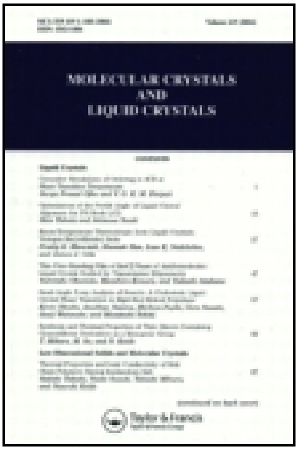

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# Liquid Crystalline Catalysis, 3[1], Monomolecular Rearrangements of Terpene Derivatives in Liquid Crystalline Solvents[†]

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The ability of limonene and linalool to rearrange in mesomorphic media is apparently determined by the constraints exerted by the solvent structure on the translational diffusions of the reactant solute molecules. Selective conversions seem to be promoted by the different media. Alkylcyclohexyl- and alkylbicyclohexyl-carboxylic acids and their mixtures with toluic acid have been used as solvents. The B structure of their smectic phases has been demonstrated by X-ray diffraction studies.

## INTRODUCTION

The guest-host intermolecular interactions resulting from dissolving an organic substance in a thermotropic liquid crystal induce local perturbations of the ordering of the mesomorphic solvent molecules[2,3] and constraints upon conformations,[4,5] orientations and diffusion properties of the solute molecules. The stereochemistry and the rate of reactions performed in liquid crystalline solvents are expected to be influenced by the anisotropy induced in all diffusions of the guest reactant molecules by the ordered structure of the solvent. We are all aware that a bimolecular reaction (a

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dimerization is sketched, for instance, in Figure 1) is promoted by molecular collisions of two reactant molecules provided that their encounters take place with sufficient energy and the correct mutual orientation.

The structural anisotropy of the transition state defines the orientational demand of the colliding molecules required for the reaction to take place. The critical orientations of bimolecular collisions can be induced by the restraints exerted by liquid crystalline solvents to the dynamic properties of the solute-reactant molecules (Figure 1). The ability of nematic and cholesteric solvents to influence or to "drive" a reaction appears so far to be very modest and quite discouraging.[1,6] The anisotropic solvation forces required to drive a reaction towards a decrease or an increase of its free energy of activation are actually expected to be linked to the rigidity of the molecular packing of the mesomorphic solvent.[1,6] Tightly ordered smectic solvents are thus expected to be more effective than nematic or cholesteric solvents whose orientational rigidity is very low and close to that of "normal" isotropic solvents.

By using Smectic B (SmB) solvents and by selecting reactions whose energies of activation are expected to be mainly determined by the entropy terms (i.e., with severe orientational demands in the transition states), we have obtained the first experimental evidence of relevant catalytic effects which can be exerted by a tightly ordered structure of mesomorphic solvents.[1,6]

In particular, the SmB phases of ZLI-1409 and ZLI-1544, supplied by E. Merck (Därmstadt), displayed their ability to reproduce in solution the solid state rearrangement of methyl *p*-dimethylaminobenzenesulfonate (methyl sulfonate ester, MSE), to its zwitterion.[1,6,7] This reaction was previously known only to take place by bimolecular methyl migrations within the crystals or the melt of pure MSE:[8] isotropic solutions of the reagent are in fact indefinitely stable. Nematic solvents were also unable to induce this MSE rearrangement.

The ZLI-1409 was further able[1] to induce the quaternization of the homologous allyl sulfonate ester (A. S. E.), a reaction which has been previously attempted in vain using the pure crystalline phase[8] of ASE. In the case of the MSE rearrangement, the perfect stacking of the reactant molecules for the methyl transfer to take place is assured both by the crystal lattice structure of the pure reagent and by the layered structure of the SmB solutions. On the other hand, the orientation required for the $S_N$-2′-allyl-transfer in the ASE rearrangement, while apparently prevented in the ASE crystal lattice by the bulkiness of the allyl group, can still be attained in the ZLI-1409 SmB solutions.

