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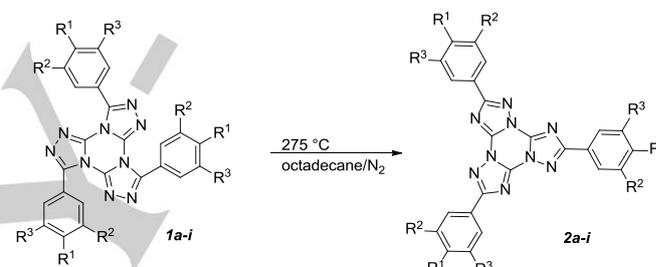
Isomerisation of Liquid-Crystalline Tristriazolotriazines

Thorsten Rieth^[a], Nico Röder^[a], Matthias Lehmann,^{* [b]} and Heiner Detert^{*[a]}

Star-shaped discotic liquid crystals with columnar superstructures constitute a highly interesting class of organic materials. Phenyl substituted tris[1,2,4]triazolo-[1,3,5]triazine, prepared by a Huisgen reaction of phenyl tetrazole and cyanuric chloride, represents an excellent core for discotic liquid crystals (DLCs). The thermal stability is not perfect, at temperatures above the clearing point, a successive threefold isomerization leads to a highly planar, C₃-symmetrical isomer, which mainly differs in the orientation of the aryl substituents to the centre of the molecule. A new class of discotic liquid crystals has been obtained: Equipped with peripheral alkoxy chains both isomers can form broad thermotropic mesophases. The optical, thermal, and physical properties were investigated by polarized optical microscopy, differential scanning calorimetry, wide-angle X-ray scattering, UV-Vis absorption and fluorescence measurements. The thermotropic properties are decisively affected by the molecular structure of the isomers, isomerisation leads to higher melting points but also the loss or even gain of mesomorphism is observed.

Organic π -conjugated systems, small molecules^[1] and polymers,^[2] are of great interest for sensing, optical and electronic applications.^[3] The group of discotic liquid crystals (DLC) offers the additional feature of self-organization, often as a columnar arrangement resulting in anisotropic properties, e.g. one-dimensional charge transport in the liquid-crystalline phase.^[4] Typical DLCs consist of electron-rich polycyclic aromatic units, e.g. triphenylene or hexabenzocoronene,^[5] whereas DLCs with an electron deficient core are rather scarce.^[6] One of the youngest members of this group is the tris[1,2,4]triazolo-[1,3,5]triazine (TTT), a tetracyclic, nitrogen-rich, and C₃-symmetrical analogue of triphenylene. The first TTT, triphenyl-TTT **1** (R¹ = H), has been prepared by Huisgen^[7], its shape is a tetracyclic plane with three phenyl rings sticking out of the bays. To avoid steric compression, the substituents are twisted out of the plane with dihedral angles up to 80°. In 2008, Gallardo^[8, 10] and Glang^[11] recognized the suitability of the TTT as a core for discotic liquid crystals. These propellers (e.g. **1b-1h**) with six to nine alkoxy groups on the outer rim can form broad mesophases. Polarized light revealed the characteristic textures of a columnar phase and X-ray diffraction (WAXS and SAXS) on pre-orientated filaments confirmed a hexagonal arrangement of the columns in the mesophase and complex helical superstructures in the solid state.^[12]

All these TTTs with a 'tangential' orientation (*t*-TTT) of the alkoxyphenyl substituents were obtained via the Huisgen route. An independent access to TTTs was reported by Tartakovsky^[13] in 2005: thermocyclization of three 5-chloro-3-phenyl-1,2,4-triazole molecules resulted in a C₃-symmetrical triphenyl tristriazolotriazine (**2**, R¹ = H) – but the different annulation pattern brings the phenyl rings to distal positions. The molecule adopts a star shape with phenyl rings as rays. This *r*-TTT with a 'radial' orientation of the substituents to the core exhibits a very high thermal stability, decomposition started only at 400 °C (TGA). Unfortunately, the scope of the synthetic method is very small.^[11] The isomeric *t*-TTT **1** (R¹ = H), when heated to 350 °C, changed to an isomeric mixture of asymmetric (*r,t*-TTTs).^[13] Herein, we present the thermal isomerization of C₃-symmetric *t*-TTTs (**1a-h**) into C₃-symmetric *r*-TTTs (**2a-h**, scheme 1, table 1), together with the impressive changes of their mesomorphous behavior, structural investigations and some optical properties.



