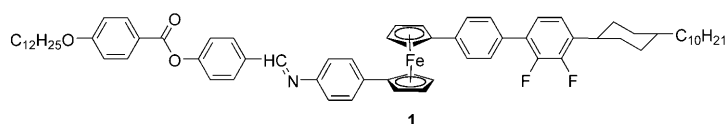


Novel Tetrahedric Smectic C and Nematic Mesophases in Unsymmetrically 1,1'-Bis-substituted Ferrocenomesogens

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Liquid crystals are anisotropic fluids that exhibit properties between those of conventional liquids and solid crystals.^[1] During the last decades liquid crystals based on ferrocene derivatives attracted significant interest of researchers engaged in the area of metal-containing liquid crystals or metallomesogens.^[2] The conformation of 1,1'-bis-substituted ferrocenes is not always known with certainty. The rotational barrier of cyclopentadienyl rings in ferrocene was estimated as $\sim 0.5 \text{ kJ mol}^{-1}$ on the basis of DFT calculations,^[3] and statistically as $\sim 4.6 \text{ kJ mol}^{-1}$ from the data of X-ray structure analysis.^[4] Flexibility in the center of the rigid rod in ferrocenomesogens may lead to non-conventional molecular organization in the liquid crystal state. We have prepared unsymmetrically 1,1'-bis-substituted ferrocenomesogen **1** (see below), and observed rather unusual thermo-optical behavior



and XRD patterns. In many respects the properties of **1** are reminiscent of the banana-shaped mesogens, though such behavior was detected in none of the earlier reported symmetrically^[5] and unsymmetrically^[6] 1,1'-bis-substituted ferrocenomesogens. In general, banana liquid crystals are characterized with the bent molecular shapes and a great variety of distinct mesophases labeled from B_1 to B_8 .^[7] They have attracted the enormous attention of the liquid-crystal com-

munity in recent years because of their extraordinary properties. Many of the banana mesophases exhibited antiferroelectric and ferroelectric properties, and also spontaneously generated chirality from achiral molecules.^[8] However, the observed properties of **1** are not comparable with the known types of banana mesophases, especially regarding their X-ray diffraction patterns. Taking into account uncommon optical textures and X-ray scattering data we suggest a tetrahedral symmetry for the observed lamellar and nematic mesophases of **1**, and the notations SmC_T^* and N_T^* , where T stands for tetrahedric order and * for chirality. Interestingly, a theoretical possibility of the tetrahedral symmetry in nematic liquid crystals was introduced earlier by Fel,^[9] and similar theoretical concept was extended later for banana-shaped liquid crystals.^[10]

Thermal phase transitions of **1** were studied by means of polarized optical microscopy (POM), microcalorimetric (DSC) and X-ray diffraction (XRD) methods (see Table 1 and SI). Schlieren textures were observed under a polarizing microscope, which are typical for smectic mesophases with tilted layers (see Supporting Information, Figure S2). Besides, the formation of garland-like and helical superstructures (see Figure 1 a, b) and large separate domains of opposite chirality were observed (Figure 1 c, d). Turning polarizer or analyzer consecutively clockwise and counter clockwise by the angle of 15° from the crossed position leads to switching in brightness of chiral domains of the opposite handedness.^[11] Beside the above mentioned banana liquid crystals spontaneously generated chirality from achiral molecules has been observed earlier in some nematics formed from hydrogen-bonded carboxylic acids^[12] and bow-shaped molecules,^[13] and also in double layered anticlinic SmCA mesophases.^[14]

In our opinion, the origin of macroscopic chiral domains and helical superstructures in **1** is adequately explainable considering pseudotetrahedric associates. One can see that there are several kinds of mirror relationships involving the central ferrocene fragment can be established in **1** (Figure 2). Firstly, conformational chirality may be caused

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Table 1. Phase transition parameters and XRD characteristics of **1** in the heating course.

Phase ^[a]	<i>T</i> [°C]	ΔH [kJ mol ⁻¹]	XRD features
Cr ₁	–	–	numerous SAXS peaks which are grouped around 3 main (4.60, 3.92, 3.41 nm) interlayer distances, numerous small and 1 sharp (0.44 nm) WAXS peak
Cr ₂	91.9	2.71	layered structure with small multiplicity in a SAXS peak (4.80), a number of small and 3 main (0.54, 0.49, 0.46 nm) WAXS peaks
SmC _T *	203.4	23.88	the same as the preceding crystal phase, a SAXS peak is gradually decreasing with increase in temperature, WAXS peaks are not changing
N _T *	215.5	0.42	two diffuse halos (4.28, 0.55 nm)
I	272.4	1.61	–

[a] Cr₁, Cr₂: crystal, SmC_T*: tetrahedral smectic C, N_T*: tetrahedral nematic, I: isotropic liquid phases.

