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ABSOLUTE ASYMMETRIC SYNTHESIS. II. (1) ON THE MECHANISM OF THE SYNTHESIS OF NONRACEMIC HELICENES WITH CIRCULARLY POLARIZED LIGHT. STRUCTURAL EFFECTS.

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Asymmetric synthesis using circularly polarized light (CPL) of hexa-, hepta-, octa-, and nonahelicene from the corresponding diaryl olefins was recently reported (1-4). Experimental evidence involving wavelength and structure dependence led us to propose a mechanism in which selective excitation of the rotameric enantiomers of the parent diaryl olefins resulted in asymmetric formation of the corresponding dihydrohelicenes, followed by stereospecific oxidation to the helicenes (1). A mechanism involving "partial photoresolution" (5) of the intermediate dihydrohelicenes with CPL was discussed and not rigorously excluded (1). Generation of optical activity by asymmetric destruction (6) of helicenes with CPL was excluded on both experimental (1-4) and theoretical (1) grounds.

It was observed that photolysis of Ia with CPL yields hexahelicene in much lower optical yield than photolysis of Ib (1-3). In order to explain this difference we proposed (1) that rotation up to ∿180° about the aryl-ethylene bond in the lowest excited singlet (S_1) state of the cis-diaryl olefin, from which the reaction presumably takes place, requires little energy. It can be seen that this rotation interchanges the enantiomers of Ia, whereas no such racemization of Ib can occur. Thus, the unequally excited enantiomers of Ia will tend to equilibrate, thereby lowering the optical yield of the hexahelicene

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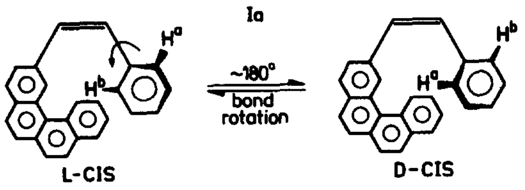
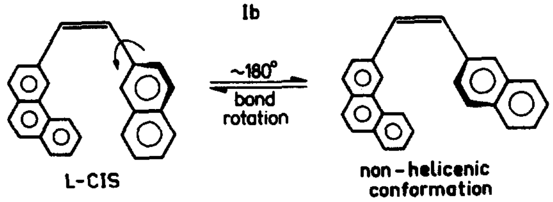
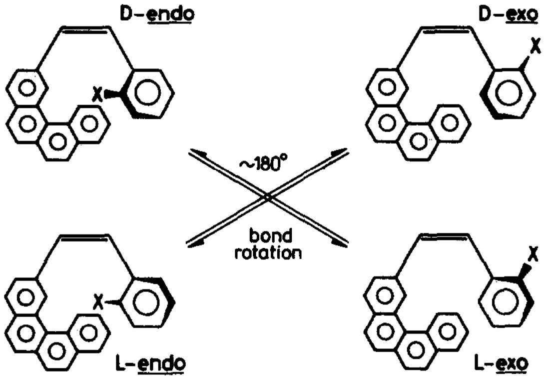
(7). This hypothesis may be tested by the irradiation of an ortho-substituted derivative of Ia with CPL.







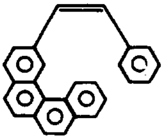
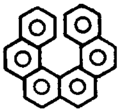
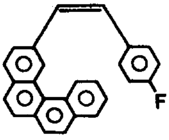
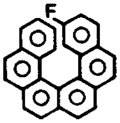
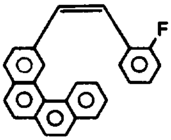
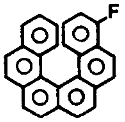
With such a compound, rotation of the phenyl group up to ∿180° no longer racemizes the cis-diaryl olefin. Furthermore, in order to reveal any electronic factors associated with this substitution, irradiations with CPL were also performed on the corresponding para-substituted compound. Otherwise, the para-substituted hexahelicene precursor was expected to behave identically with Ia.

1-(2-Fluorophenyl)-2-(2-benzo[c]phenanthryl)-ethylene (o-F-Ia) and 1-(4-fluorophenyl)-2-(2-benzo[c]phenanthryl)-ethylene (p-F-Ia) were synthesized by the Siegrist (8) method employing the appropriately substituted aldehyde anils.

Two 7.5 mg samples of each compound were irradiated at 370 nm (total dispersion, 12.2 nm) with left and right circularly polarized light (LCL and RCL) in 27 ml of toluene with a trace of I_2 added. p-F-Ia and Ia were irradiated to complete reaction, whereas o-F-Ia was irradiated to approximately 90% completion. Chromatography on neutral aluminium oxide with graded mixtures of benzene-petroleum ether separated the helicenes from the reaction mixtures.

The samples were then analyzed by polarimetry. The [α] values obtained are listed in Table 1. It is seen that irradiation of p-F-Ia with CPL produces a

Table 1. Irradiation of Hexahelicene Precursors with Left and Right Circularly Polarized Light (LCL and RCL).

Starting Material[a]	Product[b]		Optical Activity in $CHCl_3$[b,c]	
			With LCL	With RCL
 Ia		Conc.[d]	0.566	0.591
		$[\alpha]^{20}_{589}$	$+2.1\pm0.9^\circ$	$-2.4\pm0.8^\circ$
		$[\alpha]^{20}_{436}$	$+7.6\pm0.9^\circ$	$-8.0\pm0.8^\circ$
 p-F-Ia		Conc.[d]	0.535	0.534
		$[\alpha]^{20}_{589}$	$+3.4\pm0.9^\circ$	$-3.1\pm0.9^\circ$
		$[\alpha]^{20}_{436}$	$+10.7\pm0.9^\circ$	$-10.5\pm0.9^\circ$
 o-F-Ia		Conc.[d]	0.382	0.410
		$[\alpha]^{20}_{589}$	$+8.9\pm1.3^\circ$	$-10.0\pm1.2^\circ$
		$[\alpha]^{20}_{436}$	$+34.0\pm1.3^\circ$	$-31.5\pm1.2^\circ$

a) The starting material in each case was the pure trans olefin. However, the well known (9) trans-cis photoequilibration from the triplet state of stilbenes continuously generates the cis-form. b) The two fluorohexahelicenes were identified from their UV and NMR spectra. Their elemental composition was established by double focussing mass spectroscopy. c) Although neither 2- nor 4-fluorohexahelicene was resolved, it is reasonable to expect them to have the same magnitude of optical activity as hexahelicene. Since the optical activity in all three compounds is almost entirely due to the inherently asymmetric hexahelicene chromophore (10), substitution with a fluorine atom should do little to alter the electronic structures of the ground and lower excited states of this system, as shown by the fact that both 2- and 4-fluorohexahelicene have nearly the same absorption spectrum as hexahelicene itself. Indeed, Lightner *et al.* (11) have found that optically active 2-bromohexahelicene has almost the same rotatory power as hexahelicene. d) Conc. in g/100 ml.

helicene in approximately the same optical yield as from Ia, whereas *o*-F-Ia produces a helicene in significantly (x3) greater optical yield.

The observation that substitution with fluorine in the *ortho* position of Ia markedly increases the optical yield of helicene from irradiation with CPL clearly supports the above "bond rotation" hypothesis.

Furthermore, these data do not support a mechanism involving "partial photoresolution" (5) of the dihydrohelicene intermediates. Due to the inherent asymmetry of the dihydrohelicene chromophore the intermediates arising from *p*-F-Ia, *o*-F-Ia and Ia would be expected to have nearly identical CD spectra.

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