Induction of smectic A phases with calamitic molecules and 2,4,7-trinitrofluorenone: the influence of branching and chain length

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Induction of smectic A phases with calamitic molecules and 2,4,7-trinitrofluorenone: the influence of branching and chain length

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Binary systems consisting of 2,5-diphenyl-1,3,4-thiadiazole derivatives incorporating an allene unit in one of the terminal chains and the electron acceptor 2,4,7-trinitrofluorenone (TNF) have been investigated. Though the diphenylthiadiazole cores do not represent typical electron donor units, the nematic and smectic C phases observed for the pure compounds were suppressed and replaced by smectic A phases which in most cases have a higher stability than the nematic phases of the pure compounds. The substitution pattern around the allene moiety allowed a systematic study of the influence of steric effects on the mesophase induction by TNF. Compounds with long and especially those with branched terminal chains can take up a larger number of TNF molecules and can reach a higher stability of the induced SmA phase than those with shorter and unbranched chains. The induction of SmA phases is explained as the result of attractive intermolecular interaction between the diphenylthiadiazole rigid cores and TNF molecules provided by donor–acceptor interactions and quadrupole interactions, as well as a consequence of microsegregation and space filling effects.

1. Introduction

The formation of different kinds of mesophase in mixtures of electron rich and electron deficient molecules is a well known phenomenon in liquid crystal research. For instance, the induced smectic phase behaviour in binary mixtures of various rod-like systems is assumed to be based on electron donor–acceptor (EDA) interactions [1]. Somewhat later these results were adapted for discotic molecules. Columnar (Col) and nematic columnar phases (N_{Col}) have been stabilized or induced by mixing electron rich disk-like molecules and the rather flat electron acceptor 2,4,7-trinitrofluorenone (TNF) [2, 3]. Furthermore, the formation of cubic and smectic phases in the columnar mesophase sequences of double swallow-tailed and polycatenar compounds [4], and the stabilization of smectic A phases in metallomesogens [5] by doping with TNF, have been reported. We have also found that the mesomorphic properties of conventional rod-like mesogens [6], dimesogens and macrocyclic liquid crystal materials [7] can be influenced by addition of the non-mesogenic acceptor

TNF. Thereby nematic and smectic C phases observed in the pure compounds were suppressed, whereas smectic A phases were stabilized or induced.

It was surprising to find that the cyclophane molecule **1** [7], which was especially designed for EDA-interactions and which incorporates an electron donating naphthalene unit, gives a lower stability of the induced SmA phase than the cyclophane **2** incorporating exclusively 2,5-diphenylthiadiazole units, which are only poor electron donors (see figure 1) [6].

During the investigation of monomeric calamitic compounds such as **3** [8], a strong dependence of the mesophase stabilization on the chain length was found [6]. Long and branched terminal chains result in a strong stabilization of the SmA phases, whereas no smectic phases can be induced in the nematic phases of mesogens with short terminal chains [6]. From this point of view, several allene derivatives which have recently been synthesized as novel axial chiral liquid crystals with ferroelectric properties attracted our interest [9, 10]. The substitution pattern around the allenic moiety allows a systematic study of the influence of steric effects on possible mesophase induction by TNF.
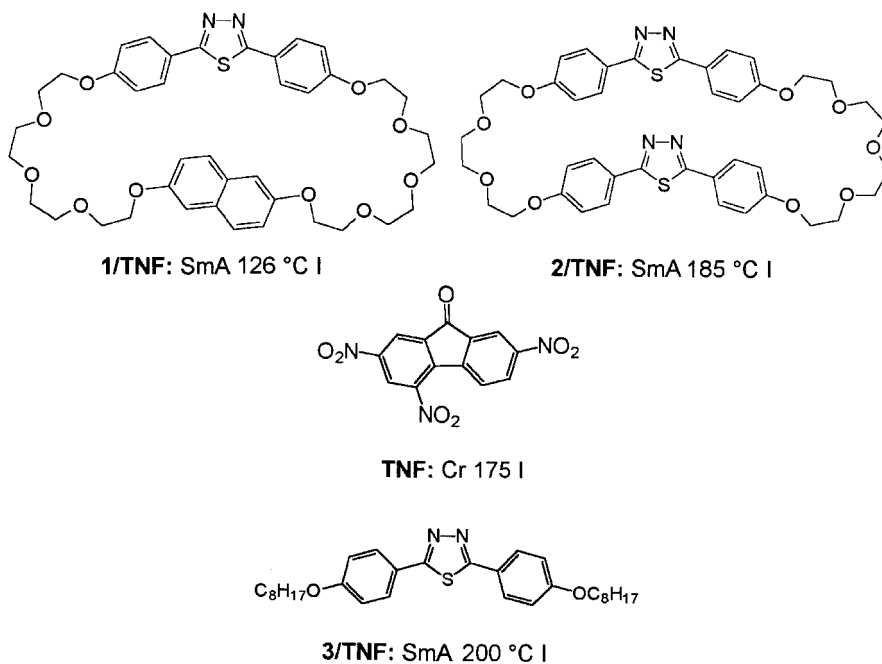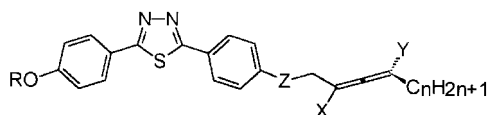
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1/TNF: SmA 126 °C I   **2/TNF:** SmA 185 °C I

