-bulb distillation in vacuo to give chemically pure **1EZ**. In analytical scale runs with 3-mL solutions, practically the same procedures, except for the scale, were employed to obtain the pentane solution of pure **1EZ** for chiral GC analysis.

Results and Discussion

Geometrical Photoisomerization. Our previous investigations on the photosensitized enantiodifferentiating isomerization of cyclooctene^{16,21} clearly indicate that the intervention of a singlet exciplex, in which substrate interacts intimately with chiral sensitizer for a certain period, is essential in order to accomplish effective enantiodifferentiation in the excited state. However, virtually no attempt has been reported on the singlet photosensitization of 1,3-cyclooctadiene (**1**), in contrast to its well-documented photochemical behavior upon direct irradiation^{26–29} and triplet photosensitization.¹⁸

We first investigated the photosensitized geometrical isomerizations of **1** with some benzenepolycarboxylates (**2** and **3**), which are efficient singlet sensitizers for cyclooctene^{21,22,30} and 1,5-cyclooctadiene.³¹ The structures of the sensitizers employed are illustrated in Chart 1, and the *E/Z* ratios obtained are listed in Tables 1 and 2. Possessing a lower singlet energy than cyclooctene, the conjugated diene **1** was sensitized not only with benzene(poly)carboxylates but also with naphthalene(di)- and anthracenecarboxylates **4–10** to give moderate *E/Z* ratios, which

(26) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 4141.

(27) Dauben, W. G.; Cargill, R. L. *J. Org. Chem.* **1962**, *27*, 1910.

(28) Nebe, W. J.; Fonken, G. *J. Am. Chem. Soc.* **1969**, *91*, 1249.

(29) Inoue, Y.; Daino, Y.; Hagiwara, S.; Nakamura, H.; Hakushi, T. *J. Chem. Soc., Chem. Commun.* **1985**, 804.

(30) Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1672.

(31) Goto, S.; Takamuku, S.; Sakurai, H.; Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2*, **1980**, 1678.

Chart 1

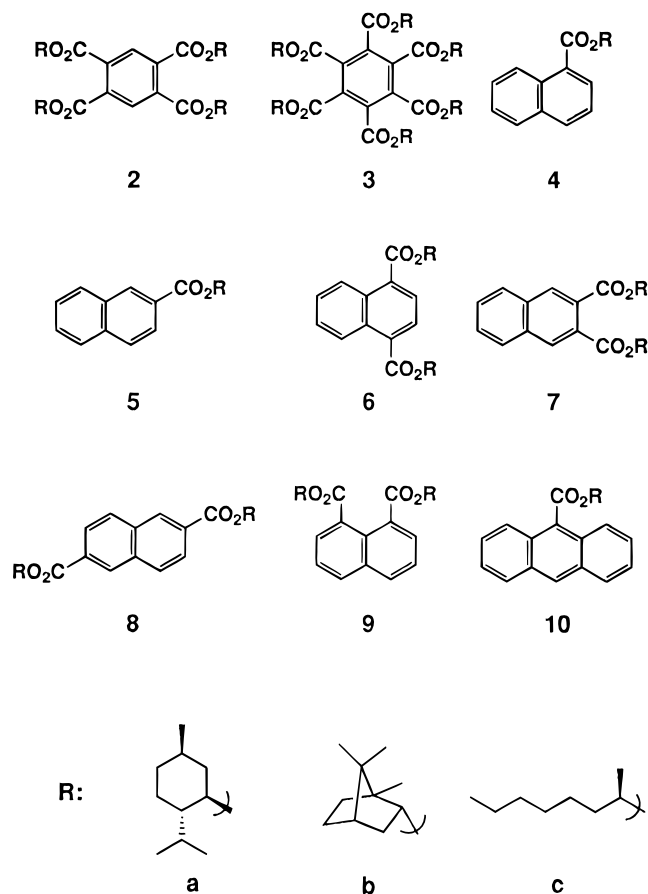


Table 1. Enantiodifferentiating Photoisomerization of (*Z,Z*)-1,3-Cyclooctadiene (**1ZZ**) Sensitized by Optically Active (Poly)alkyl Arene(poly)carboxylates in Pentane at 25 °C

