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Preliminary Communication

Induction of smectic A phases by electron donor-acceptor interaction between calamitic mesogens and 2,4,7-trinitrofluorenone

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(Received 20 September 1996; accepted 12 October 1996)

The mesomorphic properties of conventional rod-like liquid crystals (diphenyl-1,3,4-thiadiazoles, diphenylpyrimidines, diphenyltriazines, diphenyltetrazines and *p*-terphenyl derivatives), of macrocyclic liquid crystals and of dimesogens can be influenced by addition of the electron acceptor 2,4,7-trinitrofluorenone (TNF). Thereby nematic and smectic C phases are suppressed and smectic A phases can be stabilized or induced. Long and branched terminal chains result in a strong stabilization of the S_A phase, whereas no smectic phase is induced to accompany the nematic phases of mesogens with short terminal chains.

The formation of columnar and nematic columnar (N_{Col}) mesophases by electron donor-acceptor (EDA) interactions between electron rich disc-like liquid crystal molecules and the rather flat electron acceptor 2,4,7-trinitrofluorenone (TNF) is a well known phenomenon [1]. More recently, the induction of cubic and smectic phases into the columnar mesophase sequences of double swallow-tailed and polycatenar compounds by doping with TNF has been reported [2]. It was argued that the small TNF molecules are incorporated into the gaps between the aromatic cores of the swallow-tailed molecules. Therefore it was concluded that, not only EDA-interactions, but also steric reasons mainly contribute to the phase induction [3].

Several examples of mesophase induction by mixing two different rod-like compounds of different polarity have also been described [4]. However, attempts to induce smectic phases additional to the nematic phases of rod-like mesogens by EDA-interactions with TNF and other small molecules have not been successful [5]. Therefore it is generally assumed that mesophase induction into the nematic phase sequences of conventional rod-like molecules by flat and non-mesogenic TNF molecules is not possible due to their unfavourable shape.

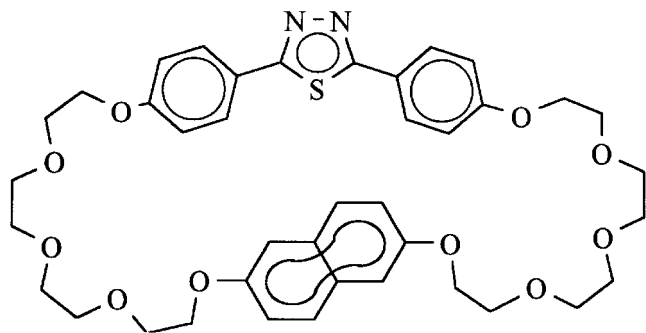
Recently we have reported on novel liquid crystal-line macrocycles tailored to realize improved donor

properties [6]. They represent macrocycles in which a calamitic rigid core is connected with an electron-rich naphthalene ring. In one of these nematic compounds (1) it was indeed possible to induce a smectic A phase on addition of TNF.

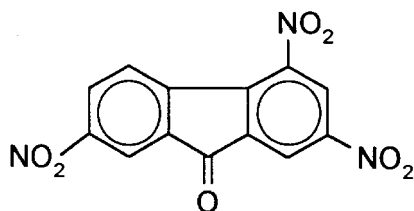
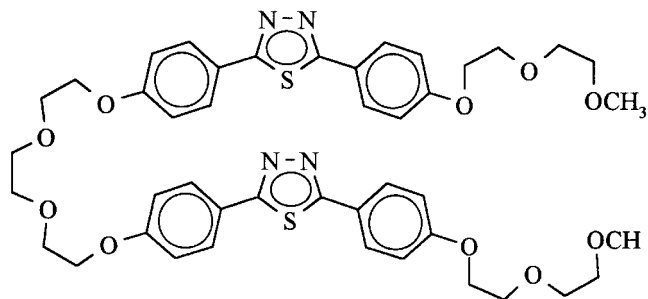
At first we assumed that the electron rich naphthalene ring due to its electron donor properties, must be responsible for the mesophase induction. In order to confirm this, we have investigated macrocycle 2 [7] incorporating exclusively 2,5-diphenylthiadiazole rigid cores. The system 2/TNF was investigated using the penetration technique; thereby compound 2 and TNF were placed side by side between two cover slips. Dependent upon the temperature and the concentration of TNF, different mesophases develop in the contact region.