If the effects exerted by nematic and cholesteric solvents in bimolecular reactions are modest, in the case of unimolecular processes, the results

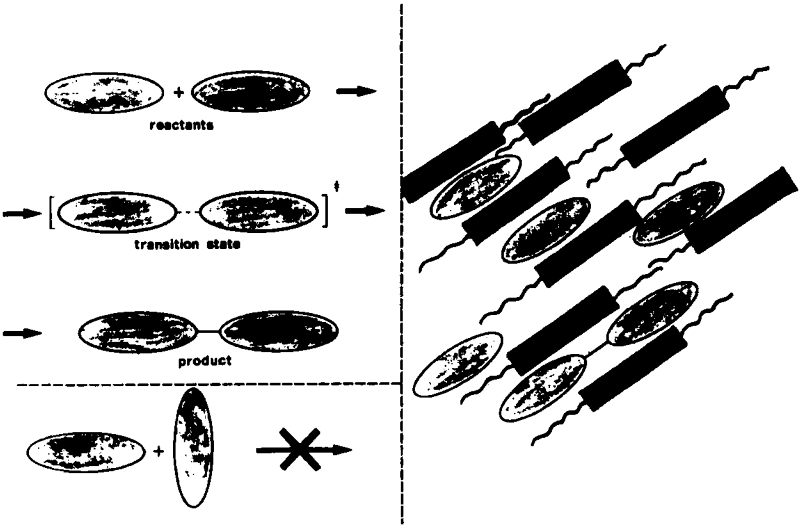


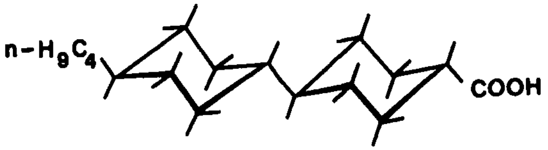
FIGURE 1 A dimerization reaction is sketched on the left side where the reagent collisions can provide, or do not provide (below), the correct mutual orientation, as required by the structural anisotropy of the transition state. A liquid crystalline solvent (right) may be able to induce the critical reagent orientation.

were even more discouraging. The preliminary report of the catalytic effect of a nematic solvent in a Claisen rearrangement was not further confirmed, and the increase in the rate of the thermal isomerization of 2,4,6 trimethoxy-*s*-triazine, observed when a nematic solvent was used, was very modest and its origin in a counterbalancing of the effects of the entropy and the heat of activation was clearly shown.[10] Hence, we decided to probe the ability of smectic solvents to influence the pathway of monomolecular thermal reactions. The sensitivity to reaction solvents of the acid-catalyzed rearrangements of monoterpenes (pinane derivatives, limonene and linalool) has been so far ascribed to a complex system of rapidly interconverting classical, or even non-classical, ionic intermediates[11] which is very easily affected by solvation. Such thermal rearrangements have been widely studied using aqueous and non-aqueous acidic media[11] and abietic acid and pine resin[12–14] matrices. Limonene and linalool, owing to their elongated shapes, have been chosen as reactivity probes. Mesomorphic media containing a carboxylic group, i.e., able to exert the required acid catalysis, have been provided by the carboxylic acids related to cyanoalkylbicyclohexyl and -cyclohexyl liquid crystals, kindly supplied by Merck (Därmstadt) for this investigation.

## X-RAY DIFFRACTION AND CALORIMETRIC STUDIES OF THE LIQUID CRYSTALLINE SOLVENTS

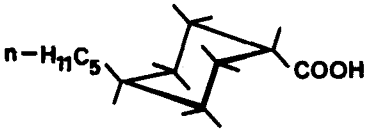
The transition temperatures of the liquid crystals used in this investigation are reported in Table I. The B assignment of the Sm phase of ZLI-1756 is mainly based on the diffraction pattern shown in Figure 2a. A single narrow ring is apparent at high angle, as it is usual for a Debye-Scherrer X-ray picture of a SmB phase,[15,16] i.e., a tightly ordered phase in which the molecular long axes are perpendicular to the Sm layers and hexagonally ordered within the layers. At low angles only the first order due to the diffraction from the Sm layers is visible. According to the notations of

