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ABSOLUTE ASYMMETRIC SYNTHESIS. I. ON THE MECHANISM OF THE PHOTOCHEMICAL ABSOLUTE ASYMMETRIC SYNTHESIS OF HELICENES WITH CIRCULARLY POLARIZED LIGHT. WAVELENGTH DEPENDENCE OF THE OPTICAL YIELD OF OCTAHELICENE

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Absolute Asymmetric Synthesis. I. On the Mechanism of the Photochemical Absolute Asymmetric Synthesis of Helicenes with Circularly Polarized Light. Wavelength Dependence of the Optical Yield of Octahelicene

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Abstract: The synthesis of nonracemic yields of hexa-, hepta-, octa-, and nonehelicene with circular light was observed, and the structural and wavelength dependence of the induced optical yields was examined. The results obtained, together with a detailed consideration of the mechanism of helicene synthesis from the parent diarylolefins, indicate that the induced optical activity is due to selective reaction of enantiomeric conformations of the parent cis diarylolefins by circular light.

Numerous attempts have been made to induce asymmetric synthesis in photochemical reactions by employing circularly polarized light.[1-3] Until recently, however, the rotations found were marginal, and in no case was the source of the rotation positively identified. Furthermore, in only one experiment[4] were opposing rotations found with right and left circularly polarized light (RCL and LCL), and in this case the optical activity disappeared upon prolonged irradiation. All recent attempts to reproduce many of these results have failed.[1,5]

After the work reported here was completed, Moradpour et al.[6] reported that irradiation of compounds Ia and Ib leads to nonracemic yields of hexahelicene.

We wish to report irradiations of the 1,2-diarylethylenes (I-IV) in the presence of iodine to the helicenes VI-IX with LCL and RCL.[7-10] All resulted in the formation of an unequal mixture of enantiomers of the respective helicenes (Scheme 1).