TNF: Cr 175 I

Figure 1.   Examples of the induction of SmA phases by TNF in macrocyclic and classical mesogenic 2,5-diphenyl-1,3,4-thiadiazole derivatives [6].

3/TNF: SmA 200 °C I

2.   Materials

The following allene derivatives have been used for the investigations:

4-12:   R = C_4H_9, C_8H_{17}
n = 1,5,7,11
X = H, CH_3, C_2H_5, C_4H_9
Y = H, C_2H_5
Z = O, OOC

These compounds are 2,5-diphenyl-1,3,4-thiadiazole derivatives to which an allene unit is attached via an oxymethylene bridge† (compounds **4–11**) and in one case via an ester group (compound **12**). The synthesis of the compounds **4**, **8** [9(*b*)] and **12** [10] has recently been reported in detail. The preparation of the other compounds will be reported in a separate paper [11].

† All the compounds are chiral, because the allenic moiety bearing two pairs of different substituents at each end represents an axis of chirality. For the investigation of their liquid crystalline and ferroelectric properties [9(*b*), (*d*)], some materials have been obtained as racemic mixtures, whereas others have been synthesized in their enantiomerically enriched form. However the chirality is not of importance for the investigations described herein. We have used racemic and optically active compounds as they were available. All compounds without specification of the absolute configuration are racemic mixtures, despite the fact that their formulae are shown in only one enantiomeric form.

3.   Experimental

The contact regions of the compounds with TNF were first observed microscopically using crossed polarizers. To study the phase diagrams of the binary systems, the phase transitions of mixtures of known concentration were then determined by polarized light microscopy.

4.   Results

4.1.   *Mesomorphic properties of the pure compounds*

The transition temperatures of the compounds investigated are given in the tables 1–3. All compounds display broad range smectic C phases and also nematic phases. Remarkably, no SmA phases have been found. This is a typical feature of liquid crystals containing the 2,5-diphenylthiadiazole unit [12]. In the series of ether compounds **4–11**, the broadest SmC phase regions were found for the disubstituted allene derivatives **4** and **8**. As expected, replacement of the hydrogen at C2 of the allene moiety by alkyl groups leads to a decrease of the mesophase stability (see tables 1 and 2). However, the influence on the SmC–N transition temperature is less pronounced than on the clearing temperature. Even for the butyl substituted compound **7**, the smectic C phase can be observed. The influence of the length of the aliphatic chain at the allene moiety for the 2-methyl substituted compounds **5** is shown in table 3. Remarkably the SmC phase is most stable for the short chain compound **5a** and its stability is decreased by elongation of the aliphatic chain attached to the allene moiety. This

is contrary to results for most other calamitic liquid crystal materials, where SmC phases are stabilized on elongation of the chains.