sensitizer	irradiation time, h	conversion, %	yield, %	E/Z	% ee/op
2a	12 ^a	29.9	19.1	0.272	-0.3 ^c
2b	86 ^b	17.7	10.4	0.132	0.1 ^d
2c	95 ^b	18.7	8.2	0.101	0.1 ^d
3a	37 ^b	29.6	8.3	0.119	-10.1 ^c
3b	117 ^b	^e	4.4	0.044	-0.5 ^d
	9 ^a	12.8	4.5	0.052	-1.5 ^c
3c	180 ^b	20.5	7.8	0.098	-0.9 ^d
	11 ^a	22.7	8.9	0.115	-2.5 ^c
4a	69 ^b	12.7	9.1	0.104	0.4 ^d
	10 ^a	16.8	9.8	0.118	0.3 ^c
5a	29 ^b	9.2	4.6	0.050	0.8 ^d
	10 ^a	11.0	6.8	0.077	-0.3 ^c
6a	87 ^b	21.1	10.0	0.127	0.9 ^d
	14 ^a	20.0	9.5	0.119	1.2 ^c
7a	72 ^b	9.8	5.9	0.065	0.6 ^d
8a	72 ^b	19.8	10.6	0.132	0.2 ^d
	13 ^a	29.8	8.7	0.124	-0.3 ^c
9a	72 ^b	19.8	10.6	0.132	0.3 ^d
10a	24 ^a	16.3	6.8	0.081	-1.1 ^c

^a Reaction scale: 3 mL. ^b Reaction scale: 300 mL. ^c Percent ee determined by capillary GC. ^d Percent op calculated from specific rotation. ^e Not determined.

are of similar magnitude. In all cases, the major course of photolysis was the *Z*-*E* isomerization as was the case with direct photolysis²⁶⁻²⁹ and triplet sensitization.¹⁸ The chemical yields of **1EZ** based on the consumed **1ZZ** are moderate to high (40-70%) in most cases even upon prolonged irradiations or at low temperatures, as shown in Table 2.

Sensitization Mechanism. In order to elucidate the excited state(s) involved in the photosensitization process, we performed

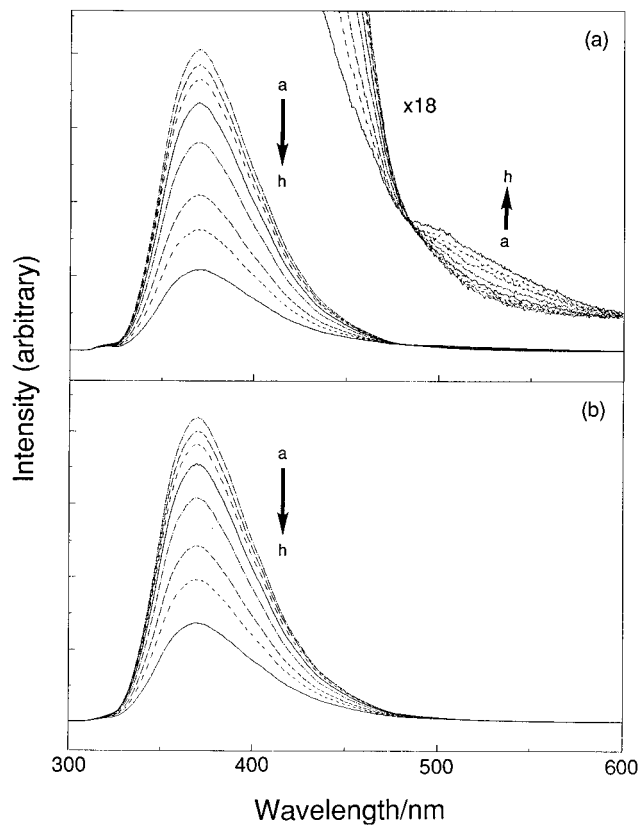


Figure 1. Fluorescence spectra of hexamethyl mellitate (**3**, R = Me; 0.1 mM) excited at 290 nm in pentane (upper traces) and in acetonitrile (lower traces) in the absence/presence of (*Z,Z*)-1,3-cyclooctadiene (**1ZZ**) of varying concentrations: (a) 0, (b) 2.5, (c) 5, (d) 10, (e) 20, (f) 40, (g) 60, and (h) 100 mM.