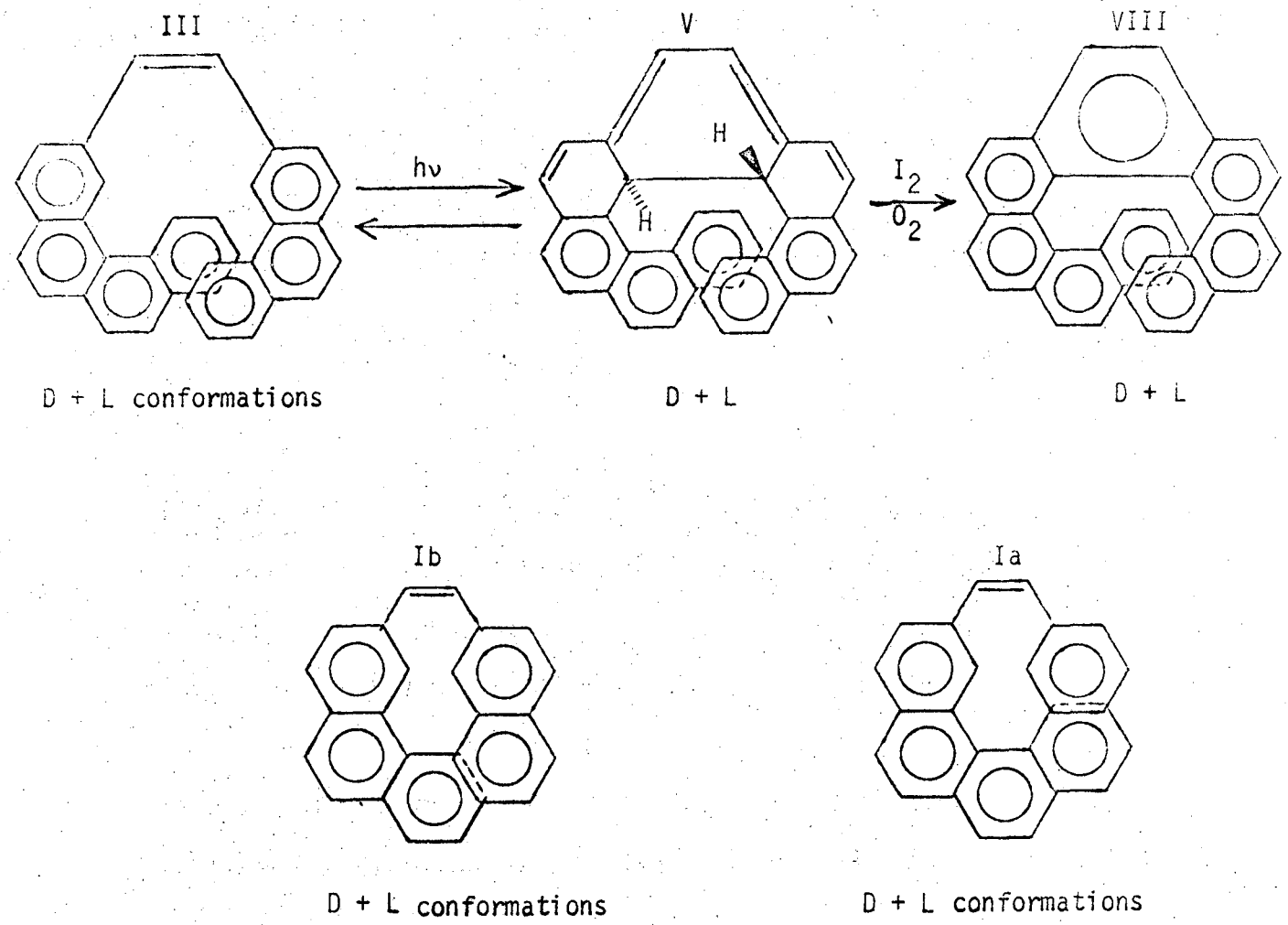
Results and Discussion

With each of the substrates I-IV, two samples were irradiated under identical conditions with RCL and LCL, and except for the marginal optical activity reported for irradiation of Ia, significant optical activity was observed.

Equal and opposite rotations were obtained in the products resulting from irradiation with RCL and LCL, and the compounds responsible for the optical activity were identified by chromatography and by the characteristic shape of the induced ORD and CD curves as the expected helicenes (Table I).

In each case it was found that irradiation with LCL led to a positive rotation, whereas irradiation with RCL led to a negative rotation.

Scheme 1



1-Phenyl-2-(2-benzo[c]phenanthryl)ethylene (Ia) → Hexahelicene (VI).

1-(2-(Naphthyl)-2-(3-phenanthryl)ethylene (Ib) → Hexahelicene (VI).

1-(2-Naphthyl)-2-(2-benzo[c]-phenanthryl)ethylene (II) → Heptahelicene (VII).

1-(3-Phenanthryl)-2-(2-benzo[c]-phenanthryl)ethylene (III) → Octahelicene (VIII).

1,2-bis-(2-Benzo[c]phenanthryl)ethylene (IV) → Nonahelicene (IX).

Table I. Irradiation of 1,2-Diarylethylenes with Circularly Polarized Light[13]

Starting Material[a]	Maximum Rotation (in °) between λ_1 and λ_2 (nm)[b]			Time (min) Irradiated	% Completion of Photolysis[c,d]
		λ_1	λ_2		
Ia[e]	0.0007 ± .0004	500	400	30	50
Ib	0.0086 ± .0004	500	370	30	20
II	0.0044 ± .0004	520	385	20	30
II	0.0100 ± .0004	520	385	45	60
II	0.0132 ± .0004	520	385	90	80
III	0.0174 ± .0004	500	410	60	30
III[f]	0.0320 ± .0004	500	410	120	30
IV	0.0144 ± .0004	500	415	120	15

a. 1 mg/ml except when otherwise stated.

b. Recorded with the Cary 60 recording spectropolarimeter in the ORD mode. The rotation are expressed as the difference between the two curves equalized at λ_1, from the samples irradiated with LCL and RCL, respectively. E.g., the last entry in the table indicates that the scan for both samples was started at the same ordinate on the chart at 500 nm (λ_1), and that at 415 nm (λ_2) the curve of the sample irradiated with LCL was 0.0144° above the one of the sample irradiated with RCL. All rotations were measured in a 2 cm quartz vessel.

c. % Completion estimated by tlc.

d. The helicenes were identified by their UV spectra and by comparison of their ORD spectra with those of authentic samples. Also the CD spectra of hexa-, hepta- and nonahelicene were compared with those of authentic samples.

e. Ia was irradiated in benzene solution, Ib - IV in toluene.

f. 2 mg/ml.