4.2. *Influence of TNF on the mesomorphic properties*

Figure 2 presents the phase diagram of compound **6** with the non-mesogenic 2,4,7-trinitrofluorenone (TNF, m.p. 175°C). Small concentrations of TNF lead to a depression of the melting point and the SmC–N transition temperature. The nematic phase was stabilized by very small amounts of TNF, a maximum of 96°C occurring at x_{TNF} about 0·05. Further increase of the TNF concentration leads to a destabilization of the nematic phase. At a TNF concentration of $x_{TNF} = 0·1$ a SmA phase suddenly appears which was identified because of its typical fan-shaped texture which can be aligned homeotropically by shearing. It is interesting that the smectic C phase is completely suppressed on addition of TNF (see figure 2) and there is no direct transition from the SmC to the SmA phase.

The stability of the SmA phase rapidly rises on further increasing the concentrations of the acceptor compound. The maximum of 137°C is reached at a TNF concentration of $x_{TNF} \approx 0·35$, and afterwards the clearing temperature slowly decreases again. Thus, the mixture with the non-calamitic compound TNF has a significantly increased mesophase stability in comparison with the pure calamitic mesogen. The difference in the clearing temperatures of the nematic phase of the pure compound **6** ($T_{N–I}$) and the maximum of the clearing temperature of the induced SmA phase of the doped system ($T_{maxSmA–I}$) is $\Delta T = T_{maxSmA–I} - T_{N–I} = 41$ K. We are aware
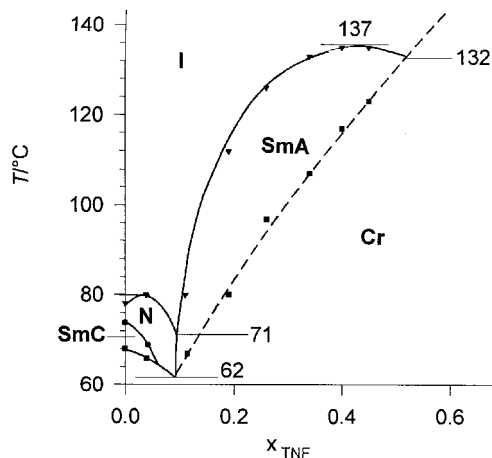
Figure 3. Simplified phase diagram of the binary system of compound **7** with TNF ($\blacksquare$ = melting point; $\blacktriangledown$ = clearing temperature; $\bullet$ = SmC–N transition).

that the mesophases of the pure compound (N) and the doped systems (SmA) are different, and therefore their transition temperatures should not be directly compared. Nevertheless, the clearing temperatures of the nematic phases of pure compounds could give us information about the inherent ability of the molecules to organize in mesophases. Therefore we will use the ΔT values, as defined above, to evaluate the amount of mesophase stabilization obtained by doping the systems‡.

The binary phase diagram of the system **7**/TNF (figure 3) is very similar to that of the system **6**/TNF with the difference that the maximum in the stability of the SmA phase is shifted to higher TNF concentrations ($x_{TNF} = 0·45$).

The maxima observed in the clearing temperatures of the smectic A phases in the contact regions between the thiadiazole derivatives **4**–**12** and TNF are summarized in tables 1–3.

In tables 1 and 2, the effects of substituents at the allene moiety are compared. In the series of butoxy substituted compounds **4**–**7** (table 1), the SmA–I transition temperatures of the induced smectic A phases seem to be independent of the size of the C2-substituent X. Thus, the clearing temperature of the induced phase of the unbranched compound **4** ($X = H$) is nearly identical with the clearing temperatures of the induced phases of the C2-branched compounds **5**–**7**. This could be the result of at least two opposite effects. First, in the undoped materials, the nematic phases are significantly destabilized on enlarging the substituents. The mesophase destabilization on enlarging a branching group is a general phenomenon in calamitic liquid crystals
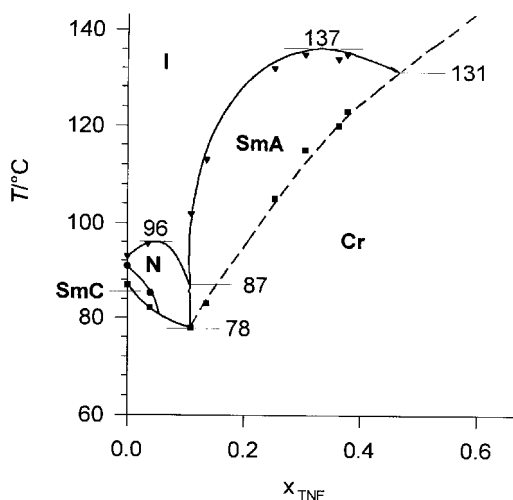