Scheme 1. Thermal isomerisation of tristriazolotriazines

Table 1: Substitution pattern and isomerization yields of *r*-TTTs

Comp.	R ¹	R ²	R ³	Yield.
1a/2a	OC ₃ H ₇	H	H	65 %
1b/2b	OC ₁₀ H ₂₁	OC ₁₀ H ₂₁	H	43 %
1c/2c	OC ₁₂ H ₂₅	OC ₁₂ H ₂₅	H	38 %
1d/2d	OC ₁₄ H ₂₉	OC ₁₄ H ₂₉	H	18 %
1e/2e	OC ₁₆ H ₃₃	OC ₁₆ H ₃₃	H	21 %
1f/2f	OC ₈ H ₁₇	OC ₈ H ₁₇	OC ₈ H ₁₇	26 %
1g/2g	OC ₁₀ H ₂₁	OC ₁₀ H ₂₁	OC ₁₀ H ₂₁	22 %
1h/2h	4-ethyloctyloxy	4-ethyloctyloxy	4-ethyloctyloxy	32 %

Heating alkoxy-substituted *t*-TTTs like **1a** to 350 °C results in mixtures with varying composition of non-symmetric isomers and decomposition products. The latter are drastically reduced if the reaction is performed in an inert solvent and below 300 °C, the time required for a complete transformation increases to four to six days. Isomerization of the *t*-TTTs was achieved by heating solutions of **1a-h** in octadecane for several days at 235 °C under exclusion of oxygen. Time-dependent ¹H-NMR (figure 1) revealed a stepwise process; the first rearrangement was fast, starting material vanished within 14 h, but it took 4 days to complete the cascade of rearrangements to C₃-symmetrical **2a**.

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For the mechanism (scheme S1), a heterolytic bond fission of a triazine bond, rotation of one ring around the triazole-triazole bond and recombination was proposed^[13] for each isomerization step.

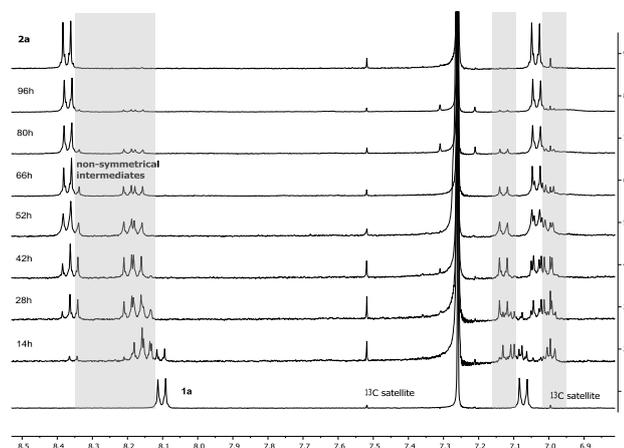


Figure 1. Stepwise rearrangement of **1a** to **2a**, monitored by time-dependent ¹H-NMR-spectroscopy (grey: signals of non-symmetrical intermediates)

NMR-Spectroscopy clearly reveals the three steps of the cascade of rearrangements. Asymmetric isomers (*tr*-TTT and *trr*-TTT) generate different sets of signals for the protons of any phenyl substituent (gray) whereas C₃-symmetrical *t*-TTT **1a** and *r*-TTT **2a** provoke only one set of signals each. Resonances of *ortho*-protons from radially orientated phenyl rings are significantly shifted towards lower field while the *meta*-protons appear at slightly higher field. The impact on the chemical shift is caused by different overlap of the anisotropy cones of the phenyl substituents and the isomeric TTT-cores due to planarization. Furthermore, ¹³C-NMR signals of phenyl substituted triazole carbons are strongly shifted to lower field (*t*-TTT: 151 ppm, *r*-TTT: 165 ppm). Likewise ¹⁵N-NMR confirmed the complete isomerization of the core (*t*-TTT:^[8] $\delta = -69.2, -99.8, -226.6$; *r*-TTT **2b**: $\delta = -119.7, -116.1, -192.2$ ppm). DFT calculations show that the transformation of **1** ($R^1 = \text{OCH}_3, R^{2,3} = \text{H}$) to the first isomer (*tr*) is exothermic by 8.3 kcal/mol, the following rearrangements reduce the energy by 12.3 kcal/mol each - the final product *r*-TTT **2** is about 32.9 kcal/mol lower in energy than the *t*-isomer.

