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Liquid crystalline behaviour of thienyl-enaminoketone derivatives containing halogen atoms

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New homologous series containing a thienyl-enaminoketone-phenyl (TEP) core substituted by a halogen atom have been synthesized. It is shown that the stability of the orthogonal phases decreases with the decreasing electron-accepting properties of the halogen atom. Generally the materials studied form orthogonal smectic phases, but in additional, tilted smectic phases are observed in iodine-substituted series as well as for two homologues containing bromine in the thienyl ring. For comparison, a homologous series containing a terminal cyano group was also studied.

1. Introduction

The formation of thermotropic mesophases is caused predominantly by the anisometric rod-like or disc-like shape of the single molecule [1]. Recently, however, considerable attention has focused on molecules which depart from this simple geometry. For example, strongly bent molecules have been studied and it has been shown that they form new types of polar phases [2]. Here we present results for materials with a slightly bent molecular shape, and our goal was to understand the relationship between the chemical nature of the terminal group and the type of phases formed, as a first step towards understanding structure–property relationships in strongly bent molecules. The three-ring thienyl-enaminoketone-phenyl fragment was chosen as the core (see the scheme). The thienyl ring slightly bends the molecular structure. Based on an X-ray single crystal investigation, it is known that the angle between the moieties attached to the thienyl ring is 146° [3]. In the terminal positions, groups differing in terms of their dipole moment, size and electron-donating properties were introduced. Previous studies of enaminoketone derivatives showed that bent molecule structure strongly promotes the formation of tilted smectic phases [4] while terminal substituents that withdraw electrons from the mesogenic core promote orthogonal phases [5]. For weak or moderate electron acceptors, for example halogen atoms, the phase sequence SmA–SmB$_{\text{Hex}}$–B is often observed [5–7]. By introducing terminal halogen atoms into a bent molecule, one can observe how the competing tendencies towards the formation of either tilted or orthogonal phases are resolved.

X	Series
F	*n*TEPF
Cl	*n*TEPCl
Br	*n*TEPBr
I	*n*TEPI

X	Series
Cl	ClTEP*n*
Br	BrTEP*n*
I	ITEP*n*
CN	CNTEP*n*

Scheme. Molecular structures of compounds studied.

2. Experimental

The enaminoketone thienyl derivatives were synthesized using standard methods from the appropriate 5-alkyl-2-acetylthienyls and 4-halogenoanilines for the *n*TEP*X* series, from 5-halogeno-2-acetylthienyls and

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4-alkoxyanilines for the halogenated *X*TEPO*n* series, and from 5-cyano-2-acetylthienyls and 4-alkoxyanilines for the CNTEPO*n* series. The products were purified by crystallization from nonane.

A typical synthetic procedure is described for 1-[2-(5-pentylthienyl)]-3-(4-iodophenylamino)-2-propen-1-one (5TEPI). The sodium salt of 3-[2-(5-pentylthienyl)]-3-oxopropanal was obtained by a Claisen formylation reaction; 2-aceto-5-pentylthienyl (15 mmol) and ethyl formate (5 ml) were added to sodium powder (0.4 g) dispersed in diethyl ether (25 ml) and the mixture stirred for 12 h. The diethyl ether and excess ethyl formate was evaporated and the crude sodium salt (yield *c.* 70%) dissolved in methanol (20 ml). To this solution (*c.* 10 mmol), 4-iodoaniline (10 mmol) in methanol (20 ml) was added, and the resulting mixture was neutralized with acetic acid and left for 12 h. Crystals of product were filtered off and recrystallized from nonane; yield 87%. ^{1}H NMR ($CDCl_3$): $\delta = 0.88$–1.76 (m, 9H, $CH_2(\mathit{CH}_2)_3\mathit{CH}_3$); 2.87 (t, $J = 7.6$ Hz, 2H, $\mathit{CH}_2(CH_2)_3CH_3$); 5.57 (d, $J = 7.9$ Hz, H, H2); 6.80 (d, $J = 3.8$ Hz, H, $H4'$); 6.82 (d, $J = 8.9$ Hz, 2H, $H2''$, $H6''$); 7.35 (dd, $J = 7.9$; 12.2 Hz, H, H3); 7.48 (d, $J = 3.8$ Hz, H, $H3'$); 7.62 (d, $J = 8.9$ Hz, 2H, $H3''$, $H5''$); 11.78 (d, $J = 12.2$ Hz, H, NH). Elemental analysis: calc. C 50.70, H 5.01, N 3.29, S 7.56, I 29.69; found C 50.87, H 4.99, N 3.34, S 7.48, I 29.77%.