Figure 2. Simplified phase diagram of the binary system of compound **6** with TNF (Cr = crystalline solid; SmA = smectic A phase; SmC = smectic C phase; N = nematic phase; I = isotropic liquid; $\blacksquare$ = melting point; $\blacktriangledown$ = clearing temperature; $\bullet$ = SmC–N transition).

‡Alternatively the SmC–N–transition temperature, which is a measure of the tendency to form smectic phases, can be used for this comparison. The results are qualitatively the same.

Table 1.   Phase transition temperatures ($T/°C$) of the racemic† thiadiazole derivatives **4**–**7**, maximum clearing temperatures ($T/°C$) of the induced SmA phases in the contact region with TNF, and temperature differences between the clearing temperatures of the nematic phases of the pure compounds and the maximum clearing temperatures of the induced SmA phases ($\Delta T = T_{\mathrm{maxSmA}} - T_{\mathrm{N–I}}$).
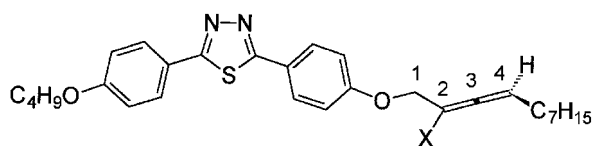
Compound	Ref.	X	Pure compound: $T/°C$	+ TNF: $T_{\mathrm{max}}/°C$	$\Delta T/K$
4	[9(b)]	H	Cr 61 SmC 115 N 132 I	SmA 137 I	+5
5c	[9(c)]	CH_3	Cr 60 SmC 91 N 101 I	SmA 137 I	+36
6	[9(c)]	C_2H_5	Cr 87 SmC 91 N 96 I	SmA 137 I	+41
7	[9(c)]	C_4H_9	Cr 68 SmC 74 N 78 I	SmA 137 I	+59

Table 2.   Phase transition temperatures ($T/°C$) of the racemic† thiadiazole derivatives **8**–**10**, maximum clearing temperatures ($T/°C$) of the induced SmA phases in the contact region with TNF, and temperature differences between the clearing temperatures of the nematic phases of the pure compounds and the maximum clearing temperatures of the induced SmA phases ($\Delta T = T_{\mathrm{maxSmA}} - T_{\mathrm{N–I}}$).
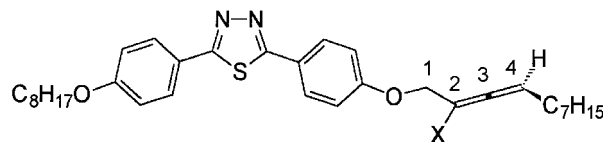
Compound	Ref.	X	Pure compound: $T/°C$	+ TNF: $T_{\mathrm{max}}/°C$	$\Delta T/K$
8	[9(b)]	H	Cr 55 SmC 130 N 131 I	SmA 151 I	+20
9	[9(a)]	CH_3	Cr 64 SmC 98 N 101 I	SmA 146 I	+45
10	[9(c)]	C_2H_5	Cr 50 SmC 92 N 95 I	SmA 143 I	+48

Table 3.   Phase transition temperatures ($T/°C$) of the optically active thiadiazole derivatives **5**[a], maximum clearing temperatures ($T/°C$) of the induced SmA phases in the contact region with TNF, and temperature differences between the clearing temperatures of the chiral modifications of the nematic phases of the pure compounds and the maximum clearing temperatures of the induced SmA phases ($\Delta T = T_{\mathrm{maxSmA}} - T_{\mathrm{N*/BP–I}}$).
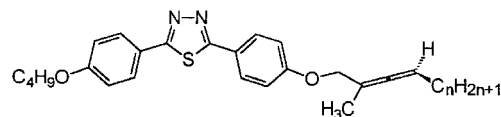