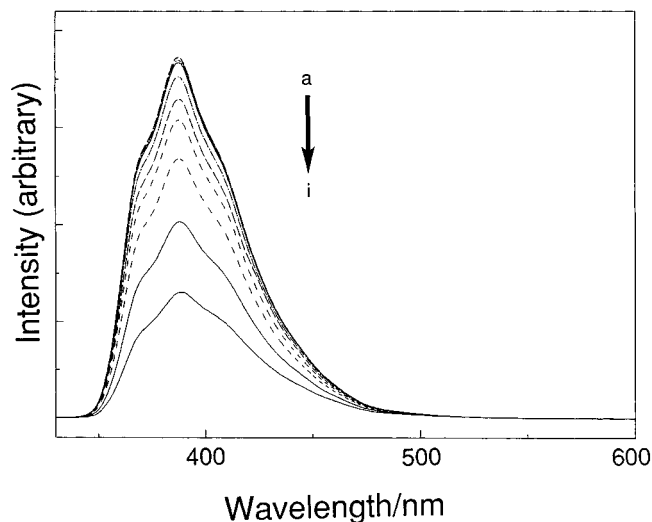


Figure 2. Fluorescence spectra of (-)-dimenthyl 1,4-naphthalenedicarboxylate (**6a**; 0.01 mM) excited at 320 nm in pentane in the absence/presence of (*Z,Z*)-1,3-cyclooctadiene (**1ZZ**) of varying concentrations: (a) 0, (b) 5, (c) 10, (d) 20, (e) 40, (f) 60, (g) 100, (h) 200, and (i) 400 mM.

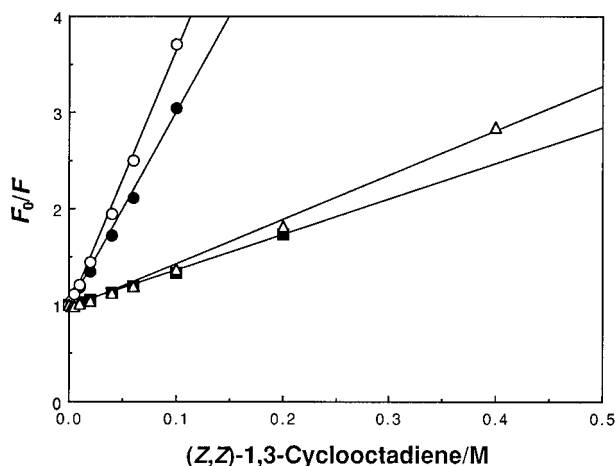
the fluorescence-quenching experiments with some representative sensitizers. As exemplified in Figures 1 and 2, the fluorescence of methyl and (-)-menthyl mellitates **3** and (-)-menthyl 1,4-naphthalenedicarboxylate (**6a**) in aerated pentane and/or acetonitrile was quenched efficiently by the substrate **1ZZ** up to 400 mM concentration.

As can be seen from Figure 1a, as the fluorescence intensity decreases gradually by adding quencher **1ZZ** into a pentane solution of **3** (R = Me), a new weak emission attributable to

Table 2. Temperature and Solvent Effects upon Product's ee in Enantiodifferentiating Photoisomerization of (Z,Z)-1,3-Cyclooctadiene (**1ZZ**) Sensitized by Optically Active (Poly)alkyl Arene(poly)carboxylates^a

sensitizer	solvent	temperature, °C	irradiation time, h	conversion, %	yield, %	E/Z	% ee
2a	pentane	25	12	29.9	19.1	0.272	-0.3
		-40	12	31.5	15.2	0.223	1.2
3a	pentane	25	37 ^b	29.6	8.3	0.119	-10.1
		-40	8	21.1	12.8	0.162	-17.6
		25	14	12.4	6.4	0.073	-1.3
3b	pentane	25	20	3.8	1.6	0.017	0.2
		-74	10	20.2	11.1	0.139	-5.8
		25	9	12.8	4.5	0.052	-1.5
3c	pentane	25	11	22.7	8.9	0.115	-2.5
		-74	11	24.5	16.0	0.212	-1.2
4a	pentane	25	10	16.8	9.8	0.118	0.3
		-40	10	19.7	10.5	0.131	-0.3
6a	pentane	25	14	20.0	9.5	0.119	1.2
		-40	12	24.5	10.4	0.138	0.6
8a	pentane	25	13	29.8	8.7	0.124	-0.3
		-40	12	17.0	11.2	0.136	-0.5

^a Reaction scale: 3 mL, unless noted otherwise. ^b Reaction scale: 300 mL. ^c Sensitizer concentration less than 1 mM, due to low solubility.