A priori three mechanisms could be invoked to explain the observed asymmetric formation of helicenes: 1) Primary formation of racemic helicenes with subsequent light-induced asymmetric destruction; 2) primary light-induced formation of racemic mixtures of dihydrohelicenes, *e.g.*, compound V, with subsequent light-induced asymmetric ring-opening to the starting olefin, *i.e.*, partial photoresolution[11] of the dihydrohelicene, this intermediate being oxidized at a slower rate to give the optically active (nonracemic) helicenes; 3) the diarylolefin precursors, which exist in conformeric D- and L- forms in rapid equilibrium at room temperature, give rise when irradiated with circular light to different amounts of excited D- and L- forms, which ring-close at a faster rate than they racemize in the excited state.

Had mechanism 1 been operative, long wavelength irradiation of the olefin with LCL would have resulted in the development of negative long wavelength optical activity (ORD and CD), while RCL would have resulted in positive optical activity. The opposite is observed.

In order to further examine the applicability of mechanism 1, asymmetric destruction of racemic hepta- and octahelicene was attempted under identical experimental conditions: no rotations were developed. (Indeed, upon prolonged irradiation of hexahelicene with RCL and LCL, Moradpour *et al.*[6] found small rotations opposite to those induced by synthesis of hexahelicene with RCL and LCL.)

Mechanism 2 involves the establishment of a III $\rightleftharpoons$ V photostationary state with an unequal distribution of the enantiomers of V resulting from their unequal absorption of circular light. Nonracemic yields of helicenes would reflect this "partial photoresolution" of V. Muszcat and

Fischer[12] have shown for a group of substituted stilbene-dihydrophenanthrene systems that the rates of the forward (III → V) and reverse (V → III) photolyses are comparable, and that the dihydrophenanthrenes aromatize quite rapidly at even low concentrations of oxidant (V → VIII). Since many of the photolyses described below required several days, even in the presence of a relatively powerful oxidant (molecular iodine with atmospheric exposure), the rate of the forward reaction to the dihydrohelicene must be slow from the cis compound. (The trans → cis conversion is rapid compared to succeeding steps.) Since the reverse reaction is of comparable rate,[12] no dihydrohelicene can accumulate for its photoreversal back to the diarylolefin to occur. Thus, if the results of Muszcat and Fischer may be applied here, it appears that mechanism 2 is highly unlikely.

In order to further clarify the above mechanistic possibilities, compound III (cis + trans) was irradiated at seven different wavelengths. The relative optical yields are plotted on Figure 1. Note that the sign of induced optical activity changes at ca. 305 nm. The sample irradiated with LCL at 410 nm was 2.7% resolved with reference to an octahelicene sample partially resolved by crystallization by Professor R. H. Martin.[13] Since the actual purity of the crystallized sample is not known, the true optical yield of the 410 nm sample may be significantly lower than 2.7%. This, taken together with an extrapolation to octahelicene from the CD of hexahelicene, led us to assume an optical yield of 2.0% for the 410 nm sample.

From our optically active octahelicene solutions the CD of octahelicene (based on the assumed 2.0% resolution of VIII in the 410 nm sample) was obtained (Figure 2). Had mechanism 1 been operative, the wavelength

dependency of the optical yield of VIII would have followed the anisotropy[14] factor ["g" = $(\varepsilon_{\ell}-\varepsilon_{r})/(\varepsilon_{total})$] of octahelicene and the induced optical activity would have changed sign at ca. 335 nm: it does not (Figure 1).

The wavelength dependence data are quite consistent with the absorption spectrum of the cis isomer of compound III, isolated by chromatography from the synthesized cis-trans mixture. Compound V, on the other hand, would in all probability have many transitions well out into the visible, if studies of the absorption of 4a,4b-dihydrophenanthrenes[12] are applicable here. Thus, if mechanism 2 were valid, one would expect a change in sign of the induced optical activity, reflecting a change in the sign in the CD of V, well above 305 nm where it actually occurs. A final result which is inconsistent with mechanism 2 is the observation by Moradpour et al. that irrdiation of Ib gives approximately four times the optical yield of hexahelicene as the irradiation of Ia.[6] Our data indicate this difference to be even greater (see Table I). Both Ia and Ib should form similar dihydrohelicenic structures, and it is reasonable to expect them to have similar capabilities for asymmetric destruction.

However, mechanism 3 can account for this difference. Hammond has noted[15] that in the S_1 state of unsymmetrical stilbenes, from which all stilbene photoclosures take place, the excitation is "localized" in the aryl group with the lower S_1 energy. Thus, in the S_1 state of cis Ib, we would expect rotation up to 180° about the napthyl-ethylene bond to be nearly free, the excitation being localized on the larger phenanthryl group. Similarly, we would expect similar rotation about the phenyl-ethylene bond in S_1 cis Ia to be nearly free. Due to the symmetry of

the phenyl group, rotation about the phenyl-ethylene bond (∿180°) in cis Ia results in interchange of its enantiomeric conformations, whereas corresponding rotation about the naphthyl-ethylene bond in cis Ib does not, due to the dissymmetry of the 2-naphthyl group.