TABLE I



ZLI-1756

$\mathrm{K}\ \underline{\ 155\,^{\circ}\mathrm{C}\ }\ \mathrm{SmB}\ \underline{\ 202\,^{\circ}\mathrm{C}\ }\ \mathrm{N}\ \underline{\ 235\,^{\circ}\mathrm{C}\ }\ \mathrm{I}$



ZLI-1153

$\mathrm{K}\ \underline{\ 54\,^{\circ}\mathrm{C}\ }\ \mathrm{N}\ \underline{\ 105\,^{\circ}\mathrm{C}\ }\ \mathrm{I}$

ZLI-1756+ZLI-1153 (3:1, wt/wt) Mix. 2

$\mathrm{K}\ \underline{\ 49^{\circ}\text{–}81\,^{\circ}\mathrm{C}\ }\ \mathrm{SmB}\ \underline{\ 150^{\circ}\text{–}179\,^{\circ}\mathrm{C}\ }\ \mathrm{N}\ \underline{\ 195^{\circ}\text{–}227\,^{\circ}\mathrm{C}\ }\ \mathrm{I}$

ZLI-1756+Toluic Acid (3:1, wt/wt) Mix. 3

$\mathrm{K}\ \underline{\ 68^{\circ}\text{–}86\,^{\circ}\mathrm{C}\ }\ \mathrm{SmB}\ \underline{\ 115^{\circ}\text{–}132\,^{\circ}\mathrm{C}\ }\ \mathrm{N}\ \underline{\ 160^{\circ}\text{–}203\,^{\circ}\mathrm{C}\ }\ \mathrm{I}$

ZLI-1153+ Toluic Acid (6:1, wt/wt) Mix. 1

$\mathrm{K}\ \underline{\ 33^{\circ}\text{–}51\,^{\circ}\mathrm{C}\ }\ \mathrm{N}\ \underline{\ 72^{\circ}\text{–}80\,^{\circ}\mathrm{C}\ }\ \mathrm{I}$

Ref. 15, the high angle peak corresponds to the 100 hexagonal reflection. By applying Bragg's law to a similar diffraction pattern obtained at 200°C, i.e., near the SmB–N transition, a $d_{100}$ = 4.87 ±0.04 Å spacing and hence an intermolecular distance of 5.62 ±0.05 Å were obtained. From the low angle Bragg peak, an interlayer distance $d_{001}$ = 35.0 ±0.4 Å resulted. Taking into account that the molecular length deduced from a fully extended Dreiding model is about 16 Å, the dimeric association of the structural repeating units is hence clearly demonstrated.

The diffraction pattern from a ZLI-1756 sample at 203° under a 1.1 KGauss magnetic field is reported in Figure 2b. It is a typical pattern from a nematic phase in which the molecules are aligned parallel to the magnetic field direction. The distance between the two crescents is about the same as the diameter of the low angle ring of Figure 2a. The dimeric molecular association is thus preserved in the nematic phase also, and the parallel alignment of the molecules to the normal of the SmB layers can also be argued. Moreover by the modified[17] Bragg law,