**Figure 3.** Stern–Volmer plots for fluorescence quenching of hexamethyl mellitate by **1ZZ** in pentane (○) and acetonitrile (●), (–)-hexamethyl mellitate in pentane (■), and (–)-dimethyl 1,4-naphthalenedicarboxylate (Δ) in pentane.

exciplex intermediate emerges at a longer wavelength, accompanying the isoemissive point at 480 nm; see the inset. The net exciplex fluorescence, obtained by the spectrum subtraction, showed maxima at ~450 nm. Similar fluorescence behavior was observed with **3a** (R = Men) upon quenching by **1ZZ** in pentane.

In contrast, the quenching profile of **3** (R = Me) in acetonitrile differs considerably. In the polar solvent, the fluorescence intensity decreases similarly upon addition of **1ZZ**, but no emission appears at longer wavelengths (Figure 1b). The efficient quenching and the lack of exciplex emission jointly indicate that the exciplex, if formed, is not emissive at all or, more probably, the spontaneous electron transfer from **1ZZ** to **3**, generating a radical ion pair, is the dominant process in polar acetonitrile. The fluorescence of naphthalenedicarboxylate **6a** was also quenched efficiently by **1ZZ** in pentane without producing any new emission (Figure 2).

According to the conventional Stern–Volmer treatment of the quenching data,²¹ the relative fluorescence intensity F_0/F was plotted as a function of the concentration of added **1ZZ** to give a good straight line for each sensitizer examined, as shown in Figure 3. From the Stern–Volmer constant ($k_q\tau$) obtained as a slope of the plot and the fluorescence lifetime (τ) determined independently by the single-photon-counting technique, we can calculate the quenching rate constant (k_q) for each sensitizer (Table 3).

Table 3. Fluorescence Quenching of Aromatic Esters with (Z,Z)-1,3-Cyclooctadiene (**1ZZ**)^a

sensitizer	solvent	τ , ns ^b	$k_q\tau$, M ⁻¹	k_q , M ⁻¹ s ⁻¹
hexamethyl mellitate (3, R = Me)	pentane	1.1	26.9	2.4×10^{10}
	CH ₃ CN	0.6	20.1	3.4×10^{10}
(–)-hexamethyl mellitate (3a) ^c	pentane	0.7	3.68	5.3×10^9
(–)-dimethyl 1,4-naphthalenedicarboxylate (6a)	pentane	4.0	4.62	1.2×10^9

^a Measured in aerated solvents at 18 °C. ^b Determined independently by single-photon-counting technique. ^c Methyl mellitate gives a usual single fluorescence peak, while the menthyl ester **3a** is known to exhibit unusual dual fluorescence behavior induced by steric hindrance (see ref 23). The listed values were determined for the relaxed state emission that appears at a longer wavelength (372 nm).

It is noted that the fluorescence quenching by **1ZZ** occurs with high efficiency at rates much faster than 10^9 M⁻¹ s⁻¹. In particular, the fluorescence of methyl mellitate was quenched by **1ZZ** near the diffusion-controlled rate both in pentane (2.4×10^{10} M⁻¹ s⁻¹) and in acetonitrile (3.4×10^{10} M⁻¹ s⁻¹), while the bulky menthyl groups in **3a** and the lower singlet energy of naphthalenedicarboxylate **6a** evidently decelerate the quenching process to 5.3×10^9 and 1.2×10^9 M⁻¹ s⁻¹, respectively. It is also emphasized that the exciplex emission observed upon quenching of mellitates **3** (R = Me or Men) in pentane is missing in acetonitrile, probably owing to the facile formation of a nonemissive radical ion pair upon quenching. Although no further spectroscopic search for the transient ionic species was made, the sudden drops of the product's ee in polar solvents described below indicate experimentally the loss of intimate and long-lived interactions between chiral sensitizer and substrate.