Thus, if mechanism 3 is operative, it can be seen that although irradiation of cis Ia with circular light excites its enantiomeric conformations unequally, this imbalance of the D- and L- excited forms is greatly reduced through the above described bond rotation. Unequally excited cis Ib, on the other hand, cannot similarly racemize in the excited state, and thus produces higher nonracemic yields of dihydrohexahelicene, which forms nonracemic hexahelicene. The same is true for the III-V-VIII system, and all of the other systems here studied.

Experiments to further clarify the mechanism of nonracemic helicene production with circular light are underway.

Experimental

Synthesis of I-IV. Forty g of 2-naphthylmethylenyltriphenylphosphonium bromide was dissolved in 120 ml 1 N LiOMe-MeOH, and 10 g p-tolualdehyde was added slowly. The mixture was stirred vigorously for 5 to 10 min and filtered. Crystallization from benzene-ethanol gave 8 g (39%) 1-(2-napthyl)-2-(p-tolyl)ethylene (X), mp 188-9°. Two g X was irradiated 12 hr in a Rayonet reactor (3500 Å lamps) in 2 l cyclohexane with a few crystals of iodine and exposure to the air. The volume of the mixture was reduced to ca. 10 ml, and chromatographed (cyclohexane on neutral alumina) yielding 1.7 g (86%) crude 2-methylbenzo[c]phenanthrene (XI), mp 77-9° (lit 80-1° [17]). The crude XI was dissolved in 20 ml reagent grade CCl_4 with 1.4 g NBS and a trace of dibenzoyl peroxide, and stirred at a gentle reflux for 3 hr. The succinimide was filtered off, the

solvent removed from the filtrate by rotary evaporation, and the residue of crude 9-bromomethylbenzo[c]phenanthrene (XII) dissolved in 20 ml xylene, and stirred at reflux for 45 min. The nearly colorless, high melting (>360°) powder, 4-benzo[c]phenanthrylmethylenyltriphneylphosphonium bromide (XIII) was filtered off, and washed with xylene and pet ether. (Yield = 4 g, 96%). Addition of XIII to equimolar amounts of 1 N LiOMe-MeOH and benzaldehyde, 2-napthaldehyde, 3-phenanthraldehyde, or 9-benzo[c]phenanthraldehyde, and work-up and purification as in the preparation of X gave Ia (50%, mp 144-5°, lit 144-5° [8]), II (60%, mp 200-2°, lit 200-1° [8]), III (65%, mp 176-8°, lit 199-200° [8]; the samples obtained by this synthesis were shown by chromatography [benzene on neutral alumina] to consist of cis [mp 200-2°] and trans [mp 202-4°] olefins. Further crystallization of the synthesized mixture from benzene yielded pure trans compound, giving the mp reported by Martin[8]), and IV (40%, mp 230-2°, lit 229-230° [8]), respectively. 9-Benzo[c]phenanthraldehyde was prepared by the procedure of Angyal <u>et al.</u>[16] from crude XII. 3-Phenanthraldehyde was similarly synthesized from 3-bromomethylphenanthrene. Condensation of 3-phenanthraldehyde with 2-naphthylmethylenyltriphenylphosponium bromide in 1 N LiOMe-MeOH and crystallization from benzene-ethanol gave Ib (mp 213-5°).

<u>Irradiation procedure</u>. The light source used in all work was an SP-200 super-high pressure mercury lamp. For all experiments except the wavelength dependence the beam was collimated with a fused silica lens and passed through a chemical filter[18] to give light of wavelengths 340-400 nm. The beam was then passed through an ultraviolet polarizing filter (Polacoat Inc., PL-40) followed by a quarter wave plate centered at 390 nm (Gaertner Inc.), followed by the sample.

For the wavelength dependence the lamp was attached to a monochromator (Bausch & Lomb, 33-86-25) with UV and visible gratings (Bausch & Lomb, 33-86-25-01 and 33-86-25-02, respectively). The beam was collimated with a fused silica lens and passed through a PL-40 plate and fused silica Fresnel rhomb (Karl Lambrecht Inc.). The ellipticity of the light was calculated as the ratio of minimum to maximum intensity of the beam transmitted by a rotating PL-40 plate. At all wavelengths the light was measured at 75% circularity. Irradiations were done at 410, 390, 370, 350, 330, 310, and 290 nm with a total dispersion of 12.8 nm at each wavelength.

