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Spontaneous mirror symmetry breaking in a re-entrant isotropic liquid

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An achiral double-swallow tailed tetracatenar compound forms a re-entrant isotropic liquid between a bicontinuous cubic phase and a nematic liquid crystalline phase. This isotropic liquid was found to represent a conglomerate of two immiscible chiral liquids. The chirality is retained and eventually becomes uniform at the transition to the cubic I432 phase.

According to natural laws a decrease in temperature should lead to an increase of molecular order, which is the reason for the well-known observation that compounds melt upon increasing the temperature. But there are also rare cases of inverted phase behaviour, where the more symmetric isotropic liquid phase is formed as temperature is decreased (or pressure is increased). This so-called re-entrant behaviour has attracted significant interest as it apparently contradicts fundamental thermodynamic rules according to which a high temperature phase always has higher entropy than a low temperature phase. The re-entrant behaviour was previously investigated mainly for liquid crystalline phases and especially for nematic phases (N_{re}).¹ Re-entrant isotropic liquids (Iso_{re}) were first observed by Yu and Saupe in lyotropic systems² and were related to a change in the shape of micellar aggregates.³ First indications of Iso_{re} phases in solvent free systems came from disc-like molecules with naphthalene⁴ or truxene cores.⁵ Re-entrant isotropic phases were also found at the transition from columnar to lamellar organization of disc-like molecules^{6,7} where formation of a bicontinuous cubic phase is suppressed. Another group of compounds forming Iso_{re} phases are rod-like oligomers. An Iso_{re} phase occurring between a lamellar and a nematic phase was observed for rod-like poly(dialkylsilanes) with narrow molecular weight distribution.⁸

Percec *et al.* observed the existence of an Iso_{re} phase for oligomers with polycatenar (taper-shaped) side chain mesogenic units with a degree of polymerization around ~ 5 below a hexagonal columnar phase.⁹ A re-entrant isotropic phase was

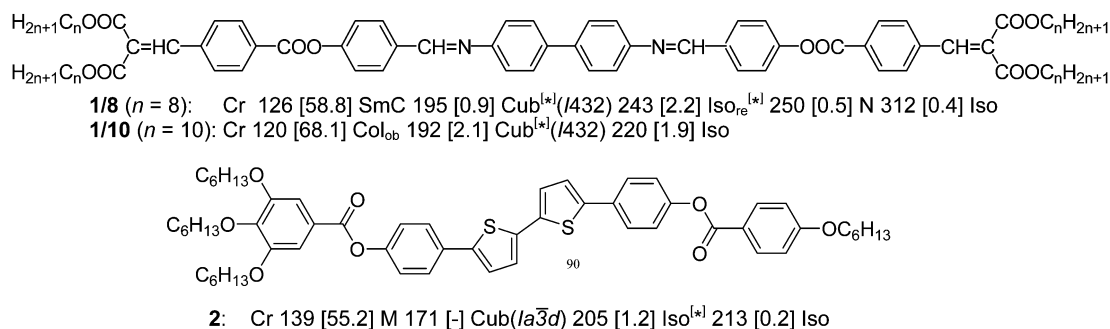
also found for a bent-core molecule, in this case occurring below a nematic phase and above a 3D tetragonal phase.¹⁰ The first observation of a re-entrant isotropic liquid for a rod-like molecule was reported for the tetracatenar double-swallow tailed compound **1/8** by Weissflog *et al.*[†]¹¹