These results demonstrate unequivocally that the sensitization of **1ZZ** with arene(poly)carboxylates proceeds in the singlet manifold as in the case with cyclooctene.^{21,22} The lower singlet energy of **1ZZ** compared with cyclooctene will accelerate the singlet energy transfer in pentane, and virtually the same sensitization/enantiodifferentiation scenario operative in the cyclooctene case²¹ may be applicable to the present case at least in pentane. However, in sharp contrast to the negligible solvent effects upon ee in the cyclooctene case,²¹ the effect of polar solvents is much more drastic for the conjugated diene **1ZZ**. This is presumably because the lower ionization potential of **1ZZ** (8.68 eV),³² compared to that of cyclooctene (8.82 eV),³²

(32) Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *Energetics of Gaseous Ions*; American Institute of Physics: New York, 1977.

facilitates the electron transfer producing solvent-separated or free radical ion pair in polar solvents.

Enantiodifferentiation. Optical purity (op) and/or enantiomeric excess (ee) of **1EZ** isolated from the photolysate were determined respectively by measuring the product's optical rotation and integrating the enantiomer peaks separated on chiral GC. The product's op or ee values obtained in the enantiodifferentiating photosensitizations at 25 °C with several chiral arenecarboxylates are summarized in Table 1. Of these sensitizers examined, only benzenhexacarboxylates **3** afforded moderately optically active **1EZ** of 2–10% ee in pentane at 25 °C, whereas the other sensitizers, including benzenetetracarboxylate **2** and naphthalene(di)- and anthracenecarboxylates **4–10**, gave poor ee's, less than 1% even in pentane. One should be cautious however in evaluating the enantiodifferentiating ability of a chiral sensitizer, since the product's ee has amply been shown to depend significantly upon the irradiation temperature especially in the asymmetric photosensitization with sterically congested benzenepolycarboxylates.^{21,22}

Temperature and Solvent Effects. To explore the temperature effect upon ee, the enantiodifferentiating photosensitizations with **2a**, **3a–c**, **4a**, **6a**, and **8a** were performed in pentane at two different temperatures. As shown in Table 2, the ee values exhibit relatively small temperature dependences in most cases. This indicates that the enthalpic, as well as entropic, differences ($\Delta\Delta H^\ddagger$ and $\Delta\Delta S^\ddagger$) for the enantiodifferentiating process producing (*R*)- and (*S*)-**1EZ** are not as great as in the cyclooctene case.^{21,22} Nonetheless, the ee value obtained with **3a** was improved considerably from 10.1% at 25 °C to 17.6% at –40 °C, and similar enhancement of ee was observed with **3b**.

In several cases, the product chirality is switched indeed within the temperature range employed or expected to be inverted by changing the temperature. These results clearly demonstrate that, although the ee's obtained are not particularly high in the present cases, the entropy term still plays an essential, but less important, role in the enantiodifferentiating process within exciplex intermediates for the reasons discussed below.

However, in view of the high ee's and the drastic temperature effect observed in the cyclooctene case,^{21,22} these low ee's and minimal entropic contributions are totally unanticipated. The conjugated diene **1** was expected to form a tighter exciplex in nonpolar solvents by virtue of the increased charge transfer (C-T) interaction, which guarantees in principle more intimate interactions within the exciplex, but the results are opposite. The increased C-T character of the intervening exciplex is evident from the remarkable solvent effects upon the exciplex fluorescence and the product's ee. The low ee's and the missing exciplex emission in polar solvents are reasonably interpreted in terms of the facile formation of a solvent-separated or free radical ion pair ($1^{\bullet+}\cdots 3a^{\bullet-}$), components of which are separated from each other and therefore not expected to contribute to the chiral recognition.

It is inappropriate however to postulate such a solvent-separated or free radical ion pair in nonpolar pentane. Judging from the moderate enantiodifferentiations attained in pentane, diene **1** is evidently located in proximity to the excited chiral sensitizer, forming an exciplex, but the stereochemical interaction between the components does not appear to be as intimate as in the cyclooctene case. In contrast, the photosensitizations of cyclooctene under analogous conditions never show such a drastic solvent effect and give comparable ee's in polar and nonpolar solvents.²¹ This is also the case even in the photosensitization of cyclooctene with triplex-forming sensitizers possessing electron-donating phenyl group(s) in the side arm.²²

Table 4. Specific Rotations of Strained (*E*)-Cyclooctenes and (*E,Z*)-Cyclooctadienes^a

cycloalkene	$[\alpha]_D$ (solvent)	ref
(<i>E</i>)-cyclooctene	426 (CH ₂ Cl ₂)	<i>b</i>
(<i>E</i>)-1-methylcyclooctene	106 (CH ₂ Cl ₂)	<i>c</i>
(<i>E,Z</i>)-1,5-cyclooctadiene	152 (CH ₂ Cl ₂)	<i>d</i>
(<i>E,Z</i>)-1,3-cyclooctadiene (1EZ)	1380 (CH ₂ Cl ₂)	<i>e</i>
	895 (EtOH)	<i>f</i>

^a Measured at 20–25 °C, unless stated otherwise. ^b Reference 10. ^c Reference 16. ^d Reference 13; measured at 0 °C. ^e This work. ^f Reference 8; sample used was >90% ee.

