As far as the last molecules are concerned, apparent geometrical distortions arise whenever the interacting nuclei are associated with small values of order parameters ($S_{ij}$) giving small values of direct dipolar couplings ($D_{ij}$). The observed dramatic geometrical effects have been explained by admitting a two-site (or multi-site) exchange mechanism within the ordered solvent, each site having its own geometry and orientation [2, 5].

We have recently found, however, that this kind of solute–solvent interactions is confined by no means to small molecules and the results concerning partially oriented spectra of two types of medium sized molecules will be discussed:

*a*) Substituted anilines: 3,5-dichloro and 3,5-dibromoaniline; 2,4,6-trichloroaniline;

*b*) Heterocyclic compounds: selenophene; tellurophene; isoxazole.

In the case of molecules *b*), in particular, it has been possible, by means of FT techniques, to obtain $^{13}C$–$^{1}H$, $^{77}Se$–$^{1}H$ and $^{125}Te$–$^{1}H$ dipolar couplings which, after correction for the effect of molecular vibrations, allow a satisfactory determination of molecular geometry, so that a meaningful comparison with Microwave (M.W.) findings can be performed.

The geometrical incongruencies invariably found in the accurate treatments of overdetermined systems in liquid crystal mesophases suggest that solvent induced distortions and in particular multisite exchange are quite a common phenomenon in the NMR of thermotropic mesophases.

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## Solute–Solvent Interactions in Ordered Phases: Asymmetric Induction in Cholesteric Liquid Crystals

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It is well known that diastereotopic solute–solvent interactions between a prochiral center and a chiral solvent can lead to some extent of asymmetric induction.

A cholesteric liquid crystal is indeed a chiral organized medium having a macrostructural helical shape. The question at the start of this work was to determine if the macrostructural handedness of the cholesteric liquid crystal used as a solvent of a chemical reaction can control the stereochemistry of the reaction.

Recently several papers pointed out a large controversy on such question. On the one hand, several research groups reported moderate extents of asymmetric induction during high temperature reactions conducted in cholesteric mesophases such as the Claisen rearrangement of O-allylarylethers [1], enantiomeric decarboxylation [2] or enantiomeric equilibration of sulfoxides [3]. On the other hand, Kagan and co-workers [4] did not succeed in reproducing these literature results and reported no detectable asymmetric induction during several photochemical processes. On the basis of these results these authors concluced by doubting that a cholesteric mesophase could afford appreciable asymmetric induction and that the effect of mesomorphic anisotropy ordering on asymmetric induction remains to be clearly established.

Our own results dealing with Hofman pyrolysis of quaternary salts in cholesteric medium and enantiomeric equilibraition of *trans*-cyclooctene offer evidence that the stereochemical outcome of the reaction conducted in liquid crystals is dependent on the *nature of the mesophase* and that the asymmetric induction is governed by the *'local' asymmetry of the mesophase and solute–solvent interactions* and not by the macrostructural handedness of the mesophase. The photochemical synthesis of chiral hexahelicene in a compensated nematic phase confirms strongly these conclusions. Some typical results: (*see overleaf*)

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| | | *Trans*-cyclooctene (–) *R* | |
|---|---|---|---|
| | | Yield | e.e. |
| Pyrolysis of | 180 °C-cholesteric A | 46% | 3.6% |
| Trimethylcyclooctyl | 130 °C-cholesteric B | 52% | 7.1% |
| Ammonium | 162 °C-isotropic phase C | 57% | 0% |
| Enantiomeric | 180 °C-cholesteric A | 53% | 1.9% |
| Equilibration of | 185 °C-cholesteric D | 61% | 1.4% |
| Racemic *trans*- | 185 °C-cholesteric E | 64% | 0% |
| -Cyclooctene | 180 °C-isotropic phase F | 62% | 0% |
| | | Hexahelicene (+) *P* | |
| | | Yield | e.e. |
| Photo-asymmetric | 27 °C-cholesteric G | 75% | 0.66% [5] |
| Synthesis of | 42 °C-compensated nematic H | 75% | 0.7% |
| Hexahelicene | 57 °C-isotropic phase G | 75% | 0.2% |

A: 3-(*p*-anisyl)3,5-cholestadiene. B: a mixture of 44.5% of A, 40.2% of C and 15.3% of *p*-azoxyanisole. C: 3-phenyl-3,5-cholestadiene. D: 3-(*p*-tolyl)3,5-cholestadiene. E: cholesteryl *p*-nitrobenzoate. F: compound A diluted by decaline. G: mixture of cholesteryl nonanoate and chloride in the ratio 3/2. H: mixture of cholesteryl chloride and myristate in the ratio 1.75/1.

## Empirical Models of Hydration of Small Peptides

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In the course of a general study of peptides hydration, different aspects of solute–solvent interactions have been examined for a cyclic dipeptide C–(L-Thr–L–His). This dipeptide belongs to a series of model peptides containing polar side chains which have been investigated elsewhere.

A qualitative study based on the concept of 'static accessibility' to water, allows to analyse the various processes of hydration. The maximum solvation criterium involves large destabilization of the conformations governed by intramolecular interactions. The amphiphilic character of the solute molecule seems to determine conformations which are in better agreement with those found experimentally.

A quantitative study based on energy calculations has been carried out. The stabilities of the hydration sites of the cyclic dipeptide have been evaluated by two empirical potential treatments: the Caillet–Claverie's potential and a simplified method (EMPWI) [1] using a suitable charge distribution. The agreement between the results obtained by the two methods allows to use the simplest model for calculations of more complex molecules.

The conformations of cyclic dipeptides *in vacuo* [2] have been calculated elsewhere and investigated in the solid state by crystallography [3] and in solution by NMR experiments [4]. A general comparison between all these different approaches allows to propose a semi-quantitative picture of the hydration of a small peptide.

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