

## A Study of the Thermal Racemisation of (-)-3,3-Diphenyl-2-(*t*-butyl)oxaziridine and (-)-1-Chloro-2,2-diphenylaziridine in Several Nematic Solvents using a Microscopic Technique

Gian Piero Spada,\* Anna Tampieri, and Giovanni Gottarelli\*

Dipartimento di Chimica Organica, Università di Bologna, via S. Donato 15, I-40127 Bologna, Italy

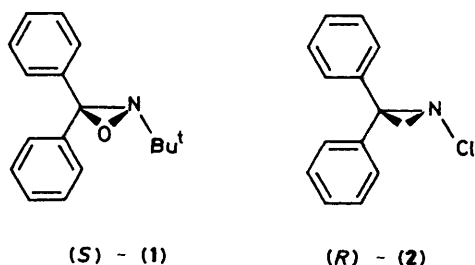
Irene Moretti and Giovanni Torre

Dipartimento di Chimica, Università di Modena, via Campi 183, I-41100 Modena, Italy

The thermal racemisation of (-)-3,3-diphenyl-2-(*t*-butyl)oxaziridine [(*S*)-(1)] and (-)-1-chloro-2,2-diphenylaziridine [(*S*)-(2)] in nematic liquid-crystal (LC) solvents has been followed directly on a thermostatic microscopic stage by measuring the variations in time of the diameters of the Grandjean–Cano disclination circles, which are associated with the induced cholesteric structure. With respect to isotropic solvents, the nematic phases exert relevant influences on the process, affecting both the activation enthalpy and entropy. Although the two variations partially compensate, the first-order rate constants are smaller in the nematic solvents.

The study of solutions of optically stable chiral solutes in nematic LCs (induced cholesteric solutions) has provided information about the stereochemistry of the solute and about the solute–solvent interactions.<sup>1</sup> In the case of rigid biaryl derivatives<sup>2</sup> and heptalenes,<sup>3</sup> the solute is well aligned in the matrix and exerts relevant influence on the nematic host, modifying, in a co-operative process, its conformer population. We reasoned that a study of the influence of the LC matrices on the thermal racemisation of chiral solutes would be interesting and should also give complementary information. We have previously researched the thermal racemisation of 1,1'-binaphthyl in several nematic matrices<sup>4</sup> and the results gave information on the compression exerted by the ordered solvent on the flexible guest and on the solute–solvent interactions in the transition state.

*N*-Alkyloxaziridines and *N*-chloroaziridines, appropriately substituted, are chiral owing to the relatively high barrier of pyramidal nitrogen inversion. The thermal racemisation of these compounds in isotropic solvents has already been studied in detail<sup>5</sup> and, at temperatures compatible with the existence of several LC phases, the process can easily be followed. Here we present a report on the effect of several nematic matrices on the racemisation of (1) and (2).



### Method and Results

When a chiral solute is dissolved in a nematic LC, a cholesteric phase is induced.<sup>6</sup> The twisting power  $\beta_M$  is a parameter which describes the ability of a solute to twist the nematic phase and can be defined as:<sup>7</sup>

$$\beta_M = (pcr)^{-1} \quad (1)$$

where  $p$  is the pitch of the macroscopic helix,  $c$  the concentration (in mol solute per mol solvent) and  $r$  the optical purity of the dopant. Equation (1) is valid for solute concentrations which do not disturb significantly the nematic phase (usually <10% w/w;<sup>8</sup> our experiments were carried out with concentrations of 1–2%, far below this limit). During the racemisation process, the pitch ( $p$ ) increases due to the decrease of optical purity  $r$ .

The pitches of the cholesteric solutions can easily be measured with an ordinary microscope following the Grandjean–Cano method:<sup>9</sup> a drop of the cholesteric solution is placed between a flat glass and a plane convex lens (radius  $R$ ), both rubbed in the same direction; a series of concentric disclination circles appears under these boundary conditions<sup>10</sup> (Figure 1). The diameter of the circles can easily be measured with a  $x$ - $y$  translator or, more accurately, with a micrometric scale in the ocular of the microscope. The pitch is obtained through the relation:<sup>10</sup>

$$p = d_n^2/[4R(n - \frac{1}{2})] \quad (n = 1, 2, \dots) \quad (2)$$

where  $d_n$  is the diameter of the  $n$ th disclination circle.