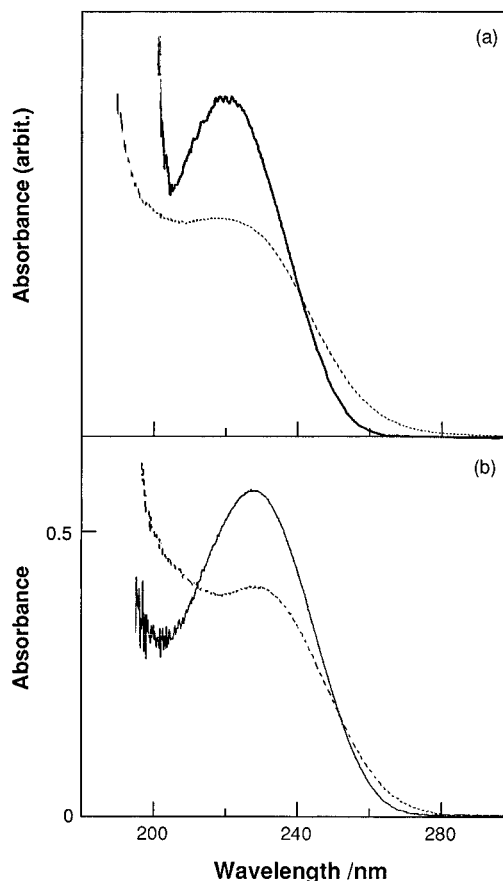


Figure 4. Absorption spectra of (*Z,Z*)- and (*E,Z*)-1,3-cyclooctadiene (**1ZZ**, solid line; **1EZ**, dashed line): (a) vapor (saturated at 23 °C) and (b) cyclohexane solution ([**1ZZ**] = 0.099 mM; [**1EZ**] = 0.111 mM).

Hence, the high C-T character itself does not immediately mean low ee's especially in nonpolar solvents, for which other factor(s) must be responsible.

Examining the crystallographic structures³³ and CPK molecular models of some mellitates **3** (R = Me, *t*-Bu, and Men), we found that placing the **1ZZ** molecule over bulky alkyl mellitate causes significant steric hindrance and the intimate face-to-face interaction becomes more difficult to attain than in the cyclooctene case. Experimentally, the following observations are indicative of more severe steric hindrance upon interaction of excited mellitate with **1ZZ** rather than (*Z*)-cyclooctene: (1) the rate of fluorescence quenching by **1ZZ** dramatically decreases by a factor of 4.5 by replacing the sensitizer's methyl with a bulky methyl group (Table 3) and (2) in spite of the much lower singlet energy of **1ZZ**, the quenching rate constant for **1ZZ** ($5.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) is of a magnitude similar to that for (*Z*)-cyclooctene ($3.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).²³ A similar unfavorable

(33) Yasuda, M.; Kuwamura, G.; Nakazono, T.; Shima, K.; Inoue, Y.; Yamasaki, N.; Tai, A. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 505.