$$1.117\lambda = 2d \sin \vartheta$$

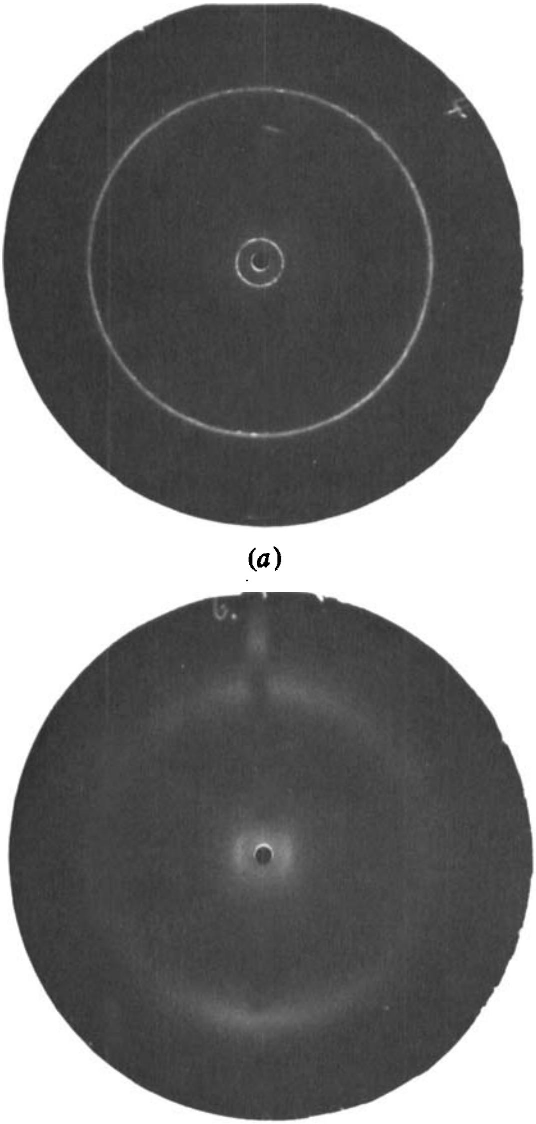
from the large angle broad peak (Figure 2b), a lateral intermolecular distance $d$ = 5.67 ±0.06 Å was obtained in good agreement with that for the SmB phase.

The transition temperatures of the mixtures ZLI-1756 + Toluic acid (3:1, wt/wt; Mix. 1), ZLI-1756 + ZLI-1153 (3:1, wt/wt; Mix. 2), and ZLI-1153 + Toluic acid (6:1, wt/wt; Mix. 3) obtained by d. s. c. measurements are reported in Table I. The structural parameters of the ZLI-1756 mixtures are the same, within experimental accuracy, as those for the pure ZLI-1756. Within the wide temperature ranges of the SmB–N transitions, a coexistence of the two phases occurs. This coexistence can also be observed with pure ZLI-1756.[17]

## RESULTS FOR THE LIMONENE AND LINALOOL REARRANGEMENTS AND A DISCUSSION OF THE SOLVENTS EFFECTS

The reactions have been carried out at 90°, 103° and 175.5°C in different isotropic and mesomorphic media and the results are reported in Tables II and III. The strict requirement of the acid catalysis is clearly emphasized by the complete stability of both terpenes, even at 175.5°C, when they are kept as pure liquids or dissolved in a non-protic solvent such as decalin.

The mesomorphic solvent molecules are all hydrogen-bonded dimers and, on passing from the isotropic to the SmB phases, a progressive segregation of aliphatic residues and dimeric carboxylic cores into separate,



(*a*)

(*b*)

FIGURE 2 X-ray diffraction pattern from the smectic (a) and nematic (b) phases of ZLI-1756. The latter is recorded at 203°C under a 1.1 KGauss magnetic field.

TABLE II

Reaction products of limonene rearrangements in different media.

| | Solvent | Temp °C | Phase | Reaction products | | | | | Others |
|---|---|---|---|---|---|---|---|---|---|
| | | | | limonene | terpinolene | α-terpinene | γ-terpinene | *p*-cymene | |
| (1) | None | 90°, 175.5° | Pure liquid | 100 | – | – | – | – | |
| (2) | decalin | 90°, 175.5° | Isotr. (no $H^+$) | 100 | – | – | – | – | |
| (3) | ZLI-1153 | 90° | Nem | 100 | – | – | – | – | |
| (4) | OBA | 103° | Nem | 100 | – | – | – | – | |
| (5) | Mix. 1 (ZLI-1153 + T. A.) | 90° | Isotr. | – | 14 | 9 | 22 | 55 | |
| (6) | ZLI-1756 | 175.5° | SmB | 100 | – | – | – | – | |
| (7) | Mix. 2 (ZLI-1756 + 1153) | 175.5° | SmB + N | 60 | 40 | – | – | – | |
| (8) | Mix. 3 (ZLI-1756 + T. A.) | 175.5° | Nem + Is | 23 | – | – | – | 37 | thymol (40) |