Small concentrations of TNF lead to a depression of the clearing temperature of the nematic phase and to a depression of the S_C-N transition temperature. In regions with increased TNF content, another liquid crystalline phase becomes observable. This mesophase exhibits a fan-like texture which can be aligned homeotropically by shearing. This indicates a smectic A phase. Further increase of the TNF concentration leads to a stabilization of the S_A phase up to a maximum at 185°C. The S_C phase cannot be observed in the centre of the contact region. This mesophase induction is a rather amazing finding, because no typical strong electron donor is incorporated in this macrocyclic compound.

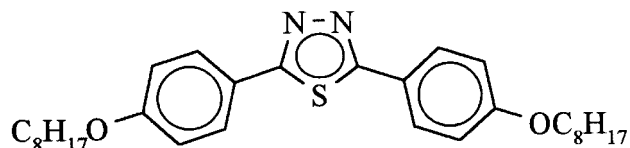
* Author for correspondence.

**1**

C 120 (g 22) N 164 I

**TNF****1/TNF** T_{\max} (SA): 126 °C**3**C 139 S_C 155 N 207 I**3/TNF** T_{\max} (SA): 172 °C

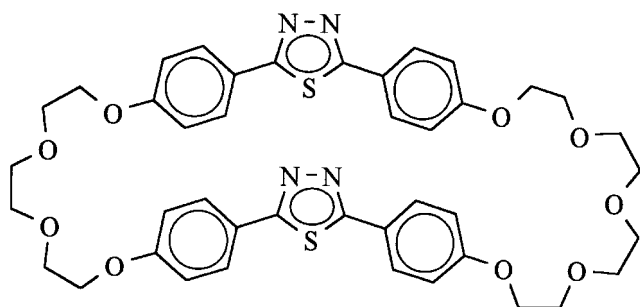
also be influenced by addition of TNF. The 2,5-bis(4-octyloxyphenyl)-1,3,4-thiadiazole **4** [8] which represents the main constituent of the macrocycles **1** and **2** and the dimesogen **3** was therefore investigated in detail.

**4**C 101 S_C 195 N 198 I**4/TNF** T_{\max} (SA): 200 °C

The pure compound **4** has an N–S_C dimorphism. Again in the contact region between **4** and TNF, a smectic A phase is induced (figure 1).

The mesophase behaviours of several mixtures containing various ratios of **4** and TNF are summarised in the simplified phase diagram given in figure 2.

Small amounts of TNF (m.p.: 175°C) lead to a depression of the clearing temperature of the nematic phase and destabilize the S_C phase. On increasing the content of TNF to about 5 mol %, a smectic A phase is observed. Further increase of the TNF concentration leads to a stabilization of the smectic A phase up to a maximum of 200°C at a concentration of approximately 20 mol % TNF. Thus the clearing temperature of the mixture with the non-calamitic compound TNF has a slightly increased mesophase stability in comparison with the pure calamitic mesogen. Obviously, attractive electron-acceptor/electron-donor interactions force the individual molecules to adopt a positional order such that the

**2**C 168 S_C 221 N 330 I**2/TNF** T_{\max} (SA): 185 °C

In the next step, we investigated the dimesogen **3**, which can be regarded as an open chain analogue of the cyclophane **2**. In this case also, the induction of an S_A phase was observed.