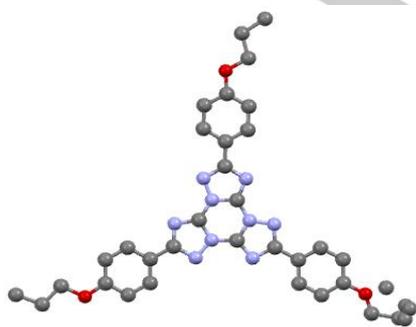


Figure 2. Molecular structure^[14] of tris(*p*-propoxyphenyl)-*r*-TTT (**2a**).

Single crystals of *p*-propoxyphenyl substituted *r*-TTT (**2a**) were obtained via slow evaporation of a solution in toluene. X-ray scattering verified the postulated isomeric arrangement of the atoms in the triazole rings (figure 2.) and provides information about the molecular packing in the solid state. Crystallographic data exhibit a nearly planar molecule: The dihedral angles between the central TTT core and the peripheral phenyl rings are below 5° whereas the phenyl substituents in crystalline *p*-alkoxy phenyl *t*-TTT are twisted up to 80°.^[8,9] The organization of the molecules in the solid state is based on π - π interactions between the electron-rich alkoxyphenyl substituents and the electron-poor TTT cores. A distance of 3.3 Å between adjacent molecules is in the typical range of π - π interactions.

Investigations of the di- and trialkoxyphenyl substituted *t*-TTTs and *r*-TTTs (**1b-g**, **2d-g**) with a polarized optical microscope show the typical fan-shaped and dendritic textures of columnar mesophases. The fluid nature of the materials was confirmed by shear experiments, which resulted in a planar alignment of the phases. Only *r*-TTT **2h** with branched side chains displays banana-leaf like textures (Figure 3., right). While dialkoxy-*t*-TTTs **1b**, **1c** are mesomorphous over a broad temperature range, their radial isomers **2b** and **2c** crystallize upon cooling from the isotropic melt. Noteworthy, thermal isomerization of **1h** remarkably converted an originally non-mesomorphous *t*-TTT into the liquid-crystalline isomer **2h** (figure 3.).



Figure 3. POM-textures (crossed-polarizers) of *t*-TTT **1h** at 120 °C (left) and *r*-TTT **2h** at 210 °C (right)

Mesomorphous behaviour was also studied by differential scanning calorimetry (DSC), the transition temperatures are summarized in table 2. DSC of *t*-TTTs **1** confirms the broad mesophases and reveals that compounds **1d**, **1e** with longer side chains display a second mesophase. But the prime result of the calorimetric measurements on *t*-TTTs **1** is their thermal instability above 200 °C! Repeated DSC scans up to 260 °C clearly reveal a shift of phase transitions to lower temperatures (fig. S43) by some degrees per scan. It appears that even this short exposure to thermal stress is sufficient to initiate the rearrangement.

Transition temperatures and the resulting widths of the mesophases are not only dependent on number and length of the alkoxy chains; the orientation of the alkoxyphenyl substituents plays a pivotal role. DSC and POM revealed that the width of the enantiotropic mesophases of dialkoxyphenyl substituted TTTs **1d** ($\Delta T_M = 113$ °C) and **1e** ($\Delta T_M = 103$ °C) drastically shrunk upon isomerization to **2d**, **2e** (**2d**: $\Delta T_M = 8$ °C) or even vanished completely (**2c**). The opposite effect, an astonishing broadening of the mesophases was observed upon isomerization of trialkoxyphenyl TTTs: *t*-TTTs **1f** ($\Delta T_M = 58$ °C), **1g** ($\Delta T_M = 39$ °C) were transformed to *r*-TTTs with significantly

higher clearing points and mesophase ranges **2f** ($\Delta T_M = 170$ °C), **2g** ($\Delta T_M > 165$ °C). These highly viscous LC phases of **2f** and **2g** do not show crystallization peaks on cooling and the second heating scans reveal only one endothermic transition with very low transition enthalpies. Whereas star-shaped TTT **1h** is not mesomorphous, its radial isomer **2h** provokes two endothermic transitions (DSC: Cr \rightarrow Col: 75 °C; Col \rightarrow I: 207 °C, $\Delta H = 4.8$ kJmol⁻¹, $\Delta T_M = 132$ °C). Cooling with 10°/min shifted the crystallization peak to 38 °C. This supercooling by $\Delta T = -40$ °C and the puny enthalpy of fusion ($\Delta H = 2.8$ kJmol⁻¹) are attributed to a very slow and incomplete crystallization from the highly viscous mesophase.