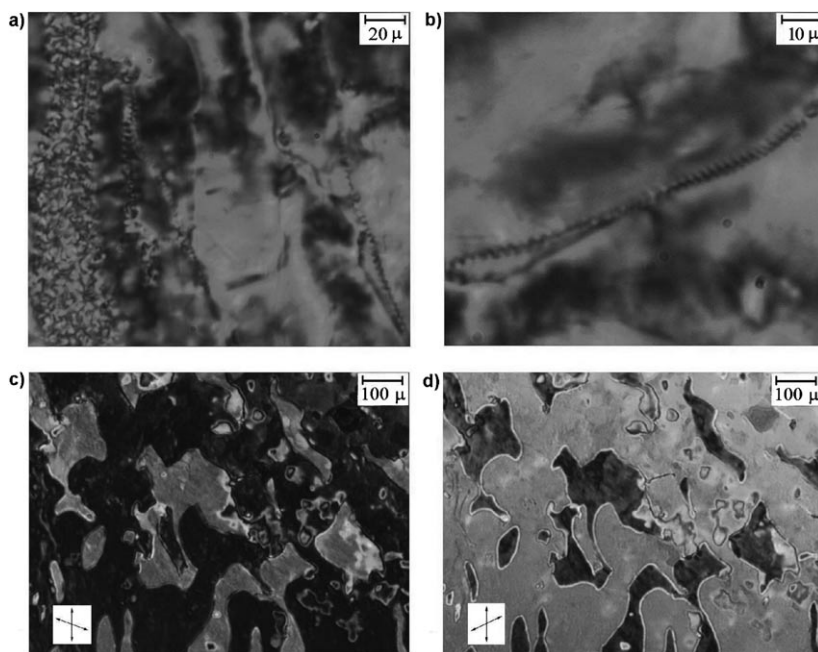


Figure 1. POM textures of the SmC_T* mesophase of **1**: a) a magnified area with garland-like and helical formations at 210°C; b) a magnified area with a helical string; c-d) spontaneous chiral resolution in the SmC_T* mesophase at 205°C.

by different orientation of the fluoro-substituents in relation to a three-dimensional structure of ferrocene. Obviously, such conformers are characterized by relatively small degree of asymmetry, and it would be rather difficult to elucidate the observed macroscopic chiral domains basing solely on this. Secondly, chiral relationship occurs between the bended conformers. Spontaneous organization into chiral smectic layers in this case is also questionable, as it should be considered that the arm substituents have different lengths and random orientation, and the chiral conformations are easily interconvertible because of flexibility in the central part of **1**. And finally, the bended conformers can be coupled in four different kinds of dimers, or two kinds of enantiomeric pairs. The internal order of the mesophases comprised of such kind of coupled conformers will be similar to some of the specifically classified mesophases with a tetrahedral symmetry theoretically described by Lubensky and Radzihovsky.^[10b]

The pseudotetrahedral dimers seem to be more capable of preserving their shapes in comparison with the single flexible conformers. Perhaps, plain-to-plain π - π electronic interactions of the benzene rings and n - π interactions between the free electron pair of the nitrogen atom and aromatic rings are the main driving forces for the dimer formation. Coplanarity of the conjugated aromatic system with the cyclopentadienyl rings of the ferrocene moiety could be a very important factor as well. The majority of the earlier reported symmetrically and unsymmetrically 1,1-bis-substituted ferrocenomesogens are derivatives of the carboxylated or alkyl substituted ferrocenes,^[5-6] where such a rigidly conjugated aromatic system is missing. In the reported cases of 1,1'-bis-arylated ferrocenomesogens^[5f,i] the formation of dimeric molecular associates seems to be prevented by repulsion between the free electronic pairs of the azomethine nitrogens. Computer-aided calculations of the pseudotetrahedral dimers gave the energy drop of