Herein we report that the Iso_{re} phase of this compound undergoes spontaneous mirror symmetry breaking with the formation of a liquid conglomerate. The phase transition temperatures and transition enthalpies of **1/8** are shown in Scheme 1. Upon heating a SmC phase forms first, which is then replaced by an optically isotropic cubic phase (Cub) at around 195 °C and this cubic phase melts into a first isotropic liquid (Iso_{re}) at 243 °C. Upon further heating, at 250 °C the birefringent texture of a nematic phase appears (N), and disappears again at the transition to the second isotropic liquid (Iso) at $T = 312$ °C. Thus there are two distinct isotropic liquid phases separated by a nematic phase; the low temperature phase is considered as a re-entrant isotropic liquid, leading to the phase sequence Cub- Iso_{re} -N-Iso. Between crossed polarizers the two isotropic liquids are indistinguishable; they are optically isotropic and have approximately the same low viscosity. However, if investigated under a polarizing microscope with an analyzer rotated by a small angle of ~ 2 – 5° out of the precise 90° position with respect to the polarizer, these two liquid phases appear to be very distinct. In the high temperature Iso phase there is no visible change, compared to the view through crossed polarizers, except that the area of view becomes slightly brighter.

In contrast, in the Iso_{re} phase dark and bright domains become visible. Rotating the analyzer in the opposite direction leads to an inversion of the brightness of these domains (see Fig. 1a and b). If the sample is rotated between crossed polarizers no change is observed. The combination of these two experiments indicates that this liquid is formed by chiral domains with opposite handedness ($Iso_{re}^{[k]}$ phase). The chirality is retained at the transition to the cubic phase (Cub^[*]), where growth of the cubic phase starts inside the domains. The domain chirality determines the chirality of the developing cubic phase which rapidly grows with the once chosen chirality

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Scheme 1 Formula, transition temperatures (observed on heating; $T/^\circ\text{C}$) and associated enthalpy values (in brackets; $\Delta H/\text{kJ mol}^{-1}$) of the compounds under discussion;^{11,17} abbreviations: Cr = crystalline solid; SmC = tilted smectic phase; Col_{ob} = columnar phase with oblique lattice; Cub = cubic phase with space group in brackets; Iso_{re} = re-entrant isotropic liquid; N = nematic phase; M = unknown mesophase; Iso = isotropic liquid; [*] indicates the presence of chirality.

sense over the field of view, leading to a conglomerate of very large chiral domains (several μm^2 –1 mm^2) or even uniform chirality of the whole sample (several mm^2 –1 cm^2). In the case of uniform chirality rotating the analyzer in the clockwise or the anti-clockwise direction gives rise to a darker or brighter image due to the distinct direction of the rotation of the polarized light (see Fig. 1c and d).[‡] Uniform chirality results if only one germ is formed which rapidly grows, leading to a cubic single LC. Though the growth slows down at the transition to a liquid domain with opposite chirality, the chirality sense once selected is retained. The outcome is stochastic, *i.e.* in the absence of external chirality either chirality is formed with equal probability. No indications of chirality could be detected in the SmC phase¹² and the nematic phase.^{13,14}

Unfortunately, due to the high temperature regions of these mesophases, all being above 240 $^\circ\text{C}$, XRD investigation of the Iso and N phases was not possible. However, based on the molecular structure, involving a very long rod-like aromatic unit combined with several alkyl chains, a cybotactic structure^{15,17} could be assumed for the N and Iso phases, similar to that reported for compound **2** (Scheme 1).¹⁷ The self-assembly of the polycatenar compounds **1/n** is strongly affected by the strength of segregation of the alkyl chains from the rod-like aromatic cores. This gives rise to a transition from the nematic to positionally ordered LC phases (SmC, Cub, Col) upon increasing the chain length or decreasing the temperature. The change in the interface curvature leads to a transition from lamellar (SmC) to cubic (Cub) and columnar (Col_{ob}) phases upon increasing the chain length or rising the temperature (see Fig. 2a).^{11,16}

Spontaneous mirror symmetry breaking with chiral conglomerate formation in isotropic liquids was previously reported for the tetra-catenar compound **2** and related compounds with a non-symmetric distribution of the terminal alkyl chains (see Scheme 1).^{17–19} In this case the conglomerate liquid occurs above a cubic phase, followed by a second transition to an achiral isotropic liquid phase. In contrast to compound **2** in compound **1/8** the chiral Iso_{re}^[*] phase and the achiral Iso phase are separated by an additional nematic phase.