Table 2: Phase transitions of *t*-TTTs **1** and *r*-TTTs **2**

TTT	transitions	TTT	transitions
1b	Cr 89 M 207 I	2b	Cr 136 I
1c	Cr 92 Col _h 208 I ^[6]	2c	Cr ₁ 90 Cr ₂ 131 I
1d	Cr -11 M ₁ 68 M ₂ 181 I	2d	Cr 128 Col 136 I
1e	Cr 19 M ₁ 68 M ₂ 171 I	2e	Cr 36 M ₁ 97M ₂ 125 Col _h 132 I
1f	Cr 126 M 184 I	2f*	Cr 35 Col _h 205 I
1g	Cr 126 M 165 I	2g	Col _h 181 I
1h	Cr 124 I	2h	Cr 75 Col _h 207 I

* only visible in the first heating scan

The self organization of the discotic mesogens was studied in detail by X-ray diffraction on oriented filaments, obtained by extrusion of **2e,f,g,h** in the LC phase. Figure 4 exemplifies the typical diffraction pattern found for the two different columnar LC phases in **2f** and **2h**. Main signal is the halo (4.5 Å) that corresponds to the mean distance of the liquid aliphatic chains. Furthermore, a broad meridional signal and a small number of intense equatorial reflexes were observed. The latter can be indexed for hexagonal unit cells of **2e-f** with cell parameters a_{hex} according to the diameter of the columns. a_{hex} increases with the number and length of the side chains: **2f**: $a_{\text{hex}} = 29.8$ Å (150 °C), **2g**: $a_{\text{hex}} = 31.5$ Å (115 °C), and **2e**: $a_{\text{hex}} = 36.3$ Å (130 °C). Intracolumnar distances of the discotic mesogens provoke broad meridional signals at 3.3 Å (25 °C) to 3.6 Å (167 °C), these distances correspond to attractive interactions between π -systems. Correlation lengths range up to 3-10 molecules within the π -stack, thus showing the LC character of the phase.^[15] Interestingly, a set of weak and diffuse intensities very close to the reflections 10 along the meridian indicates a correlation along the columnar axis, with a correlation length of 1-2 repeating units. Closer inspection of these signals could be successfully done for compound **2f**, which reveal a *c*-parameter of 51 Å in which 14 molecules stack along the column at 150 °C. This large repeating distance can be explained only by helical stacking of the radial star mesogens. Contrary to the hexagonal phases formed from TTTs with linear side chains, the branched chains in **2h** result in a different volume ratio. Tilting of the mesogens allows to maintain a strong interaction of the aromatic units, but the structure of the mesophase changes to centered rectangular with two columns in the unit cell, as confirmed by the

diffraction pattern (fig. 4; at 115 °C: $a_{\text{rec}} = 34.7$ Å, $b_{\text{rec}} = 29.5$ Å). Two broad meridional reflexes located on the layer line (hk3) correspond to a periodicity with $c = 43.2$ Å along the columns. The density is 0.97 g/cm³, equivalent to 14 mesogens in two columns. Again, such a large periodicity can only be explained by a helical stacking of seven tilted mesogens along one column with a mean distance of 6.2 Å. A tilt of 53° allows a mean distance of the aromatic rings of 3.7 Å. This and the relatively poor correlation along the column are reasons for only few meridional reflexes and the lack of the typical π -stacking reflection. A fibre diffraction simulation of the pattern on a geometry-optimized model is in perfect agreement with the experimental data (fig. 4). The helical arrangement in the liquid crystal state allows best the filling of the void space between the arms of the star mesogens by simultaneous optimization of the nanosegregation and is found recently for many star LC systems.^[17, 18]

Cooling below the melting transition results in crystallization of **2e**, **2f**, and **2h** to form higher ordered phases with preserved orientation of the columns (SI). Only **2g** maintains the columnar-hexagonal structure of the LC phase. Lower temperatures provoke increasing diameters a_{hex} of the columns due to a stretching of the aliphatic chains - thereby reducing the π - π distances of the coplanar aromatic nuclei to 3.3 Å.