Now the question arose as to whether the mesophases of conventional calamitic liquid crystal materials can

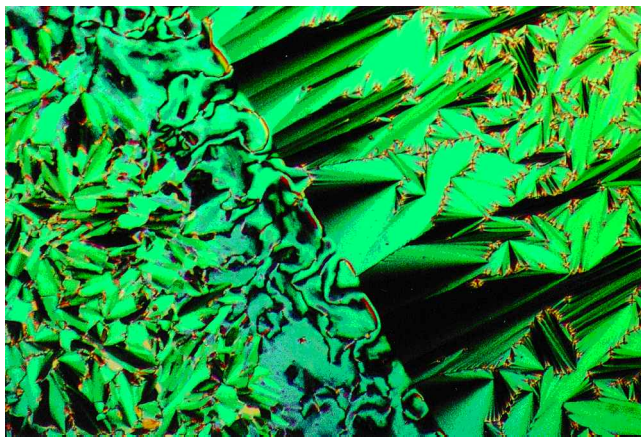


Figure 1. Optical photomicrograph (crossed polarizers) of a section of the contact region between compound **4** and TNF at 193°C; from the left hand side to the right hand side, the TNF concentration increases and in the same direction the phase sequence S_C -N- S_A is observed.

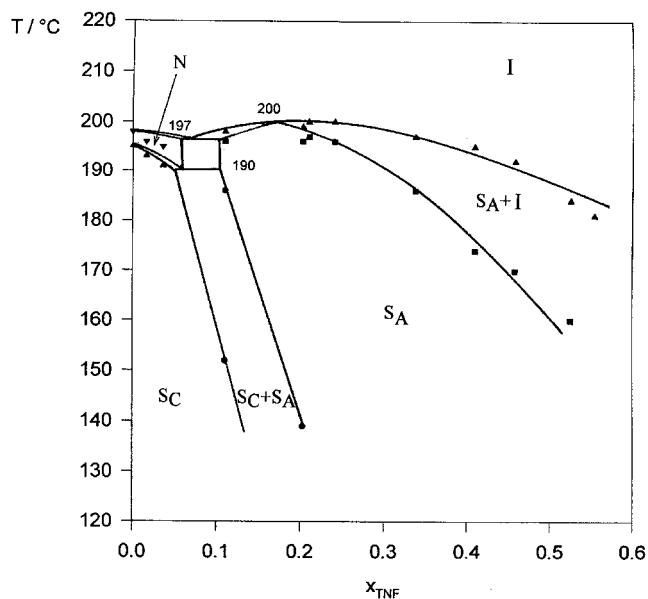


Figure 2. Simplified phase diagram of the binary mixture of **4** with TNF as determined by polarizing optical microscopy; only the transitions between liquid crystalline phases and the clearing temperatures are displayed.

formation of a smectic layer structure occurs. These interactions are strong enough to prevail over the unfavourable disturbance caused by the non-mesogenic TNF molecules.

Other calamitic compounds incorporating different heterocyclic structural units (see the table) were also investigated by the penetration technique (contact preparations). A deep red colour occurs in the contact regions with TNF indicating charge transfer interactions.

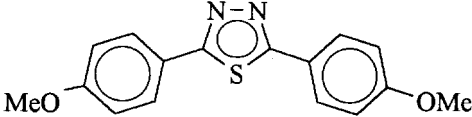
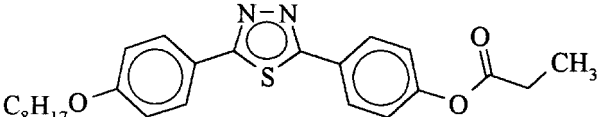
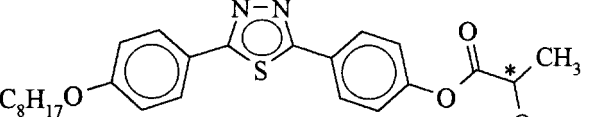
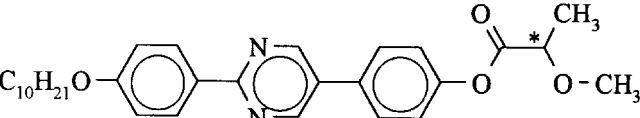


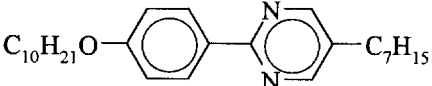
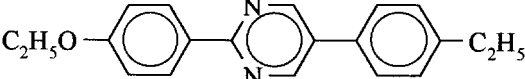
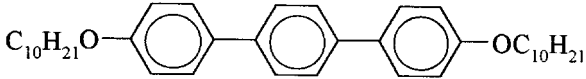
With one exception (compound **5**), in all cases S_A phases were induced or the existing S_A phases were stabilized (compounds **8** and **11**), whereas the nematic and S_C phases were destabilized. In the table, the transition temperatures of the pure compounds are compared with the maximum clearing temperatures of the induced S_A phases in the contact zones with TNF.