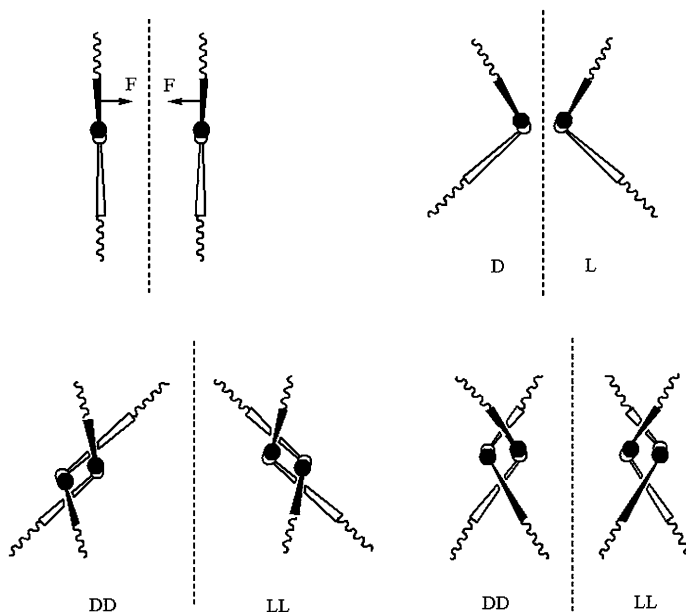


Figure 2. Possible chiral relationships in **1**.

41.2 kJ mol⁻¹ for the untilted enantiomers and 47.3 kJ mol⁻¹ for the tilted one. Accordingly, the tilted dimers are more stable thermodynamically in comparison with their untilted counterparts. In fact, the bended enantiomers of different handedness can not couple into the tetrahedric dimers, and, hence, this provides an initial mechanism for stereospecific supramolecular assembling. Notably, the untilted dimers are not well adapted for packing into the lamellar smectic C layers together with the tilted enantiomers, and, possibly, they segregate into separate helical and garland-like superstructures.

The broad nematic mesophase with non-conventional textural patterns follows the SmC_T* mesophase (Figure 3). The N_T* mesophase has a dark appearance, and only some momentary birefringent flash can be observed on transition to the isotropic liquid state. Chiral nematic droplets and birefringent walls are observed in perimeter areas of the sample. A boundary of the pseudoisotropic domains has a complex texture pointing out non-conventional supramolecular organization of the mesophase (see Figure 3d). Additionally, certain signs of optical biaxiality were detected in

the N_T* mesophase of **1**. First of all, brightness of the sample alternates when the cell is turned in relation to the crossed polarizers (Figure 4). Secondly, conoscopic observa-

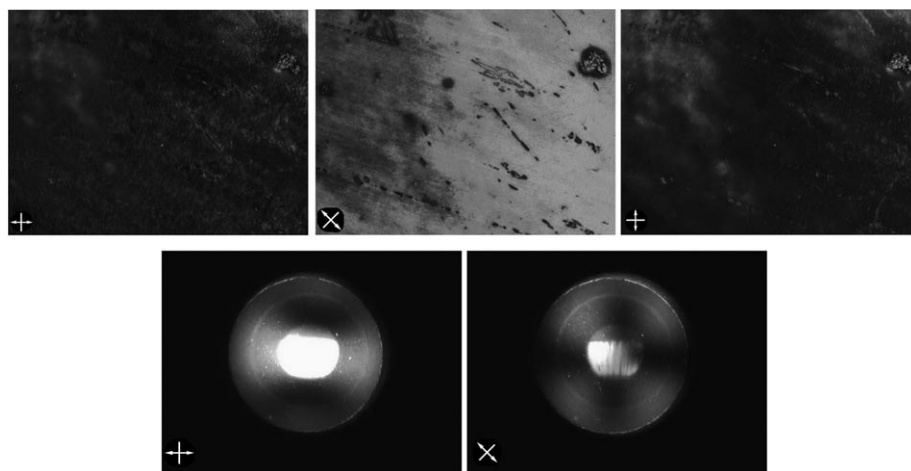


Figure 4. Possible optical biaxiality of the N_T* mesophase of **1** detected by POM experiments at 240°C: a) switching brightness of the homeotropically aligned sample of ~10 μ thickness by turning the crossed nicols from the angle 0 to 45 and 90° (top pictures); b) conoscopic pictures of the homeotropically aligned sample at the angles of 0° and 45° to the crossed nicols (lower pictures).

tions revealed a large symmetry disturbance of the “Maltese cross”. Indeed, the above optical observations might be connected with the surface alignment and not with the bulk biaxial mesophase. But at any rate these optical phenomena are indicative of biaxial geometry of the molecules. In this connection, the distorted tetrahedric dimers are very similar to rectangular board-shaped mesogens with molecular biaxiality except for two vertices are slightly twisted in relation to two others in the first case. In summary, all of the observed optical properties conform well to the suggested tetrahedric order.