T. A. = Toluic Acid; O. B. A. = *p*-n-octyloxybenzoic acid.

TABLE III

Reaction products of linalool rearrangements in different media.

| Solvent | Temp °C | Phase | Reaction products |  |  |  |  |  | Others |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | linalool | limonene | terpinolene | allo-*o*-cymene | camphene | *p*-cymene |  |
| (1) None | 90°, 175.5° |  | 100 | – | – | – | – | – |  |
| (2) decalin | 90°, 175.5° |  | 100 | – | – | – | – | – |  |
| (3) ZLI-1153 | 90° | Nem | 100 | – | – | – | – | – |  |
| (4) OBA | 103° | Nem | 100 | – | – | – | – | – |  |
| (5) Mix. 1 (ZLI-1153 + T. A.) | 90° | Isotr. | – | 21 | – | – | 60 | – | 3-carene (19) |
| (6) ZLI-1756 | 175.5° | SmB | – | 64 | – | 19 | – | – | α-terpineolo (17) |
| (7) Mix. 2 (ZLI-1756 + 1153) | 175.5° | SmB + N | – | 41 | 22 | 24 | 13 | – |  |
| (8) Mix. 3 (ZLI-1756 + T. A.) | 175.5° | Nem + Is | – | 13 | – | – | 8 | 49 | *p*-cymenene (30) |

T. A. = Toluic Acid; O. B. A. = *p*-n-octyloxybenzoic acid.

close-packed, alternating strata takes place, as clearly shown by the X-ray structural results. The constraints exerted by the layered structures of the mesomorphic solutions upon the solute translational diffusion will determine the ability of the solute to reach the solvent carboxylic groups, as required for acid catalysis to take place.

At 90° and 103°C, the nematic structures of ZLI-1153 and OBA* (see reactions 3 and 4 of Tables II and III) are not conducive to rearrangement of the terpenes. By destroying the nematic packing of the solvent by addition of the non-mesomorphic toluic acid, reaction does occur (see reactions 5 of Tables II and III). At 175.5°C, the SmB structure of ZLI-1756 prevents any rearrangement of the alicyclic limonene only; the linalool is in fact converted into limonene, allo-*o*-cymene and $\alpha$-terpineol (see reactions 6 of Tables II and III). Probably because of its open-chain and quite linear structure and particularly its polar hydroxyl group, linalool is apparently able to reach, at that temperature, a location in which catalysis can be exerted. The rearrangement of the alicyclic hydrocarbon limonene requires, on the contrary, the destruction of the SmB ordering, and the amount of the conversion increases with the destructive effects exerted by the mesomorphic ZLI-1153 together with the non-mesomorphic toluic acid.

The reaction products and their ratios drastically change with the different mesomorphic solvents. The anisotropic solvation-shell and the constraints exerted by the liquid crystalline solvent on the solute molecular[4,5] conformations are expected to play a relevant role within the complex system of rapidly interconverting ionic intermediates.

In fact the final mixtures resulting from reactions performed using isotropic solutions (see Ref. 11 and reactions 5 and 8 of Tables II and III) are more complex unless *p*-cymene, the most stable and final product of almost all the reaction paths, is mainly produced. The selective conversion of limonene into terpinolene in Mix. 2 (see reaction 7, Table II) must be particularly pointed out. The very few data presently available do not allow any structural speculation on this point. We can only mention very tentatively that in mesomorphic media, terpinolene appears to be a product preferred to its isomers $\alpha$- and $\gamma$-terpinene, and that formation of "flexible" open-chain allo-*o*-cymene seems to be better promoted than that of more conformationally rigid compounds like camphene. Terpinolene, which is able to assume half-chair conformations within the cyclohexene residue, can probably more effectively pack with the "chairs" of the solvent cyclohexyl-residues compared with $\alpha$- and $\gamma$-terpinene. In conclusion, evidence of the ability of smectic solvents to exert stereochemical and catalytic effects have been obtained by this investigation.