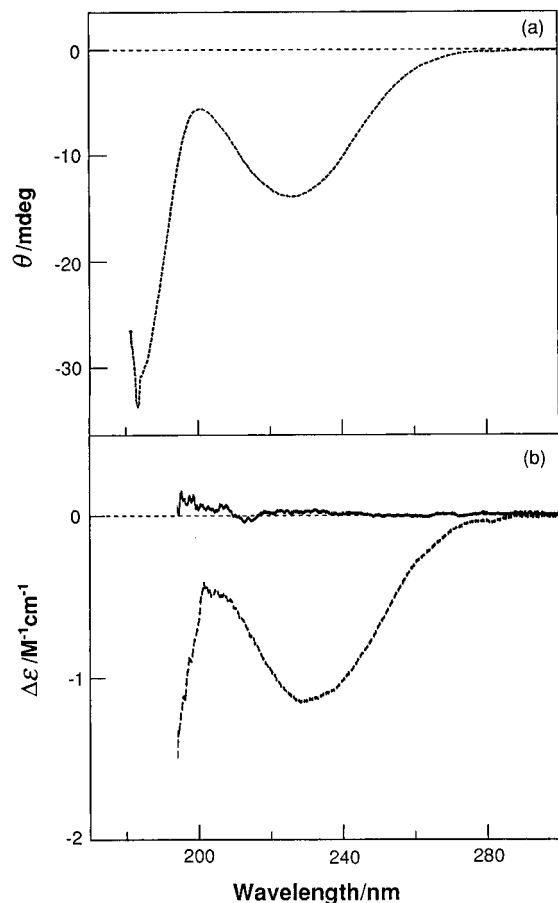


Figure 5. Circular dichroism spectra of **1ZZ** (solid line) and/or **1EZ** (10.1% ee; dashed line); the same samples and conditions as in Figure 4.

effect upon ee of increased steric hindrance in the substrate has been reported in the enantiodifferentiating photoisomerization of 1-methylcyclooctene sensitized by benzenepolycarboxylates.¹⁶ In these cases, the substrates cannot form any intimate exciplex but give rise to a more distant exciplex to afford lower ee's. We deduce therefore that there exist fairly critical steric, as well as electronic, requirements for both substrate and sensitizer structures to accomplish highly efficient enantiodifferentiation in the excited state. For a better enantiodifferentiating photosensitization system, our efforts should be directed toward a more compact substrate that forms an intimately interacting exciplex probably with high C-T character.

Chiroptical Properties of (*E,Z*)-1,3-Cyclooctadiene (1EZ**).** The enantiodifferentiating photosensitization of **1ZZ** provided us with a direct access to optically active **1EZ**, chiroptical properties of which are of much theoretical and spectroscopic interest.^{4–8,19} We carried out the preparative scale photolysis of **1ZZ** in the presence of (–)-menthyl mellitate **3a**. Isolation through the selective extraction with aqueous silver nitrate gave chemically pure **1EZ** (>99.5% by GC). The isolated sample was immediately subjected to the measurement of optical rotation and also to the GC analysis over a chiral capillary column, affording the specific rotation of $[\alpha]_D^{25} -139.6^\circ$ (*c* 1.07, CH₂Cl₂) and the enantiomeric excess of 10.1%. Repeated measurements with the same sample and independent experiments gave practically identical values within the experimental errors of $\pm 5^\circ$ in $[\alpha]_D$ or $\pm 0.5\%$ in ee. Using the specific rotation (-139.6°) and ee value (10.1%), we can determine the specific rotation of optically pure (–)-**1EZ** as -1380° (CH₂-Cl₂).³⁴

It may be interesting to compare the chiroptical properties

Table 5. Theoretical and Experimental (Chir)optical Properties of (*E,Z*)-1,3-Cyclooctadiene (**1EZ**)^a

entry	transition		relative intensity (N → V ₂ /N → V ₁)
	N → V ₁	N → V ₂	
nature ^a	$\pi_2 \rightarrow \pi_3^*$ (70%)	$\pi_1 \rightarrow \pi_3^*$ (50%)	
ΔE^b	calc. ^c	5.97	7.12
	exp. ^d	5.49 ($\Delta 0.48$)	6.77 ($\Delta 0.45$)
<i>f</i> ^e	calc. ^c	0.17	0.12
	exp. ^d	0.12 ^f	<i>g</i>
<i>R</i> ^h	calc. ^c	–35	–86
	exp. ^d	–70 ^f	–161

^a Major contribution assigned by Bouman and Hansen (ref 19). ^b Excitation energy in eV. ^c Reference 19; calculated by *ab initio* RPA calculation. ^d This work; measured in vapor phase. ^e Oscillator strength. ^f Reference 8; corrected for the underestimated absorption coefficient, see text. ^g Not determined. ^h Rotatory strength in 10^{–40} cgs.

of relevant (*E*)-cyclooctene derivatives, specific rotations of which are listed in Table 4. The $[\alpha]_D$ value of parent (*E*)-cyclooctene (426°) is exceptionally high for a simple alkene in comparison with the moderate $[\alpha]_D$ values reported for (*E*)-isomers of 1-methylcyclooctene (106°)¹⁶ and 1,5-cyclooctadiene (152°).¹³ In this context, the $[\alpha]_D$ value of **1EZ** as high as 1380°, reminiscent of the tremendously high specific rotations of helicenes,³⁵ may be attributable to the helical arrangement of the p orbitals in this highly twisted conjugated diene.