X-ray diffraction patterns of **1** at the different phase states are represented in Figure 5. At room temperature a SAXS pattern consist of a number of scattering peaks, which is suggestive of the complex internal arrangement of the molecules. In a WAXS pattern one sharp intensive peak corresponding to the interlayer spacing distance of 0.44 nm is explicitly exposed among numerous small reflections. Most likely, the latter points out strong one-dimensional plain-to-plain

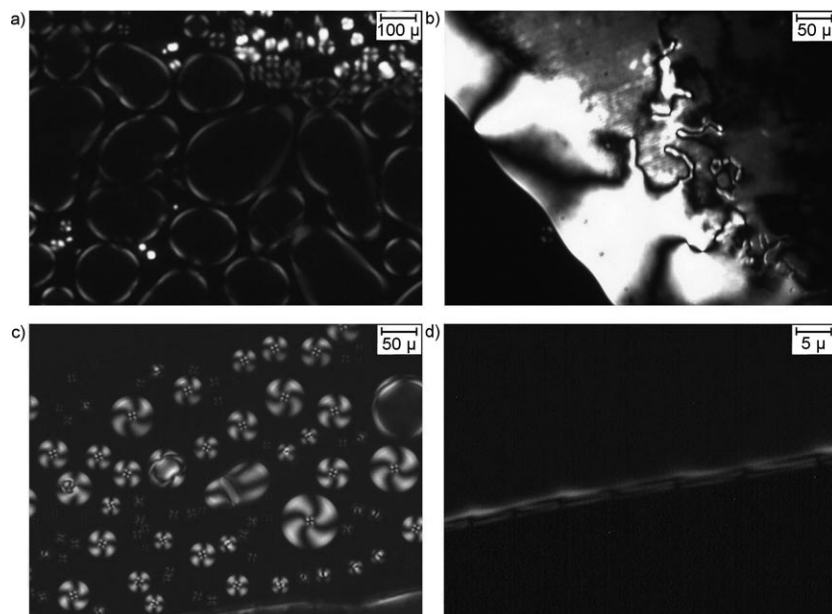


Figure 3. POM textures of the N_T* mesophase of **1**: a) dark droplets on cooling from the isotropic state at 272°C; b) an equilibrated transition from the isotropic liquid (left) to N_T* (right) mesophases at 272°C; c) chiral nematic droplets at 265°C; d) the intricate structure of the N_T* pseudoisotropic domain boundary, 245°C.

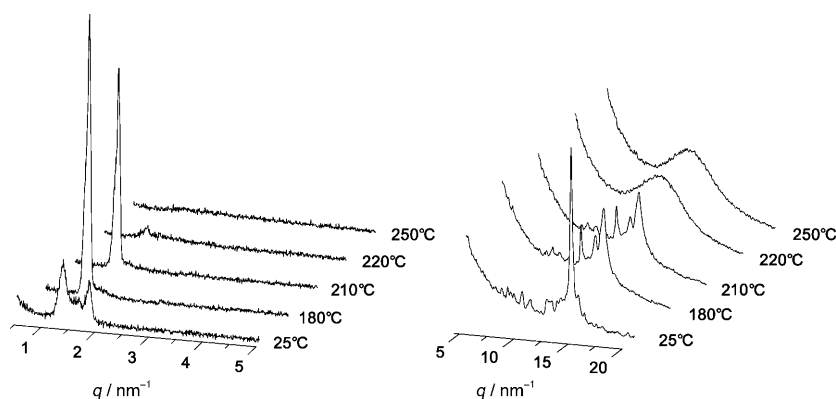


Figure 5. Selected SAXS (left) and WAXS (right) patterns of **1** in the different phase states.