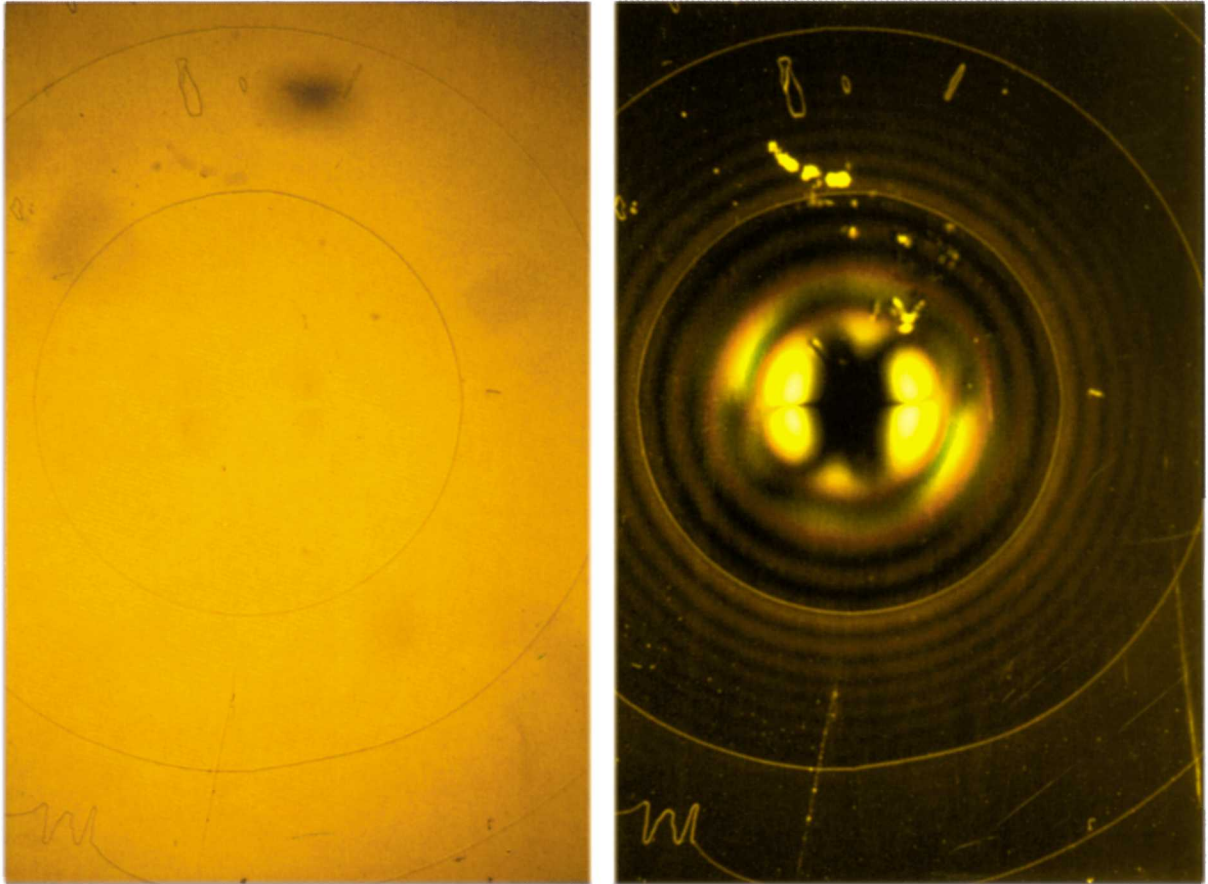
Provided the racemisation process is slow, the kinetics can be followed accurately by measuring the variation of the disclination diameters (and hence the pitch) *vs.* time according to equation (3) where  $p_0$  is the pitch at time  $t = 0$  and

$$\ln(p_0/p) = -2k^i t \quad (3)$$

$k^i$  is the rate constant for nitrogen inversion (the rate constant for racemisation,  $k^{rac}$ , being twice  $k^i$ ).

This method is new and has been briefly described without details only in ref. 4. A similar technique has been used previously to follow the diffusion of a chiral substance in nematic phases.<sup>11</sup> The interest of the method depends mainly on the fact that only a very small amount of chiral compound is needed: for derivatives (1) and (2), which do not have very high  $\beta_M$  values, an Arrhenius plot (typically with 4 points) can be obtained with less than 1 mg of compound. Using a good thermostatic platform, the kinetic constants are very accurate as each pitch is obtained by measuring at least four diameters.