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*p-n-Octyloxybenzoic acid.

## EXPERIMENTAL

The reaction solutions have been prepared by injecting at room temperature 16 $\mu$l of terpene into 0.4 g of the different mesomorphic solvents. Reaction tubes were sealed under $N_2$ and kept for 50 days at 90.3°, 103° and 175.5°C by immersion in boiling chlorobenzene-water, ethylenediamine-toluene and *o*-chlorophenol respectively. The final reaction mixtures were analyzed by G. C.-M. S.[12,13] A Varian 1400 instrument was used under the following conditions: 3% OV-17 on Silanized Chrom G 80–100 mesh column; 2.74 m long at programmed temp. (6°/min) from 90 to 170°; helium flow rate, 30 ml/min. MS spectra were taken on an AEI MS-12, coupled with a gas chromatograph (Biemann separator).

An Elliot toroidal X-ray camera was used with Nickel-filtered Cu$K\alpha$ radiation ($\lambda$ = 1.54°A) from a Rigaku-Denki rotating anode generator. In addition, a conventional X-ray powder diffractometer was used. The sample had a thickness of 1 mm and was held by two very thin Al sheets fixed to a circular hole in an Al matrix with a diameter of 8 mm. Heating was obtained by a hot stage with a temperature control of ±0.1°C. The differential scanning calorimeter measurements were performed by using a Perkin Elmer instrument.

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## References

1. For part 2 see: P. De Maria, A. Lodi, B. Samorì, F. Rustichelli and G. Torquati, to be published.
2. D. E. Martire in "*The Molecular Physics of Liquid Crystals*". (Eds. G. R. Luckhurst and G. W. Gray), Academic Press, London (1979) Chap. 11.
3. M. D. Croucher and D. Patterson, *J. Chem. Soc. Faraday Trans. 1*, **77**, 1237 (1981).
4. G. F. Pedulli, C. Zannoni and A. Alberti, *J. Magn. Res.*, **10**, 372 (1973).
5. B. Samorì, *J. Phys. Chem.*, **83**, 375 (1979).
6. B. Samorì and L. Fiocco, *J. Am. Chem. Soc.*, **104**, 2634 (1982).
7. G. Albertini, A. Lodi, G. Poeti, F. Rustichelli, B. Samorì and G. Torquati, *Nuovo Cimento Soc. Ital. Fis. B.*, in press.
8. C. N. Sukenik, J. A. P. Bonapace, N. S. Mandel, Pin-Yan Lau, G. Wood and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 851 (1977).
9. M. J. S. Dewar and B. D. Nahlovsky, *J. Am. Chem. Soc.*, **96**, 460 (1974).
10. W. E. Bacon, Jun-Ling Kuo and G. H. Brown, *Mol. Cryst. Liq. Cryst. Lett.*, **56**, 13 (1979).
11. C. M. Williams and D. Whittaker, *J. Chem. Soc. (B)*, (1971) 668 and 672 and references therein.
12. V. Mosini, M. L. Forcellese, and R. Nicoletti, *Phytochem.*, **19**, 679 (1980).

13. V. Mosini and A. Santi, *Ann. Chim. (Rome),* **72**, 521 (1982).
14. F. De Angelis, G. Ferretti, M. Botta and R. Nicoletti, *Gazz. Chim. Ital.*, 112, (1982).
15. J. Doucet, A. M. Levelut, M. Lambert, L. Liebert and L. Strzelecki, *J. Phys. (Paris),* **36**, 3 (1975).
16. L. V. Azaroff, *Mol. Cryst. Liq. Cryst.*, **60**, 73 (1980).
17. A. De Vries, *Mol. Cryst. Liq. Cryst.*, **20**, 119 (1973).
18. S. Melone, F. Rustichelli, B. Samorì and G. Torquati, to be published.