Compound	Ref.	n	Pure compound: $T/°C$	+ TNF: $T_{\mathrm{max}}/°C$	$\Delta T/K$
(R)-**5a**		1	Cr 90 SmC* 116 N* 132 I	SmA 166 I	+34
(R)-**5b**	[9(d)]	5	Cr 65 SmC1* 74 SmC2* 76 SmC3* 95 N* 99·5 BP 100·5 I	SmA 138 I	+37
(S)-**5c**	[9(a)]	7	Cr 60 SmC1* 72 SmC2* 73 SmC3* 90 N* 97 BP 98 I	SmA 137 I	+39
(S)-**5d**	[9(d)]	11	Cr 54 SmC1* 61·5 SmC2* 62·5 SmC3* 79 N* 86 BP 86·5 I	SmA 128 I	+41

[a] The SmC1*–SmC2*–SmC3* transitions most likely correspond to a SmC_A^*–SmC_γ^*–SmC* phase sequence [9(d)].

and should also have an effect in the doped systems. However, in the doped systems this effect seems to be compensated by a mesophase stabilizing effect which increases on elongation of the chains.

If one compares the N–I transition temperatures of the pure compounds **4**–**7** with the maximum clearing temperatures of the induced SmA phases, it becomes evident that this temperature difference ΔT increases

strongly with elongation of the C2-substituent. This shows, that the enhancement of mesophase stability (with respect to the nematic phases of the pure compounds) caused by the interaction with TNF is indeed increased by enlarging the size of the substituent *X*. It seems, that in the series of compounds **4**–**7** this effect completely compensates the loss of mesophase stability caused by the branching of the molecules.

The clearing temperatures of the nematic phases of the octyloxy substituted compounds **8**–**10** (table 2) are nearly identical with those of the corresponding butoxy substituted compounds **4**–**7**. Thus, the elongation of the 'non-allenic' terminal chain has no significant influence on the nematic mesophase stability of the pure compounds. However, the clearing temperatures of the induced SmA phases in the doped systems **8**–**10**/TNF are higher than those of the related system **4**–**6**/TNF. This effect is especially strong for the unbranched allene derivatives (compare **4** and **8**). This shows that elongation of the terminal chains at this end of the molecules increases the stability of the induced SmA phase.

Again, the temperature differences ΔT between the clearing temperatures of the nematic phases of the pure compounds **8**–**10** and the induced SmA phases increase with enlargement of *X*. This indicates that, also for compounds **8**–**10**, the degree of mesophase stabilization caused by the interaction with TNF is increased by enlarging the size of the substituent *X*. However, the increase of ΔT on enlarging the substituent *X* is smaller than for the series **4**–**7**. Therefore, in this homologous series the stability of the induced SmA phase decreases on enlargement of the substituent *X*.

Comparison of the ΔT values of the 2-substituted 2,3-alkadiene derivative **6** and the isomeric 4-substituted compound **11** shows that there is no significant influence of the position of the branching on ΔT.
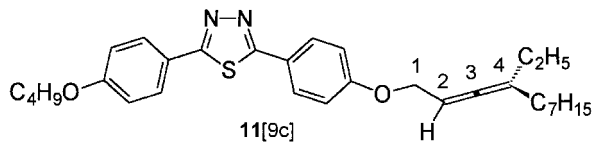
pure compound: T/°C	**11**+TNF: T_{max}/°C	ΔT/K
Cr 89 (SmC 78 N 85) I	SmA 128 I	+43