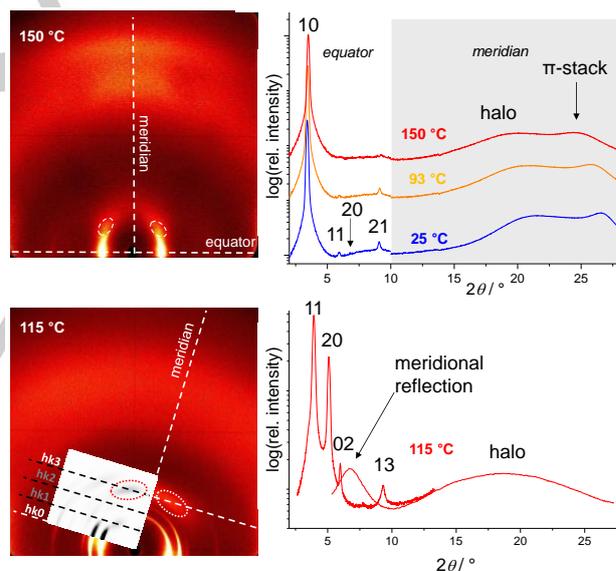


Figure 4. Diffraction pattern of **2f** at 150 °C (top left) and of **2h** at 115 °C (bottom left), Inset: simulated fibre diffraction pattern (Clearer).^[16] Top right: 2 θ -Scan along equator and meridians with indexing of the reflexes according to a hexagonal phase (**2f**). Bottom right: 2 θ -Scan along equator and meridian with indexing of the reflexes according to a centered rectangular phase (**2h**).

The isomeric TTTs are colorless and fluorescent compounds, in solution, in the solid state, and in their mesophases. Absorption maxima of tangential and radial isomers in cyclohexane peak at nearly identical positions (**1b**: $\lambda_{\text{max}} = 310$ nm, **2b**: $\lambda_{\text{max}} = 312$ nm) but the more planar *r*-isomers **2** show structured spectra and higher extinction coefficients (**1b**: $\log \epsilon = 4.63$, **2b**: $\log \epsilon = 4.77$, and not the negative solvatochromism of the *t*-isomers **1**). The structured emission bands of *r*-TTTs appear

at significantly higher energies than those of their *t*-isomers (in cyclohexane: **1b**: $\lambda_{\text{max}}^{\text{F}} = 370$ nm, **2b**: $\lambda_{\text{max}}^{\text{F}} = 348$ nm). Large Stokes shifts of *t*-TTTs and blurred spectra indicate substantial geometrical changes after excitation. Both series display a positive solvatochromism with a remarkably higher sensitivity of the *r*-isomers **2**.

Summary

Thermal rearrangements of trisiazolotriazines convert the *all-tangential* form in three steps to the *all-radial* form. An increase of the molecular diameter and planarization are responsible for changes of the thermotropic properties: increased melting points and even loss of mesomorphism appear, but also the gain of liquid crystallinity has been observed.

Acknowledgements

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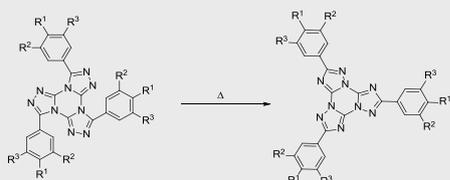
Keywords: Trisiazolotriazine • Discotic Liquid crystal • Isomerization • X-ray diffraction • Fluorescence

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Layout 2:

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A thermal rearrangement of discotic trisubstituted triazolotriazines converts Huisgen type *all-tangential*, C₃-symmetrical TTTs in three steps via two non-symmetrical isomers to also C₃-symmetrical but *all-radial* isomers. According to the substitution pattern, liquid crystallinity is changed, destroyed, or even gained.

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Matthias Lehmann and Heiner Detert*

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Isomerisation of Liquid-Crystalline

Trisubstituted Triazolotriazines

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