In all work except the wavelength studies, the diarylolefins were irradiated at a concentration of 1.0 mg/ml unless otherwise noted, with a trace of iodine and exposure to the atmosphere. The vessel used was a cylindrical quartz cell with a capacity of 6.5 ml and a 2 cm optical path. Unless otherwise noted, toluene was used as a solvent. For the wavelength dependence irradiations were performed in a similar vessel at a concentration of 0.1 mg/ml in toluene-I_2.

All samples were chromatographed (benzene on neutral alumina), and the helicenic (first) fraction was concentrated for ORD or CD analysis in a 2 cm quartz cell. Since the parent cis olefin cannot be separated from the respective helicene under these conditions, it was difficult to judge the helicene concentration by UV analysis, unless the reaction was carried to completion. (The wavelength studies demanded accurate determination of helicene concentration for the calculation of relative optical yields: thus, these reactions were irradiated to completion.)

Asymmetric destructions of heptahelicene (0.42 mg/ml and 0.12 mg/ml) and of octahelicene (0.57 mg/ml) were attempted by irradiation for 30 min and 60 min respectively, under identical conditions as the asymmetric syntheses in Table I.

UV spectra were taken on a Cary 14 spectrophotometer, CD and ORD spectra on a Cary 60 recording spectropolarimeter.