The influence of the elongation of the alkyl chain in the 'allenic' side chain of the 2-methyl-2,3-alkadienes **5** is given in table 3. The clearing temperatures of the induced SmA phases strongly decrease on elongation of the chain. However, the clearing temperatures of the mesophases of the pure compounds decrease in the same order. By comparison of the ΔT values it becomes evident, that the amount of mesophase stabilization on

addition of TNF is again increased with increasing chain length, but the effect is much smaller than the influence of the branching.
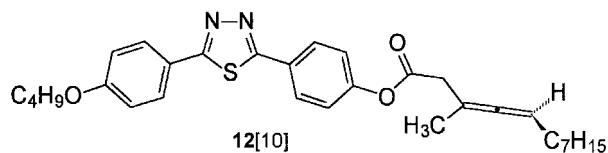
pure compound: T/°C	**12**+TNF: T_{max}/°C	ΔT/K
Cr 76 SmC 149 N 164 I	SmA 136 I	-28

Comparison of the 2,3-alkadienyl ether **5c** with the allenyl acetate **12** reveals that the replacement of the ether oxygen by an oxycarbonyl group strongly stabilizes the mesophases of the pure compound. However the induced SmA phase in the system **12**/TNF has approximately the same mesophase stability as that of the system **5c**/TNF. Thus, for this particular compound, the mesophase stability of the induced SmA phase is lower than the stability of the nematic and of the SmC phase of the pure compound **12** ($\Delta T = -28$ K).

5. Discussion

Considering the molecular structures of the components of the binary systems under investigation, electron donor–acceptor (EDA) interactions, quadrupole interactions, entropy effects, microsegregation and steric interactions should influence their self-organization.

In the binary systems presented here, the calamitic mesogens can act as weak electron donors, and TNF is a strong electron acceptor. Furthermore, TNF is a rather flat molecule and the 2,5-diphenylthiadiazole rigid core is also flat [13], because the conjugation of the aromatic π-system favours a periplanar arrangement of the aromatic rings and there is no steric hindrance between neighbouring rings which disfavours their planar arrangement. Thus, close contact between the molecules should be possible, allowing attractive EDA interactions [14] between them. The presence of EDA interactions in the mixed systems is indicated by the occurrence of a deep red colour in the contact regions between the two components. These EDA interactions should cause additional cohesive forces between the molecules.

However, there is some doubt as to whether the EDA interaction is sufficiently strong to induce a liquid crystal phase. Recently an alternative explanation has been given for the mesophase stabilization in discotic liquid crystals doped with TNF [15]. This explanation has its origin in an electrostatic quadrupolar interaction which stabilizes a face-to-face arrangement of disc-like molecule and TNF, provided that the quadrupole moments of the unlike molecules are opposite in sign. The quadrupole

moment for most peripherally alkoxy substituted disc-like compounds is negative, whilst that of TNF is positive. This interaction should weaken the face-to-face interaction for like particles (pure compounds) while strengthening it for unlike particles (mixtures with TNF). This assumption has been confirmed by Monte Carlo simulations [15] and it has also been applied for an explanation of the unusual phase behaviour of non-symmetric mesogenic dimers consisting of calamitic units [16].

Regarding the systems under discussion, the 2,5-bis-(4-alkoxyphenyl)-1,3,4-thiadiazoles should be only weak electron donors. However, they should provide a strongly negative quadrupole moment due to the donor properties of the alkoxy groups and the acceptor properties of the thiadiazole central unit. Probably the unfavourable quadrupolar interactions between the diphenylthiadiazole cores of neighbouring molecules could contribute to the preference for SmC phases and nematic phases in the pure thiadiazole derivatives [12]. The arrangement of the diphenylthiadiazole units in a smectic A phase would not allow a compensation of their quadrupole moments. Therefore, this arrangement could be destabilized in favour of a tilted SmC phase or a nematic phase in which a partial compensation of the unfavourable quadrupolar interactions is possible (see figure 4).

Insertion of TNF molecules with an opposite (positive) quadrupolar effect between the diphenylthiadiazole units could give rise to attractive quadrupolar interactions which are maximized by a non-tilted parallel arrangement of the molecules in these mixed systems. This could

