Contribution of Pitch and Solute-Solvent Interactions to the Photoasymmetric Synthesis of Hexahelicene in Cholesteric Liquid Crystals

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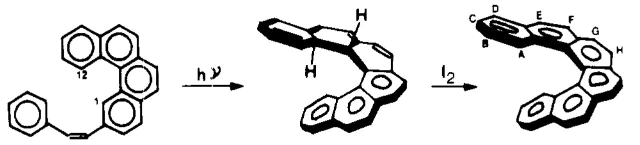
In spite of some controversy,[1-4] it seems now well established that a cholesteric liquid crystal used as a solvent for a chemical reaction can induce asymmetric synthesis.[5-7] However, mechanisms and factors governing this induction are still unclear.

Our recent results[5] during thermal reactions in cholesteric mesophases showed that asymmetric induction resulted from solute-solvent interactions without any clear evidence of a macrostructural handedness effect.

We now report some results concerning the photoasymmetric synthesis of hexahelicene in cholesteric liquid crystals, which are indicative of simultaneous contribution of pitch and solute-solvent interactions.



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For such a study, we chose a very well-documented cholesteric system, a 1.75/1.00 weight mixture of cholesteryl chloride and cholesteryl myristate. This unique system offers the possibility of running the photoasymmetric synthesis of hexahelicene in a chiral solvent which exhibits for the same chemical composition four different states of matter depending on the temperature: from room temperature to 42 °C a left-handed cholesteric, at 42 °C a compensated nematic, from 42 to 62 °C a right-handed cholesteric, and above 62 °C an isotropic liquid.[8,9]

A 1 wt % solution of olefin 1[14,28] in this cholesteric mesophase containing a small amount of iodine[10] (about 5% relative to the substrate) was sandwiched between two Pyrex plates seperated by a 0.1-mm spacer. The Pyrex upper plate was carefully polished by rubbing several times in a single direction with a lens-cleaning tissue[11] to ensure a planar alignment of the preparation (helical axis perpendicular to the plates). The uniformity of the orientation was checked with a polarizing microscope.

The required temperature was obtained by placing the cell on a thermostated plate and controlled with a microthermocouple inside the preparation. An air draft between two Pyrex plates was applied slightly above the cell to avoid any overheating from the irradiating light. The uniformity of the alignment can be again easily checked by the uniformity of the reflected color.

Table I. Photoasymmetric Synthesis of Hexahelicene in a Mixture of Cholesteryl Chloride and Cholesteryl Myristate

run	temp, °C	helix handedness	pitch, μ	$|\alpha|^{25}{}_D$ (c 1, $CHCl_3$)	% ee[a]
1	31 ± 1	left handed	−3.5	+2.0 ± 0.3	0.05
2	41 ± 1	nematic	∞	+7.0 ± 0.5	0.19
3	51 ± 1	right handed	+4.9	+10.8 ± 0.7	0.29
4	61 ± 1	right handed	+1.6	+15.5 ± 1	0.43
5	70 ± 1	isotropic		+1.0 ± 0.2	0.03
6	80 ± 1	isotopic		+0.8 ± 0.2	0.02

[a] Calculated from $|\alpha|^D{}_{max}$ +3640°.[15]

Table II. Photoasymmetric Synthesis of Hexahelicene in Compensated Nematic Phases

nematic	temp, °C	$|\alpha|^{25}{}_D$ (c 1, $CHCl_3$)	% ee
A[a]	65 ± 1	+4.7 ± 0.4	0.13
B[b]	32 ± 1	+6.1 ± 0.5	0.17

[a] Cholesteryl chloride (68%)-cholesteryl palmitate (32%).[19] [b] Cholesteryl chloride (68%)-cholesteryl nonanoate (32%).[19]

The irradiation[15] was conducted with a high-pressure mercury lamp for 1.5 h. Hexahelicene was recovered and purified by flash chromatography[12] on silica gel with hexane as eluant (85% yield[13]). Verification with an optically active sample of hexahelicene showed that no enrichment occurred during such a purification process.

From Table I, it can be seen clearly that asymmetric induction is small but the observed optical rotations were always significant[16] and several comments have to be pointed out. (1) In the isotropic phase (runs 5 und 6) the enantiomeric excess, resulting only from solute-solvent diastereoisomeric interactions, is low but in agreement with literature results.[18] (2) In a compensated nematic phase (run 2) the asymmetric induction, resulting also from solute-solvent interactions, is higher than in the isotropic phase. This clearly shows again[5] that such interactions, controlling the stereochemistry of the cyclization, are increased by the local ordering of the mesophase by a factor 10. (3) The results in the cholesteric phase indicate a clear-cut additional effect of the helical matrix: a right-handed helix affords an additive effect (runs 3 and 4) meanwhile a left-handed helix affords an opposite effect (run 1). (4) Finally, it is interesting to note that the enantiomeric excess is inversely proportional to the pitch.

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[10] A lack of iodine led to the formation of a mixture of compounds 2 and 3 which could not be separated by chromatography. Compound 2 was identified by mass spectroscopy and ^1H NMR (br s at 2.95 ppm).

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[16] We reinvestigated the experiment reported in the literature[6] using a mixture of cholesteryl nonanoate and cholesteryl chloride (3:2, left-handed helix, pitch 0.5 μ[17]). We obtained a lower enantiomeric excess: 0.29% ($[\alpha]_D$ +10.5°) instead of 1.1%. A possible explanation of this discrepancy could be the presence of a small amount of compound 2 which increases, as we have shown, the optical rotation (see footnote 10).