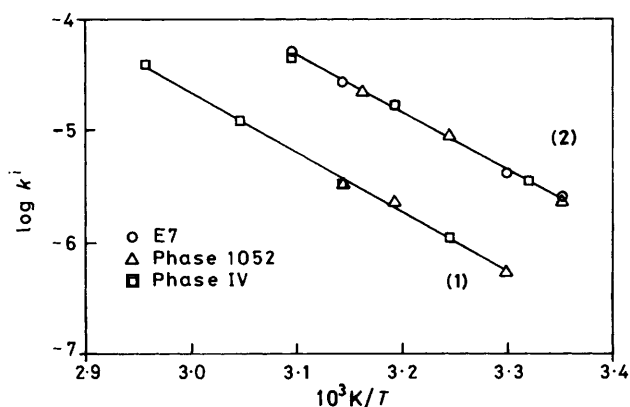
The data obtained for the racemisation of (1) and (2) are summarised in Table 1, together with those in isotropic solvents obtained from ref. 5. Also the structure of the nematic phases is



**Figure 1.** Optical microscopic textures in natural (left) and polarized light (right, crossed polars) of a cholesteric sample inserted between a plano-convex lens and a flat plate previously rubbed in the same direction (see the text). Three circular Grandjean–Cano disclinations are evident.

**Table 1.** First-order rate constants and activation parameters for thermal racemisation of (–)-(1) and (–)-(2) in liquid crystalline media compared with data in isotropic solvents. All activation parameters refer to nitrogen inversion. Errors are quoted as  $\pm \sigma$ .

| Solute               | Solvent                          | T/°C        | $10^6 k^i/s^{-1}$ | $\Delta H^\ddagger/kJ mol^{-1}$ | $\Delta S^\ddagger/J mol^{-1} K^{-1}$ |
|----------------------|----------------------------------|-------------|-------------------|---------------------------------|---------------------------------------|
| (–)-(1)              | Phase 1052                       | 30.0        | $0.55 \pm 0.05$   | $98 \pm 11$                     | $-40 \pm 8$                           |
|                      |                                  | 40.0        | $2.34 \pm 0.10$   |                                 |                                       |
|                      |                                  | 45.0        | $3.50 \pm 0.15$   |                                 |                                       |
|                      | Phase IV                         | 35.0        | $1.09 \pm 0.06$   | $101 \pm 3$                     | $-32 \pm 3$                           |
|                      |                                  | 45.0        | $3.32 \pm 0.13$   |                                 |                                       |
|                      |                                  | 55.0        | $12.1 \pm 0.6$    |                                 |                                       |
|                      |                                  | 65.0        | $39 \pm 2$        |                                 |                                       |
|                      |                                  | 60.0        | 41.7              |                                 |                                       |
|                      | Tetrachloroethylene <sup>a</sup> | 70.0        | 142               | $116 \pm 2$                     | $+19 \pm 1$                           |
|                      |                                  | 80.0        | 478               |                                 |                                       |
|                      |                                  |             |                   |                                 |                                       |
| (–)-(R)-(2)          | E7                               | 25.0        | $2.5 \pm 0.3$     | $96 \pm 3$                      | $-32 \pm 2$                           |
|                      |                                  | 30.0        | $4.1 \pm 0.2$     |                                 |                                       |
|                      |                                  | 40.0        | $16.5 \pm 0.8$    |                                 |                                       |
|                      |                                  | 45.0        | $27.1 \pm 0.6$    |                                 |                                       |
|                      |                                  | 50.0        | $52 \pm 2$        |                                 |                                       |
|                      | Phase 1052                       | 25.0        | $2.34 \pm 0.08$   | $96 \pm 5$                      | $-30 \pm 4$                           |
|                      |                                  | 35.0        | $9.3 \pm 0.4$     |                                 |                                       |
|                      |                                  | 43.0        | $22.5 \pm 0.6$    |                                 |                                       |
|                      | Phase IV                         | 28.0        | $3.46 \pm 0.04$   | $93 \pm 5$                      | $-40 \pm 3$                           |
|                      |                                  | 40.0        | $16.7 \pm 0.05$   |                                 |                                       |
|                      |                                  | 50.0        | $46.2 \pm 1.5$    |                                 |                                       |
|                      | Cyclohexane <sup>a</sup>         | 40.0        | $68 \pm 0.3$      | $104 \pm 2$                     | $+0.8 \pm 4$                          |
|                      |                                  | 50.0        | $260 \pm 0.7$     |                                 |                                       |
|                      |                                  | 60.0        | $786 \pm 3$       |                                 |                                       |
|                      | Acetonitrile <sup>a</sup>        | 40.0        | $22 \pm 0.1$      | $106 \pm 1$                     | $-1.5 \pm 2.1$                        |
|                      |                                  | 50.0        | $82 \pm 0.2$      |                                 |                                       |
|                      |                                  | 60.0        | $270 \pm 0.6$     |                                 |                                       |
|                      | t-Butyl alcohol <sup>a</sup>     | 40.0        | $63 \pm 0.2$      | $100 \pm 1$                     | $-12 \pm 4$                           |
|                      |                                  | 50.0        | $220 \pm 2$       |                                 |                                       |
|                      |                                  | 60.0        | $663 \pm 2$       |                                 |                                       |
|                      |                                  |             |                   |                                 |                                       |
|                      | CCl <sub>4</sub> <sup>a</sup>    | 60.0        | $655 \pm 3$       |                                 |                                       |
| Benzene <sup>a</sup> | 60.0                             | $481 \pm 2$ |                   |                                 |                                       |
| Ethanol <sup>a</sup> | 60.0                             | $563 \pm 4$ |                   |                                 |                                       |