Chirality is considered to arise from a local twist caused by the clashing of the bulky peripheral alkyl groups of adjacent rod-like molecules, distorting their parallel alignment if organized

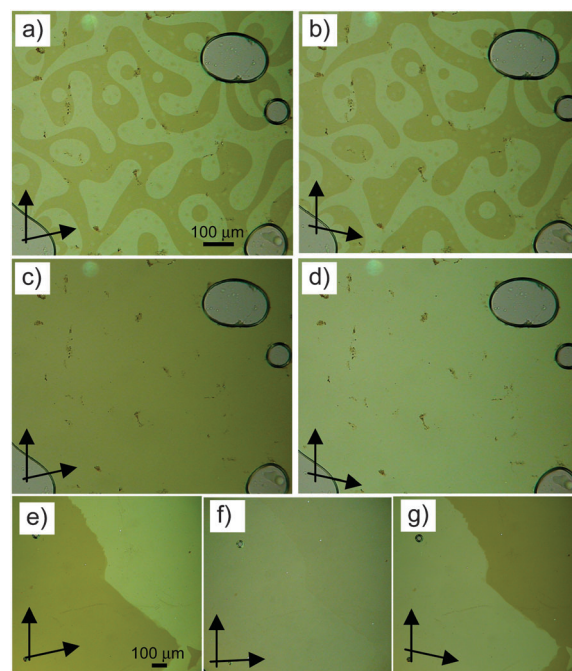


Fig. 1 (a–d) Textures of compound **1/8** as observed between slightly uncrossed polarizers (direction of the polarizers is indicated by arrows); (a and b) in the conglomerate of the Iso_{re}^[*] phase at $T = 247^\circ\text{C}$ and (c and d) in the Cub^[*](/432) phase after cooling to $T = 240^\circ\text{C}$; during the growth of the cubic phase huge domains are formed, leading to uniform chirality throughout the whole sample; indicated by distinct brightness upon changing the direction of the analyzer; (e–g) textures of compound **1/10** in the Cub^[*](/432) phase as obtained upon cooling from the achiral isotropic liquid ($T = 215^\circ\text{C}$); cooling rates were 5–10 K min^{-1} and the sample thickness is $\sim 25 \mu\text{m}$. Ordinary non-treated microscopy glass plates were used. Conglomerate formation was observed independent of the sample thickness, though the visibility is increased with growing thickness; the cooling rate only affects the domain size.

in ribbons or columns (see Fig. 2b).^{18,19} In columnar phases the lateral coupling between the ribbons or columns is weak and therefore chirality synchronization along the aggregates is only short range.^{18–20} It becomes long range in the cubic phase where the nodes of the nets of columns (ribbons) in the bicontinuous (/a3d phases) or tricontinuous networks (/Im3m/432 phases, see Fig. 2c²¹) provide an efficient transmission of chirality over



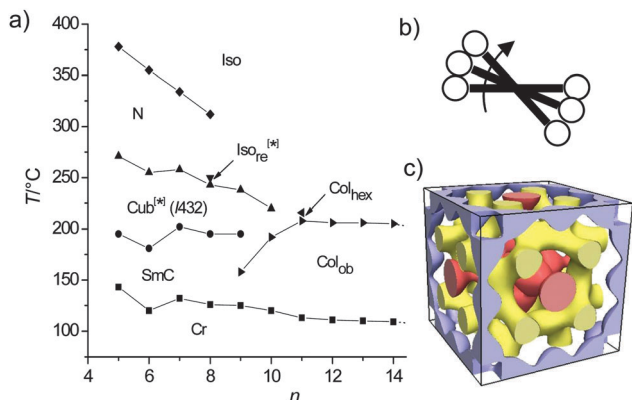


Fig. 2 (a) Mesophase types and transition temperatures of compounds **1/n** depending on alkyl chain length, for abbreviations, see Scheme 1;^{11b} (b) the development of a helical twist by clashing of bulky peripheral groups. (c) Model of the tricontinuous cubic Cub^[*]/Im $\bar{3}$ m (I432) phase formed by three networks (red, yellow and blue) involving the aromatic cores (helices or twisted ribbons) and separated by the fluid alkyl chains.¹⁸ The bicontinuous cubic phases with chiral I432 space group have the same electron density distribution and thus the same fundamental structure as proposed for the achiral tricontinuous cubic Im $\bar{3}$ m phases.^{21a}