An especially strong mesophase stabilization was observed for the lactic acid derivatives **7** and **8** which have branched terminal chains. No S_A phase can be induced below the nematic phase of the short chain thiadiazole derivative **5**. Also, in the case of the short chain pyrimidine derivative **12**, a smectic A phase can be detected in the contact region with TNF. However, the pure compound **12** is high melting and therefore we are not sure if this phase is really an induced phase or if it is observed due to the depressed melting point of the mixture.

It seems that in the case of rod-like molecules, mesophase induction with TNF is possible only if the terminal chains are sufficiently long or branched. We assume that in these compounds the chains can fill up the additional free space which results from the incorporation of the TNF molecules between the rigid aromatic cores. The TNF molecules reinforce the smectic layer structure by donor-acceptor interactions with the aromatic cores of the calamitic molecules. The strength of the EDA-interactions should be determined by two factors: the difference in the donor-acceptor properties of the interacting molecules and the closeness of the contact of their aromatic π -systems [9]. The best contact is possible if the rigid cores are flat. This is realized in the thiadiazole derivatives [10], the tetrazine **9** and the pyrimidine **11**. These molecules are flat because conjugation of the aromatic π -systems favours a periplanar arrangement of the aromatic rings. Additionally, no steric hindrance between neighbouring rings disfavours the planar arrangement. Again, in the compounds **8**, **10** and **12**, at least two of the aromatic rings can be arranged periplanar to each other. In the case of the terphenyl derivative **13** however, in the most stable conformation all aromatic rings should be twisted with respect to each other due to the steric interactions of the *ortho*-hydrogen atoms of neighbouring phenyl rings. Nevertheless, even the mesomorphic behaviour of the *p*-terphenyl derivative **13** is modified in the presence of the electron acceptor TNF.

We have to conclude that induction of mesophases by addition of the electron acceptor TNF occurs with both conventional calamitic mesogens and with mesogens composed of disc-like molecules. In the former case, nematic and smectic C phases are suppressed and smectic A phases can be stabilized or induced. Long and branched terminal chains result in a strong stabilization

Table. Transition temperatures (°C) of the calamitic liquid crystals **5–13** and the maximum clearing temperatures (°C) of the induced S_A phases in the contact region with TNF.

Compound	Reference	Transition temperatures of the pure compound	Contact region with TNF: T_{\max} (S _A)	Structures
5^a	[11]	C 173 N 264 I	—	 <p style="text-align: center;">5</p>
6	[12]	C 113 S _C 169 N 209 I	168	 <p style="text-align: center;">6</p>
7	[13]	C 95 S _C 160 N 166 I	174	 <p style="text-align: center;">7</p>
8	[14]	C 115 S _C 175 S _A 182 I	188	 <p style="text-align: center;">8</p>
9	[15]	C 127 S _C 163 N 173 I	170	 <p style="text-align: center;">9</p>
10	[16]	C 147 S _C 193 N 240 I	214	 <p style="text-align: center;">10</p>
11	[17]	C 53 S _A 54.5 N 71.5 I	69	 <p style="text-align: center;">11</p>
12	[18]	C 153 N 215 I	110	 <p style="text-align: center;">12</p>
13	[19]	C 129 S _X 172 S _Y 196 S _Z 201 S _C 214 I	212	 <p style="text-align: center;">13</p>

^aReported transition temperatures: C 171 N 260 I [11].

of the S_A phases, whereas no smectic phases can be obtained below the nematic phases of short chain molecules.

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