<sup>a</sup> From ref. 5.**Figure 2.** Arrhenius plot ( $\log_{10} k^i$  vs.  $1/T$ ) for thermal racemisation of (–)-(1) and (–)-(R)-(2) in liquid crystals E7, Phase 1052, and Phase IV.

reported. Arrhenius plots for the same reactions are reported in Figure 2.

With respect to isotropic solutions, for both derivatives the reaction rates in the nematic solvents are smaller and the activation constants show variations which are small but statistically relevant for  $\Delta H^\ddagger$  and more important for  $\Delta S^\ddagger$ : for derivative (1) the difference is  $-59 J mol^{-1} K^{-1}$ . The variations observed on changing the nematic solvent are, in contrast, within experimental error, showing that the effect of the mesophase is not specific as is also indicated by the comparable values measured for the rate constants.

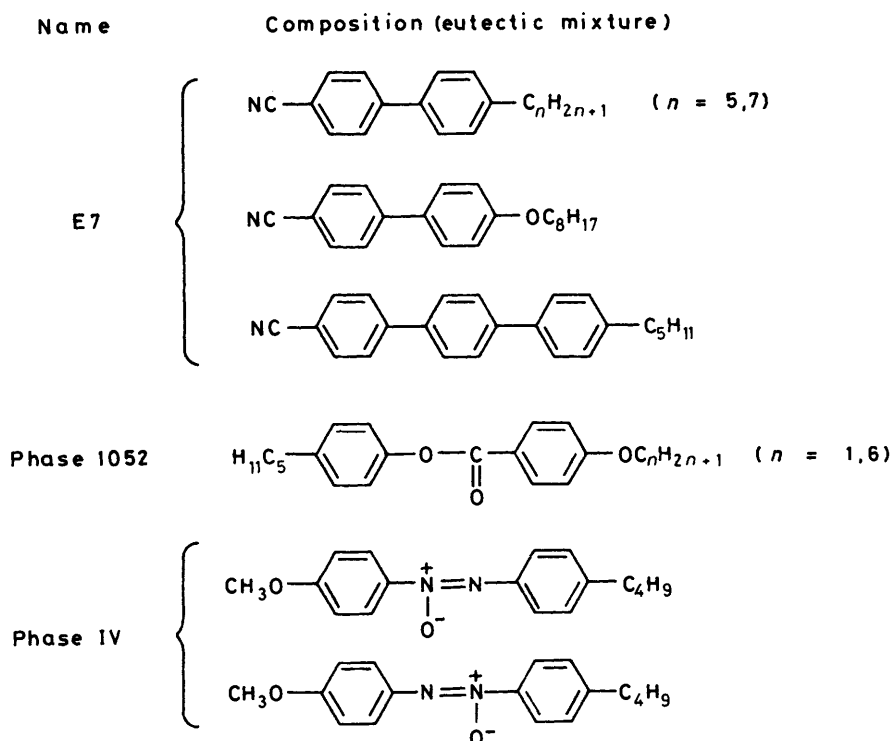
**Table 2.** Twisting power of (–)-(1) and (–)-(2) in nematic solvents. A positive value of  $\beta_M$  corresponds to a right-handed<sup>a</sup> induced cholesteric.

| Solvent    | $\beta_M/\mu m^{-1}$ |             |
|------------|----------------------|-------------|
|            | (–)-(1)              | (–)-(R)-(2) |
| E7         |                      | +22         |
| Phase 1052 | +3.1                 | +12         |
| Phase IV   | +3.2                 | +16         |

<sup>a</sup> Helical handedness was determined from the sign of the rotatory power<sup>12</sup> and from the sense of the spiral-like disclinations observed under circular boundary conditions.<sup>10</sup> For experimental details, see, for example, ref. 6(c).