Absorption and circular dichroism spectra of the same sample (10.1% ee) were measured both in cyclohexane solution and in vapor phase. As can be seen from Figure 4, both geometrical isomers **1ZZ** and **1EZ** exhibit the absorption maxima (λ_{\max}) at almost identical wavelengths around 228 nm in solution and 219 nm in vapor phase. The comparable λ_{\max} for **1ZZ** and **1EZ** may seem rather exceptional, since highly constrained *E*-isomers of cyclooctene⁶ and 1-methylcyclooctene³⁶ absorb at longer wavelengths than the *Z*-isomers do. However, the diffused and less-intensive absorption profile of **1EZ** is characteristic of a strained (*E*)-cycloalkene. Unexpectedly, the measured absorption coefficient of **1EZ**, ϵ 3625 M^{–1} cm^{–1} (λ_{\max} 229.5 nm, cyclohexane) turned out to be significantly greater than the reported value: ϵ 2630 M^{–1} cm^{–1} (λ_{\max} 230.5 nm, cyclohexane).¹⁷

As shown in Figure 5, the CD spectrum of (–)-**1EZ** (10.1% ee) in cyclohexane exhibits one negative Cotton effect peak at 228 nm ($\Delta\epsilon -1.29$ M^{–1} cm^{–1}),³⁷ in formal agreement with the previous work,⁸ while the measurement in vapor phase reveals another yet larger negative peak at 183 nm in addition to the N → V₁ band at 226 nm. Although this new peak was predicted

(34) This is much greater than the value reported previously by Isaksson et al.: $[\alpha]_D^{20} -649^\circ$ (*c* 0.017, ethanol).⁸ The reason(s) for this discrepancy will be discussed later in ref 37.

(35) Newman, M. S.; Lednicer, D. *J. Am. Chem. Soc.* **1956**, *58*, 4765.

(36) Tsuneishi, H.; Inoue, Y.; Hakushi, T.; Tai, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 457.

(37) From the ee and $\Delta\epsilon$ values obtained above, we can evaluate the $\Delta\epsilon$ value of optically pure **1EZ** as 12.8 M^{–1} cm^{–1}. Again, this $\Delta\epsilon$ value is much greater than that ($\Delta\epsilon$ 8.83 M^{–1} cm^{–1} in ethanol) reported previously by Isaksson et al.,⁸ although their CD spectrum is essentially superimposable to ours except for the intensity. However, using the corrected absorption coefficient obtained above, Isaksson's $\Delta\epsilon$ value can be recalculated to be 12.2 M^{–1} cm^{–1} (EtOH). In spite of the different solvent used, this value is well within the experimental error, taking into account the reported ee (>90%).⁸ Similarly Isaksson's specific rotation may also be corrected for the absorption coefficient, since they determined the concentration from the absorbance.⁸ However, the corrected $[\alpha]_D$ value for the >90% ee sample is only 895° (EtOH), which is much smaller than ours, i.e., 1380° (CH₂-Cl₂). Since the $\Delta\epsilon$ values are comparable in cyclohexane and ethanol, we have no reasonable explanation for this discrepancy, although at least part of the difference may be attributed to the solvent effect.

theoretically,¹⁹ its precise location and relative intensity have not been elucidated experimentally. The theoretical and experimental (chir)optical properties of **1EZ** are summarized in Table 5. The calculated transition energies for the $N \rightarrow V_1$ and $N \rightarrow V_2$ bands are in good agreement with the experimental value obtained here, taking into account the general tendency of overestimation by ca. 0.5 eV in the *ab initio* calculations.¹⁹ Furthermore, the observed relative intensity of the rotatory strengths, i.e., $R(N \rightarrow V_2)/R(N \rightarrow V_1) = 2.3$, is in excellent agreement with the predicted value (2.5). Then, the peak at

193 nm is assigned to the $N \rightarrow V_2$ transition, although some Rydberg character would be overlapping.^{19,35,38}

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JA963160C

(38) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic: New York, 1975; Vol. 2, p 176.