be a possible explanation of the fact that the SmC phase of pure 2,5-diphenylthiadiazole derivatives is destabilized in the contact region with TNF, and that in the TNF-rich regions the SmA phase is found exclusively. The importance of quadrupolar interactions for mesophase induction with TNF could also explain why a strong electron donor is not necessary for mesophase induction with calamitic molecules and macrocyclic liquid crystal materials such as **2** [7]. It is, however, hard to evaluate which of the attractive forces is dominant. Structural variations, such as for example the replacement of the electron donating ether oxygen of compound **5c** by the oxycarbonyl group which is only a weak donor (compound **12**), have a dramatic influence on the ability to form induced SmA phases. However, they give no answer to this question, because the oxycarbonyl group should not only decrease the electron donor ability of the rigid core, but also simultaneously influence its quadrupole moment and other molecular parameters. Therefore, we presently cannot decide which effect is mainly responsible for the decreased stability of the SmA phase in system **12**/TNF and the increased stability of the induced SmA phase in system **5c**/TNF in comparison with the mesophases of the pure compounds **12** and **5c**, respectively.

However donor–acceptor properties and quadrupolar interactions should not be exclusively responsible for the mesophase stabilization in the systems under discussion. TNF is a rigid and highly polar compound, whereas the calamitic thiadiazole mesogens consist of a rigid and polar central core terminated at both ends by lipophilic
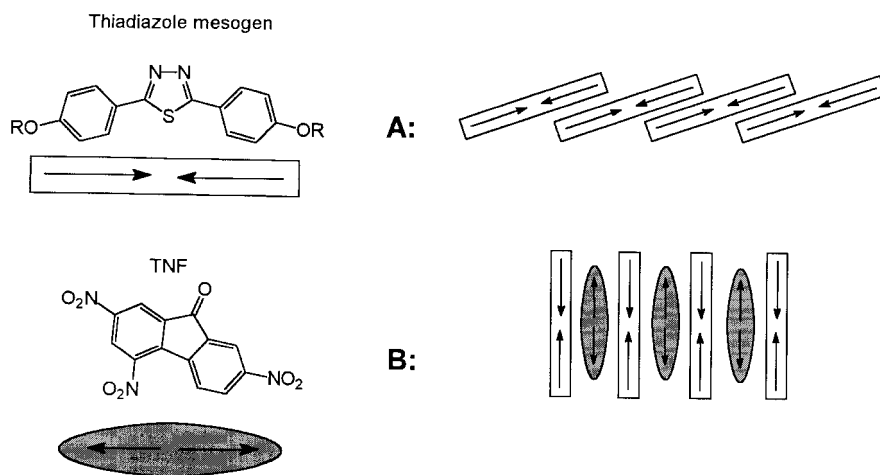

Figure 4. The influence of the quadrupole moment (symbolized as oppositely directed arrows) on the mesophase formation in pure diphenylthiadiazole derivatives (**A**) and in their mixtures with TNF (**B**). Positive quadrupole moment: the arrows are directed away from each other; negative quadrupole moment: the arrows are directed towards each other. Arrangement **A** minimizes the unfavourable quadrupolar interactions between neighbouring diphenylthiadiazole rigid cores in the pure compounds; this arrangement can be realized in nematic and in tilted smectic phases. The arrangement **B** with non-tilted molecules should be stabilized by attractive quadrupolar interactions between the diphenylthiadiazole rigid cores and the TNF molecules.

and flexible alkyl chains. Thus, these calamitic molecules can be regarded as amphiphilic§ compounds with a tendency to segregate the rigid polar parts and the flexible lipophilic parts into separate regions. The attractive interactions with the TNF molecules occur in the central rigid parts of calamitic mesogens. This means, that the polar TNF molecules are mainly built-in between the diphenylthiadiazole units and thus increase the polarity in this region. This enhanced polarity reinforces microsegregation [17–20] of the polar regions—now consisting of the aromatic cores of the calamitic molecules and the TNF molecules—from the non-polar regions of the terminal chains. This microsegregation could substantially contribute to the stabilization of SmA phases in the doped systems. Indeed, no mesophase induction by TNF can be found for calamitic molecules with short terminal chains and the stabilization of the induced SmA phases relative to the nematic phases of the pure compounds (ΔT) rises on increasing the length of the chains and on introduction of branching.