stacking of the ferrocene moieties in the room temperature crystal form. After a transition to the Cr_2 state the SAXS diagrams reveal a layered structure with interlayer spacing of ~ 4.8 nm (001 reflection). At the same time in the WAXS diagrams three relatively intensive peaks appear among numerous smaller reflections. The same aspect of the SAXS and WAXS patterns are sustained in the SmC_T^* mesophase. The interlayer spacing distance of ~ 4.8 nm is very persistent and the remnant weakly layered structure remains even in the nematic state up to 220°C . Molecular modelling explains sufficiently well the appearance of the periodicity of ~ 4.8 nm from the layered packing of the tilted pseudotetrahedric dimers (Figure 6). As for the WAXS signals it is

not straightforward in this stage to give assignments for all the reflection peaks in the SmC_T^* state. However, in a case of cross-penetrated packing of the pseudotetrahedrons X-ray scattering reflections might appear due to the electronic density periodicities other than imaginable from the simple 2D or 3D order of the molecules. For instance, some sensible interpretation of this would be a superposition of two or several 2D lattices within the smectic layers,

which certainly will give rise to a series of peaks in the wide angle region. A schematic illustration of possible periodicities of the electronic density in a case of tetrahedric smectic layers is given in Figure 6. The difference between the Cr_2 and SmC_T^* is that conformational melting of the terminal alkyl chains gives rise to fluidity and liquid crystal properties in the latter case, while the central parts of the mesogenic molecules will be arranged in a flexible interpenetrated network.

Briefly, very unusual mesophases were observed in **1**, which are distinguished by spontaneous mesoscopic and macroscopic chiral degeneracy, non-conventional XRD patterns and explicit signs of molecular biaxiality. The fairly plausible tetrahedric order can be deduced from these experimental observations. Accordingly, dark textures of the N_T^* mesophase seem to be a natural consequence of random orientation of the terminal alkyl chains from the centres of elongated tetrahedrons. Intricate boundaries of the N_T^* pseudoisotropic domains is another strong indication of complex internal organization of the observed mesophase. It should be noted that a justification of the observed properties of **1** without engaging the suggested pseudotetrahedric dimers would be quite ambiguous.

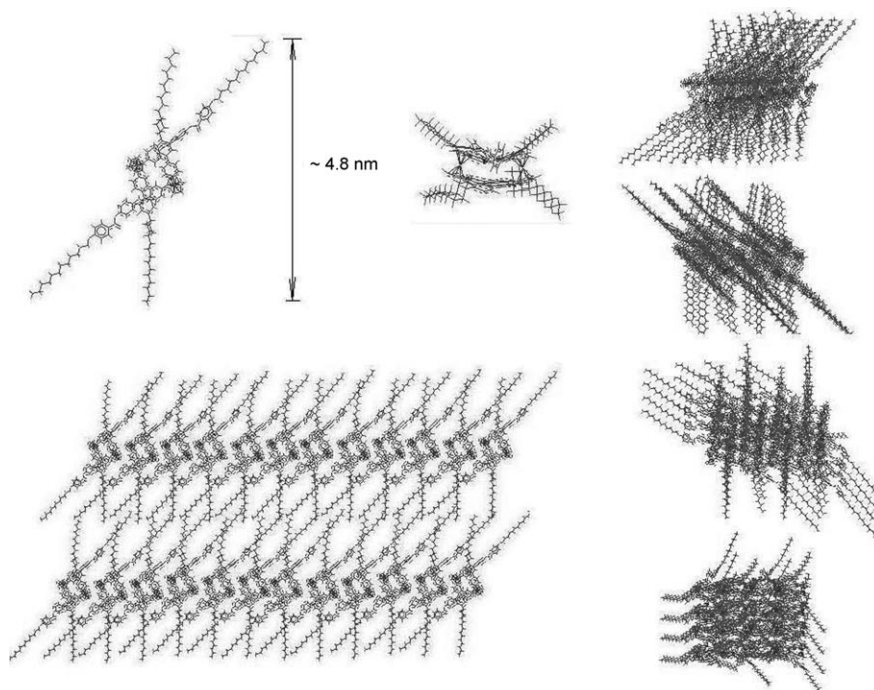


Figure 6. Molecular models illustrating tetrahedric dimers (in the upper left corner), the SmC_T^* layers with interlayer spacing distance of ~ 4.8 nm (in the lower left corner) and schematic illustration of possible different periodicities of the electronic density depending on the point of view in a case of interpenetrated packing of the pseudotetrahedric dimers within the smectic layers (in the right).

Experimental Section

The synthetic procedures for preparation of compound **1** and other experimental details are given in Supporting Information to this article.

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Keywords: chirality · ferrocenes · helical structures · liquid crystals · metallomesogen

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