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Two other experiments were performed in compensated nematic phases at 32 and 65 °C (Table II) in order to show that the observed helical matrix effect was not a temperature effect.

If these data confirm the contribution of solute–solvent interactions to optical induction, already documentated in thermal reactions,[5] they show in addition and for the first time that the asymmetric induction is simultaneously dependent upon the handedness of the pitch. As a matter of fact, recently, Nakazaki,[7] in a mechanically twisted achiral nematic phase, pointed out that this asymmetric cyclization was controlled by the handedness of the mechanical twist.

The pitch contribution lies in our case in between 0.1 and 0.24% (the enantiomeric excess obtained in the cholesteric phase minus the one obtained in the compensated nematic). It is interesting to remark that this value (corresponding to 1 to 2 cal/mol) is of the same order of magnitude as the extent of asymmetric induction observed by Kagan[20,21] and Calvin[22-24] during the photosynthesis of hexahelicene with circularly polarized light (CPL). Such pitch contribution could also arise from the formation of CPL in the mesophase.[25]

However one could argue that intimate solute–solvent interactions are responsible for all the optical activity induced by the fact that the pitch could intervene in altering the manner in and degree to which the chiral solvent interacts with the hexahelicene precursors.

Such phenomena could have some contribution to the prebiotic generation of optical activity.[11,26]

Experimental Section

1-Phenyl-2-(2-benzo[*c*]phenanthrenyl)ethylene (1). To a stirred mixture of 0.01 mol of (2-benzo[c]phenanthrenylmethyl)triphenylphosphonium bromide[14] and 100 mL of anhydrous THF was added, at room temperature, 0.01 mol of *n*-butyllithium in hexane. Almost immediately after the addition of the base to the reaction mixture, the contents became orange and soon dark red. The solution was stirred for 2 h and 0.011 mol of freshly distilled benzaldehyde was added. The uncolored mixture was then stirred for 2 h and finally the solvent was evaporated. The residue was purified by a rapid filtration on silica gel (methylene chloride eluant) and the cis–trans isomers were separated by chromatography on silica gel (hexane–cyclohexane 1:1 as solvent) and identified by NMR[27] (total yield (cis + trans) = 90%).

Cis isomer: liquid; NMR (CCl$_4$) 6.40 (br s, 2 vinylic H), 6.80–7.20 (m, 14 arom H), 8.10 (d, $|J|$ = 8 Hz, H$_{12}$), 8.70 ppm (br s, H$_1$).

Trans isomer: mp, 140 °C; NMR (CCl$_4$) 1 7.10–7.90 (m, 16 H, 14 arom and 2 vinylic H), 8.90 (br s, H$_{10}$), 8.97 ppm (d, J = 8 Hz, H$_{12}$).

Photocyclization in a Cholesteric Liquid Crystal. Olefin 1 (20 mg; either the cis or the trans isomer or a mixture of the two isomers) was mixed with 2.5 g of a mixture of cholesteryl chloride and cholesteryl myristate (in the ratio 1.75/1.00) during 2 h at 80 °C (isotropic phase) under stirring. Then 1 to 2 mg of iodine was carefully dissolved in the mixture. The pitch of this cholesteric mixture was determined by the droplet method[29] while the handedness of the mesophase, known from literature,[8,9] was also controlled either by the droplet method[30] or the Grandjean–Cano method.[31]

The reaction mixture was introduced between two Pyrex plates separated by a 0.1-mm spacer. The planar alignment obtained by rubbing the Pyrex upper plate with a lens-cleaning tissue was checked with a polarizing microscope.

After irradiation (1.5 h with a 125-W high-pressure mercury lamp, temperature being rigorously controlled with a microthermocouple inside the preparation), the plates were washed with methylene chloride. Solvent was evaporated and the residue purified by flash chromatography[12] (eluant, hexane). Finally hexahelicene was purified by chromatography on silica gel (eluant, pentane): 85% yield; mp 229 °C;[14] NMR (CCl$_4$, 250 MHz)[15] 6.65 (t, $|J|$ = 7.5 Hz, 2 H, B), 7.16 (t, $|J|$ = 7.5 Hz, 2 H, C), 7.55 (d, $|J|$ = 9.0 Hz, 2 H, A), 7.79 (d, $|J|$ = 9.0 Hz, 2 H, D), 7.90 (s, 4 H, E and F), 8.05 ppm (s, 4 H, G and H).

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Registry No. (*E*)-1, 20508-12-7; (*Z*)-1, 20508-11-6; **3**, 187-83-7; (2-benzo[*c*]phenanthrenylmethyl)triphenylphosphonium bromide, 35160-98-6; benzaldehyde, 100-52-7; cholesteryl chloride, 910-31-6; cholesteryl myristate, 1989-52-2.

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Alkoxide Variation in Complex Base-Promoted Syn Dehydrohalogenations

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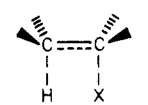
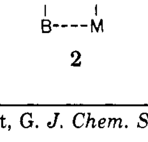
In 1972, Caubère and Coudert[1] reported a 60% yield of 1-bromocyclohexene in the reaction of *t*-BuONa-activated NaNH$_2$ with *trans*-1,2-dibromocyclohexane, 1. Under the same conditions, mostly unreacted 1 was recovered when either *t*-BuONa or NaNH$_2$ alone was the base. The unusual propensity for this complex base[2,3] to induce syn dehydrohalogenation was rationalized by Sicher's[4] transition state 2 in which interactions of the base counterion M with the leaving group X are important.



1 (60%) (36%)



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