Additionally, there are steric effects which influence mesophase formation. Incorporation of TNF molecules increases the space filling in the central polar and rigid regions¶. The space available between the rigid cores for the incorporation of the TNF molecules without disturbing the interaction of the alkyl chains is limited. It determines the TNF concentration at the maximum of the stability of the SmA phase. Accordingly, the mesophase stabilization which can be achieved is much larger for compounds with long and branched terminal chains than for those with short or unbranched chains (see tables 1–3). The comparison of the TNF concentrations at the maxima of the clearing temperatures of the induced SmA phases is given for selected compounds in table 4. Indeed, with increasing size of the lipophilic regions the maximum of the stability of the induced SmA phase is shifted to larger TNF concentrations. Compounds with long, and especially those with branched, terminal chains can take up a larger number of TNF molecules which provide additional cohesive forces in the region of the rigid cores. Therefore these molecules can reach a higher stability of the induced SmA phases than those with short and unbranched chains.

Finally we want to point out some analogies between the mesophase induction caused by addition of TNF to anisometric molecules and the formation of lyotropic

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Table 4. Comparison of the temperature differences between the clearing temperatures of the nematic phases of the pure compounds and the maximum clearing temperatures of the induced SmA phases ($\Delta T = T_{\text{maxSmA}} - T_{\text{N–I}}$) and the positions of the maxima of the induced SmA phases (x_{TNF}) in the phase diagrams of the binary systems of compounds **3** [8, 6], **6** and **7** and with TNF.

Compound	ΔT/K	x_{TNF}
3	+2	0·2
6	+36	0·35
7	+59	0·45

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mesophases by addition of protic solvents to classical amphiphiles [21]. Both binary systems consist of amphiphilic molecules and other molecules which can specifically interact with only one of the amphiphatic parts of these amphiphilic molecules. In both cases these interactions can give rise to additional cohesive forces and increase the segregation tendency of the amphiphatic parts‖. A main difference from lyotropic systems is that the number of TNF molecules which can be incorporated between the rigid cores of classical calamitic molecules without destroying the smectic order is strongly limited. Furthermore, exclusively smectic A phases are found in the TNF doped systems of calamitic mesogens as a consequence of the rigidity of the molecules, the linear pre-organization of the alkyl chains and the equivalent space filling of the antagonistic regions. On branching the terminal chains, more space becomes available between the rigid cores, and a larger number of TNF molecules can be inserted. An especially large size of the lipophilic regions is provided with polycatenar [22] and double swallow-tailed compounds [23]. This gives rise to a curvature of the interfaces between the regions of the rigid cores and the flexible alkyl chains, and a rich polymorphism including columnar mesophases is found for the pure compounds. Addition of TNF to columnar mesophases of polycatenar molecules increases the volume of the central rigid regions and—as in inverted lyotropic systems—the interface curvature between the antagonistic regions decreases giving rise to a transition from columnar phases via intermediate phases (Cub, SmC) to SmA phases with flat interfaces [4]. So it seems that columnar mesomorphism in TNF doped systems is strongly restricted to rigid disc-shaped molecules.

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§Amphiphilicity is used here in a quite general sense. It describes any chemical or structural contrast within a molecule [17–20].

¶The increased size of the rigid and polar regions in the mixed systems additionally disfavours tilted SmC phases in relation to SmA phases, because tilting of the rigid cores would further enlarge the lateral cross section. This is unfavourable, because it would disturb the packing of the alkyl chains.

‖This analogy is especially evident from comparison with the behaviour of non-ionic amphiphiles. For example, the addition of water to oligo(oxyethylene) surfactants provides additional hydrogen bonding between the polyether chains and the water molecules. This increases the cohesive forces between the polar groups. Simultaneously, the coordination of the water molecules to the polyether chains enhances their polarity, which forces the segregation from the lipophilic alkyl chains and gives rise to the formation of lyotropic mesophases.

In summary, the smectic A phases occurring in the contact region between TNF and the thiadiazole derivatives **3–12** appear to be formed due to the attractive intermolecular interaction between both molecules, provided by donor–acceptor interactions and quadrupole interactions, the microsegregation and the space filling effect of the flat TNF molecules between the rigid cores of the calamitic liquid crystal molecules. Depending on the particular structure of the interacting molecules, the different factors can contribute to a different extent to the total effect.

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