Mechanically Directed Absolute Asymmetric Syntheses of Helicenes in a Twisted Nematic Mesophase

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Summary Irradiation of the precursors (**1**) and (**3**) of hexahelicene (**2**) and octahelicene (**4**) in a mechanically twisted nematic mesophase gave optically active helicenes whose chiralities were found to be governed by the handedness of the twist.

In a preceding paper[1] we reported a successful asymmetric synthesis of (*P*)-(+)-hexahelicene (**2**) with a 1% optical yield by u.v. irradiation of the precursor (**1**) in a cholesteric liquid crystal.[2] Saeva and Olin's recent examination[3] of extrinsic c.d. of anthracene dissolved in 'twisted nematic mesophases' which were produced by placing the nematic crystalline material between rubbed surfaces held at an angle between 0 and 90°, led them to conclude that the twisted nematic mesophase is cholesteric in nature.

The natural extension of our photo-asymmetric synthesis in the cholesteric mesophase to this mechanically twisted mesophase is reported here.

The achiral nematic mesophase employed in our experiments was a 1 : 1 (wt %) mixture of *p*-cyanophenyl *p*-butylbenzoate and *p*-cyanophenyl *p*-heptylbenzoate reported by Saeva and Olin.[3] The precursor (**1**)[4] was dissolved in the heated (70—80 °C) nematic liquid crystal to yield a 1 wt% solution into which a trace of iodine (5 wt% to the precursor) was added. An aliquot portion (5 mg) of the mixture was introduced into an irradiation cell consisting of a pair of 25-mm square, 1·4-mm thick Pyrex plates separated by a $20\,\mu$m thick aluminium foil spacer having a hole 22 mm in diameter. To ensure correct molecular alignment, the Pyrex plates were polished by making 20 passes in a single direction with a piece of soft cotton before they were held together to make a 45° twist between the polishing directions.[3] After irradiation with a medium-pressure u.v. lamp (Toshiba SHL-100UV) for 1 h at room temperature, the reaction mixture was extracted with $CHCl_3$. Preparative t.l.c. (SiO_2 gel, elution with hexane) of the combined extracts from 10 irradiations afforded hexahelicene (**2**) in 70% yield, calculated from the observed optical density at 315 nm in hexane. Examination of the integrated (32 times) c.d. spectrum[5] at 300—350 nm in hexane gave information on assigning the absolute configuration as well as calculating the optical yield of the product (Table).

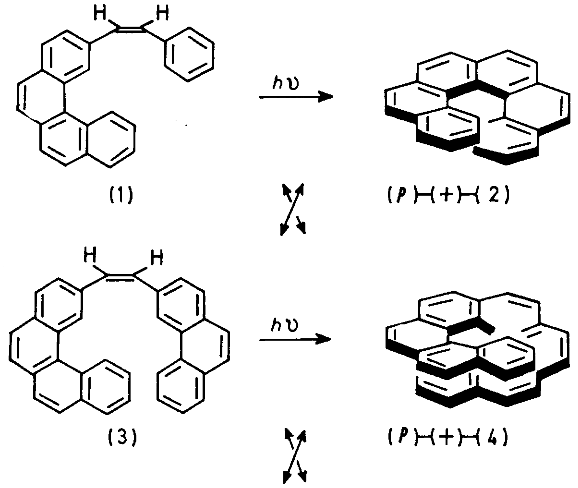

Figure. Photo-asymmetric syntheses of (*P*)-(+)-helicenes in right-handed twisted nematic mesophase.

Comparison between experiments (a) and (b) clearly indicates that the handedness of the twist of the achiral nematic mesophase determines the chirality of the photoproducts: a right-handed twist (see Figure) gives (*P*)-(+)-hexahelicene (**2**) while a left-handed twist gives the enantiomer. Experiments (c) and (d) confirm this mechanical control of the direction of the photo-asymmetric synthesis in octahelicene (**4**) affording optical yields which are five times higher[6]; irradiation in right- and left-handed twist nematic mesophases converted the precursor (**3**)[7] into (*P*)-(+)- and (*M*)-(−)-octahelicene (**4**), respectively, with 70—75% yields, whereas the reaction in the nematic mesophase having no twist gave the racemic product (experiment e).

It is interesting to note that in both cases a right-handed mechanical twist in the nematic mesophase was found to relate to *P*-chirality of the helicenes.

A preparative experiment was carried out starting from (**3**) (40 mg) and iodine (2 mg) dissolved in the nematic crystal phase. After irradiation of 200 aliquot portions in

Table. Photo-asymmetric syntheses of helicenes in twisted nematic mesophase.

Experiment	Precursor (wt %)	Handedness[b] of twist	Helicenes	$[\theta]^{d}$	% Optical yield[e]
(a)	(**1**) (1·0)	Right	(*P*)-(+)-(**2**)	$+260\pm60$	$0{\cdot}04\pm0{\cdot}01$
(b)	(**1**) (1·0)	Left	(*M*)-(−)-(**2**)	-250 ± 60	$0{\cdot}04\pm0{\cdot}01$
(c)	(**3**) (1·0)	Right	(*P*)-(+)-(**4**)	$+200\pm30$	$0{\cdot}22\pm0{\cdot}02$
(d)	(**3**) (1·0)	Left	(*M*)-(−)-(**4**)	-190 ± 30	$0{\cdot}21\pm0{\cdot}02$
(e)	(**3**) (1·0)	—[c]	(±)	*ca.* 0	*ca.* 0
(f)	(**1**) (0·5)[a]	Right	(*P*)-(+)-(**2**)	$+580\pm60$	$0{\cdot}09\pm0{\cdot}01$
(g)	(**1**) (0·5)[a]	Left	(*M*)-(−)-(**2**)	-520 ± 60	$0{\cdot}08\pm0{\cdot}01$
(h)	(**1**) (0·5)[a]	—[c]	(±)	*ca.* 0	*ca.* 0

[a] With 2·0 wt% of anthracene. [b] The handedness of a 45° twist is defined as shown in the Figure for the right-handed alignment of two polishing directions. [c] No twist. [d] $[\theta]_{325}$ and $[\theta]_{374}$, respectively, for (**2**) and (**4**). [e] Calculated from the reported $[\theta]_{325}$ $+6{\cdot}47 \times 10^{5}$ and $[\theta]_{374}$ $-9{\cdot}0 \times 10^{4}$ for (+)-(**2**) (ref. 5) and (−)-(**4**) (ref. 6), respectively.

the right-handed twist nematic mesophase, the reaction product was purified through column chromatography (Al_2O_3) followed by preparative t.l.c. (SiO_2 gel) to yield (*P*)-(+)-(**4**) (16 mg, 40% yield), m.p. 328—330 °C,[8] $[\alpha]_D^{24}$ +12° ($CHCl_3$) (0·18% optical yield)

Finally, experiments (f), (g), and (h) demonstrated an interesting effect† of added anthracene which doubled the optical yield of hexahelicene (**2**).

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† A similar effect of anthracene has been observed in the photo-asymmetric synthesis of (**2**) in cholesteric liquid crystals.

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