Acknowledgments

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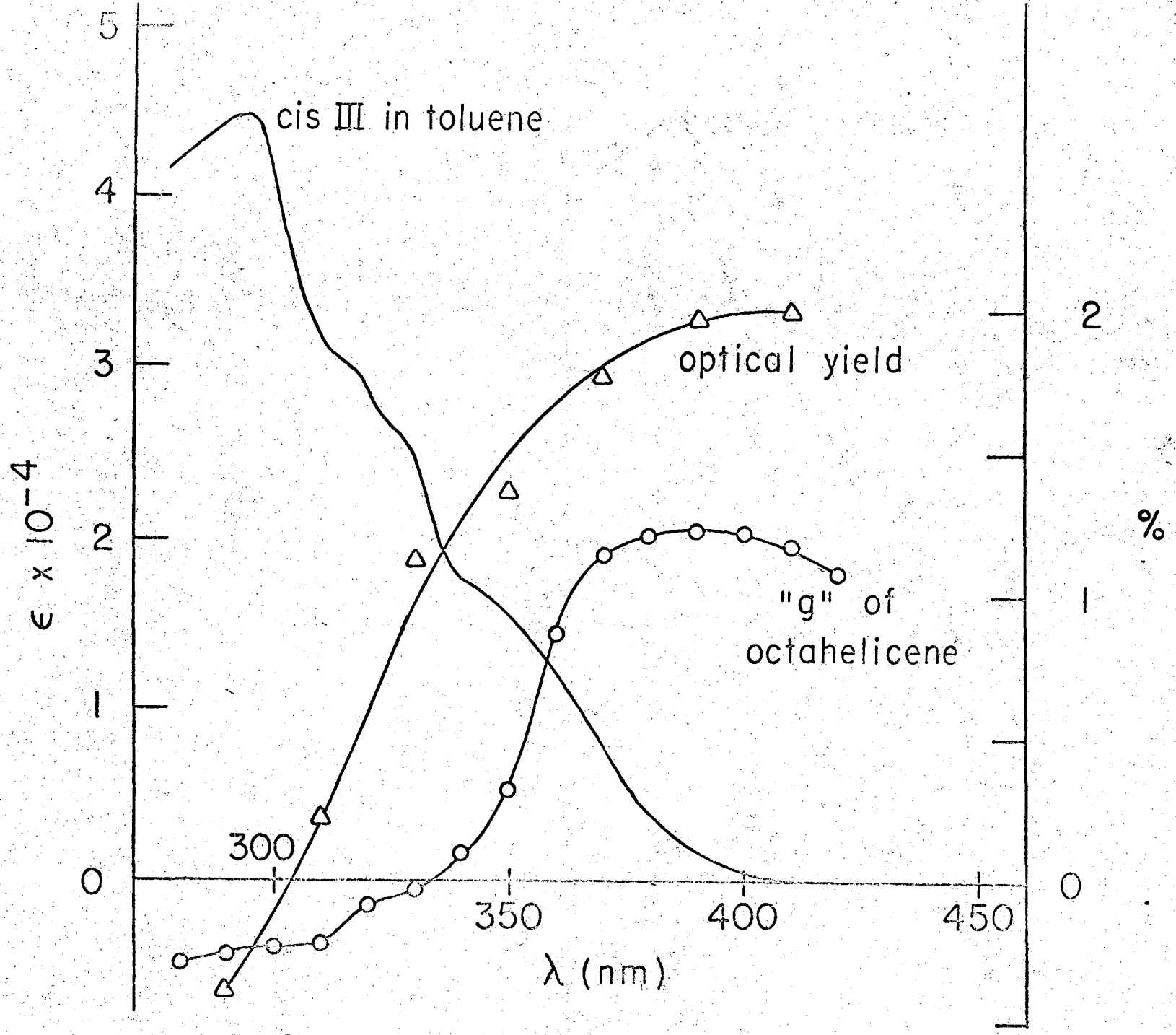
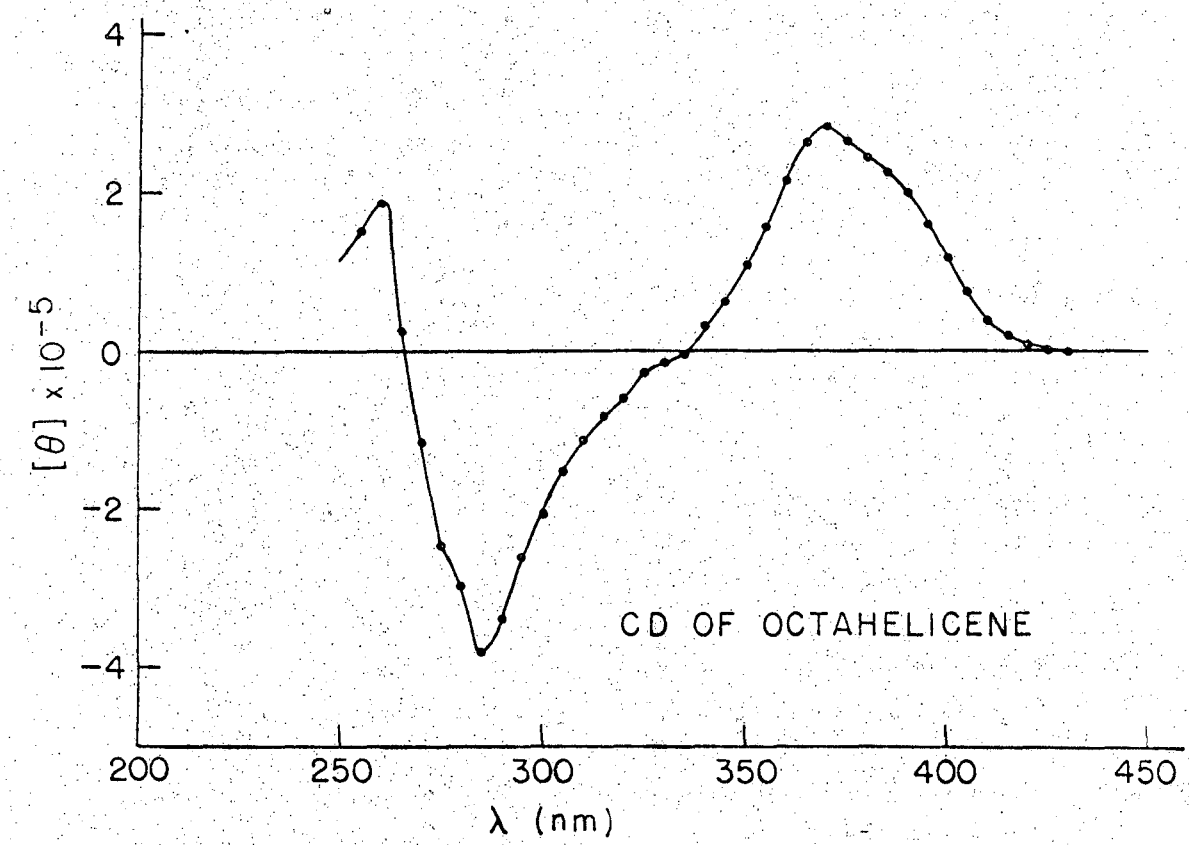


Fig. 1 XBL 715-5165



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Bernstein: Absolute Asymmetric Synthesis

Figure 2

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