macroscopic distances.¹⁸ Thus bicontinuous cubic phases provide templates for helical molecular packing supporting chirality synchronization of chiral conformations of the involved transiently chiral molecules.^{18,19} Transient chirality results if twisted chiral conformations have lower energy than non-twisted achiral conformers.²² For compounds **1/n** the chirality of molecular conformations could be provided by the twist of the carboxyl groups in the peripheral phenylbenzoate units²³ and probably also by the twist of the biphenyl core. The cubic phases of compounds **1/n** with $n = 5-10$ (see Fig. 2c) form chiral conglomerates, too (see Fig. 1e–g). Chirality confirms an I432 cubic phase (the chiral version of the Im $\bar{3}$ m lattice) and excludes an Ia $\bar{3}$ d lattice, which would be achiral,¹⁸ in line with the previous phase assignment to Im $\bar{3}$ m based on XRD.²⁴ In the Iso_{re}^[*] phase of **1/8**, occurring at temperature just above a cubic phase, a local cybotactic structure of twisted ribbons and chirality synchronization of the involved transiently chiral molecules are retained. Enantiophobic chirality synchronization^{19,22} allows a denser packing of the molecules with uniform conformational chirality, providing an enthalpy gain which is sufficient to overcome the entropic penalty of demixing even in the liquid state.^{17,19} Upon further increasing the temperature the cybotactic cluster size decreases and at a certain limit the entropy penalty of demixing becomes dominating over the chirality synchronization enthalpy gain and an achiral liquid is formed. In the case of compound **1/8** a parallel alignment of the molecules is retained and an achiral nematic phase is formed after removal of chirality synchronization. The parallel alignment of the long axes of the rod-like molecules provides an energetic advantage, compensating the energetic penalty by a less dense mixed organization of the conformers. The nematic phase then undergoes a transition to the achiral isotropic liquid upon further increasing the thermal energy as typical for rod-like LCs. Thus, the phase sequence Iso_{re}^[*]–N–Iso

with re-entrance of an isotropic liquid, being a chirality synchronized liquid, is in line with an increasing entropy with increasing temperature.

Compound **1/10** with longer alkyl chains forms no nematic phase and there is a direct transition between the chiral cubic phase and the achiral isotropic liquid without an Iso_{re}^[*] phase (see Fig. 1e–g), *i.e.* chirality develops just at the Iso–Cub^[*](I432) transition. This indicates that in this case a 3D network is required for chirality synchronization. Obviously the molecular chirality is relatively weak for compounds **1/n** and longer alkyl chains are unfavourable for chirality synchronization as they decrease the core packing density. Also for compounds **1/5–1/7** no Iso_{re}^[*] phase is observed and the Cub^[*](I432) phase directly transforms to the achiral N phase (Fig. 2a). In this case the shorter chains lead to smaller cybotactic clusters, providing less support for chirality synchronization and the parallel alignment in an N phase becomes dominating.

In summary, chirality synchronized re-entrant isotropic liquids can have a lower entropy than achiral anisotropic LC phases occurring at higher temperature, thus supporting the re-entrance of an isotropic liquid phase.^{17,18} Chirality synchronization could possibly also contribute to the stabilization of re-entrant isotropic liquids in the phase sequences of disc-like molecules, especially in cases where their occurrence is obviously not related to the frustration at the lamellar-columnar cross-over.^{4,5}

Notes and references

† Also direct transitions between two isotropic liquid phases (Iso₁/Iso₂) were observed above cubic,^{21b,25} chirality frustrated and tetragonal LC phases.¹⁰

‡ In the achiral Iso phase rotation of the analyzer in the opposite direction would give identical brightness.

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