

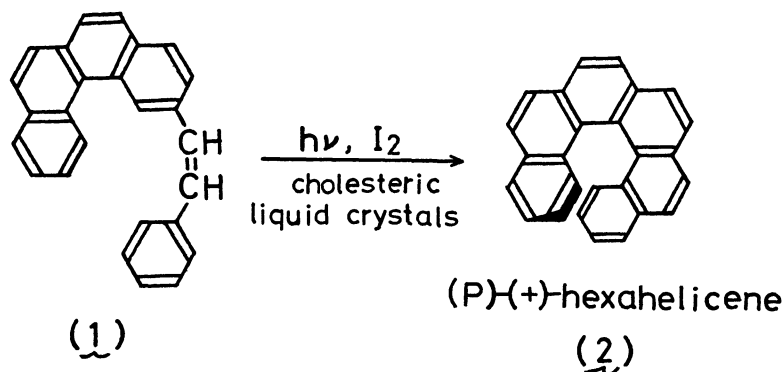
PHOTO-ASYMMETRIC SYNTHESIS OF HEXAHELICENE IN CHOLESTERIC LIQUID CRYSTALS

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Irradiation of 2-styrylbenzo[c]phenanthrene (1) in cholesteric liquid crystals yielded optically active hexahelicene (2) with optical yields around 1%.

Macroscopic helical structures formed by cholesteric liquid crystals appear attractive as solvents for asymmetric reactions, and several asymmetric reactions¹⁾ carried out in the chiral mesophases have been reported.

In this communication we describe the results of the asymmetric photocyclization of 2-styrylbenzo[c]phenanthrene (1) in cholesteric mesophases leading to optically enriched hexahelicene (2)²⁾.



A 1 wt% mixture of (1)³⁾ in a 3:2 mixture of cholesteryl nonanoate and cholesteryl chloride containing a small amount of iodine (about 5 wt% to the substrate) was sandwiched between a pair of Pyrex plates separated by an aluminum foil spacer, and was irradiated with a medium pressure UV lamp for 1.5 hr at 25°C. The reaction mixture was chromatographed on silica gel, and elution with hexane afforded a 75% yield of (P)-(+)-hexahelicene (2)⁴⁾ (run a, Table I), $[\alpha]_D^{23} +40^\circ$ (CHCl_3)⁵⁾, whose identity was established by its CD spectrum (Figure 1). Irradiation of the same starting mixture heated at 55~60°C, slightly above the cholesteric-isotropic liquid transition temperature, yielded a sample of hexahelicene with almost no optical activity (run b, Table I) suggesting that the macrostructural handedness of the mesophase controls the asymmetric induction. Although it is premature to speculate upon the details of this asymmetric transformation, it is interesting to note that a dextrorotatory hexahelicene, $[\alpha]_D^{23} +37^\circ$ (CHCl_3), was also obtained by irradiation of (1) in cholesteryl benzoate (run c, Table I) which is known to form a similar right-handed helix⁶⁾ in the cholesteric mesophase as cholesteryl nonanoate and cholesteryl chloride.

Table I. Asymmetric photosynthesis of hexahelicene in cholesteric liquid crystals

Liquid-crystal	T, °C	Time, hr	Yield	$[\alpha]_D^{23}, \text{CHCl}_3$	Optical yield ^a , %
a cholesteryl nonanoate~ cholesteryl chloride (3:2)	23	1.5	75	+40°	1.1
b cholesteryl nonanoate~ cholesteryl chloride (3:2)	55~60	1.5	74	~0°	~0
c cholesteryl benzoate	145~150	1.0	72	+37°	1.0

^a Hexahelicene, $[\alpha]_D^{24} +3640^\circ (\text{CHCl}_3)$

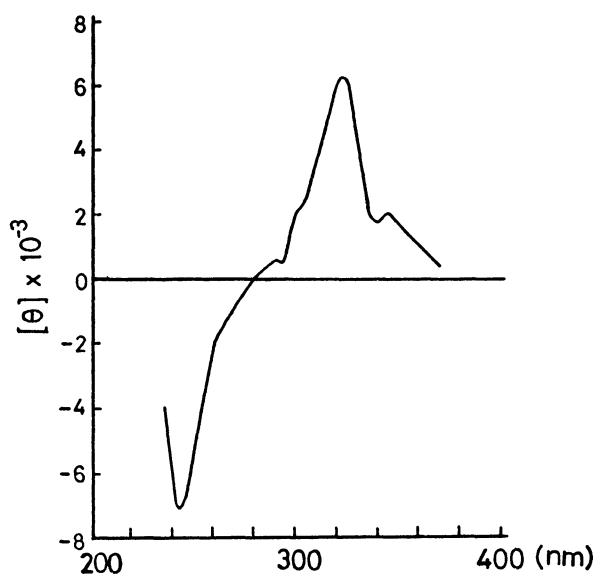


Figure 1. Circular dichroism spectrum of (+)-hexahelicene from run a in the Table I.

References and Notes

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