The general trend can be explained by considering that the nematic solvents exert a compression on the chiral compound, facilitating the attainment of the transition state, which, owing to the planarity of the molecular moiety around the nitrogen, is better aligned in the nematic host. The lack of specificity of the nematic solvents is almost certainly correlated to the bulky structure of both derivatives, which are unlikely to pack well with any of the nematic hosts.

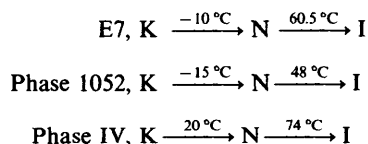
This situation is confirmed by the values of the twisting powers  $\beta_M$  (Table 2), which are relatively small,<sup>1</sup> indicating that the packing with the solvents in the ground state is not tight, especially for derivative (1). The removal of the steric hindrance in the planar transition state allows better packing, hence the decrease of  $\Delta S^\ddagger$ ; this difference is more consistent for derivative (1), which displays the smallest value of  $\beta_M$ , indicative of severe steric hindrance in the ground state. The results obtained for the



racemisation of 1,1'-binaphthyl<sup>4</sup> in several nematics are in line with the present interpretation (the activation enthalpy is smaller than in isotropic solvents and the activation entropy more negative), indicating again that the mesophases exert compression which facilitates the attainment of the planar transition state which in turn packs very efficiently with the solvent. However, in this case, the effects are, in general, greater and the variations with the structure of the nematics are relevant (for example in MBBA,\*  $\Delta H^\ddagger = 98 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -37 \text{ J mol}^{-1} \text{ K}^{-1}$ , while in E7, which is structurally similar to the solute,  $\Delta H^\ddagger = 65 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -109 \text{ J mol}^{-1} \text{ K}^{-1}$ ) as the solute-solvent interactions in both the ground and transition states are more specific.

### Experimental

**Materials.**—(–)-3,3-Diphenyl-2-(*t*-butyl)oxaziridine [(–)-(1)],  $[\alpha]_D = -224^\circ$  ( $c = 0.5$ , chloroform), 87% e.e., was obtained from *N*-(*t*-butyl)diphenylimine as previously described.<sup>5a</sup> (–)-(R)-1-Chloro-2,2-diphenylaziridine [(–)-(R)-(2)]  $[\alpha]_D = -151.7^\circ$  ( $c = 0.5$ , chloroform), 50% e.e., has been prepared from the corresponding 2,2-diphenylaziridine according to the reported procedure.<sup>5b</sup> Liquid crystals E7 (from BDH), Phase 1052, and Phase IV (from Merck) were used as received. Their structures are reported below. The undoped phase transition temperatures are:†



**Thermal Racemisations.**—Solutions of (–)-(1) or (–)-(R)-(2) (ca. 0.5 mg) in the liquid-crystalline solvent (50 mg) were

prepared by mixing the two components in a small vial, heating the mixture for several seconds above the isotropic transition temperature, and stirring it for ca. 20 min at room temperature. One drop of the solution was placed on a glass plate which had been rubbed in one direction with tissue paper. The plate was placed on a Linkam TH600 thermostatted microscopic stage, where the diameter of the hole was increased to 5 mm in order to allow the observation of several Grandjean-Cano circles.

A plano-convex lens (curvature radius ca. 40 mm), which had been rubbed previously with tissue paper, was placed over the drop so that the rubbing directions were parallel. Both lens and the plate were coated with a thin layer of polyvinyl alcohol in order to facilitate the alignment of the mesophase. The distance between the concentric circles, as they appeared through the microscope, was measured as a function of time with a micrometric scale in the ocular of the instrument. The error in the determination of the pitch values is smaller than  $\pm 3\%$ .

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\* MBBA: *N*-(4-methoxybenzylidene)-4-butylaniline.

† K: crystal; N: nematic; I: isotropic.

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