Table 1. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the *n*TEPF series.

n	Cr		SmA		I
4	•	80.8 (24.72)	•	86.59 (2.85)	•
5	•	65.0 (17.85)	•	92.2 (3.23)	•
6	•	80.1 (32.90)	•	98.1 (3.64)	•
7	•	61.6 (25.70)	•	100.1 (3.93)	•
8	•	83.4 (41.90)	•	101.9 (4.20)	•
9	•	70.6 (28.61)	•	101.7 (4.10)	•

The identification of the mesophases was based on microscopic observations of the textures observed using a Nikon polarizing microscope equipped with Mettler FP82HT heating stage. For the orthogonal liquid crystalline phases SmA, SmA_d, and SmB_{Hex} and for the crystal B phase, black homeotropic or/and focal-conic fan textures were found. When no change in texture was observed during the transitions between orthogonal phases, the phase transition temperatures were determined by either calorimetric or X-ray measurements which are discussed later. For the tilted smectic phases, SmC and SmF, characteristic schlieren textures or broken focal-conic fan textures were observed. Additionally, the SmF phase was assigned from the L-shaped patches which appear in the broken fan texture. The tilted crystal G phase was identified on the basis of characteristic paramorphotic broken focal-conic fan or mosaic textures.

Calorimetric measurements were performed using a Perkin-Elmer DSC7 differential scanning calorimeter. The X-ray studies were performed using a DRON-system for homeotropically aligned one surface free samples in reflection mode.

3. Results and discussion

The phase transition temperatures and associated enthalpy changes are collected in tables 1–8. The phase diagrams of the *n*TEPX series, in which the halogen atom (*X* = F, Cl, Br, I) is attached to the phenyl ring,

Table 2. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the *n*TEPCl series.

n	Cr		SmB_{Hex}		SmA		I
4	•	102.6 (15.82)			•	153.1 (5.94)	•
5	•	87.7 (14.21)			•	156.3 (6.24)	•
6	•	73.4 (11.43)	•	77.0 (0.55)	•	159.4 (6.57)	•
7	•	80.7 (25.20)	•	72.1 (0.18)	•	159.6 (7.05)	•
8	•	88.1 (30.68)	•	70.0 (0.56)	•	159.1 (7.13)	•
9	•	85.0 (29.52)	•	72.5 (0.47)	•	158.4 (6.93)	•

Table 3. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the *n*TEPBr series.

n	Cr		SmB_{Hex}		SmA		I
4	•	119.0 (17.29)			•	159.2 (6.30)	•
5	•	105.6 (17.08)	•	91.3 (0.45)	•	162.8 (6.88)	•
6	•	89.0 (24.07)	•	94.3 (0.90)	•	165.7 (7.10)	•
7	•	84.3 (20.02)	•	91.2 (0.57)	•	167.5 (6.78)	•
8	•	90.5 (28.73)	•	89.8 (0.92)	•	166.9 (7.73)	•
9	•	89.3 (28.64)	•	90.6 (0.82)	•	167.4 (7.77)	•

Table 4. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the *n*TEPI series.

n	Cr		G		SmF		SmB$_{Hex}$		SmA		I
4	•	136.3 (18.86)							•	154.1 (6.08)	•
5	•	116.7 (20.61)	•	97.8 (0.17)			•	109.4 (0.72)	•	159.9 (6.88)	•
6	•	106.2 (25.24)	•	93.2 (0.03)	•	96.2 (0.01)	•	111.0 (1.23)	•	162.8 (7.11)	•
7	•	99.9 (17.48)	•	90.1 (0.02)	•	94.4 (0.02)	•	110.5 (1.45)	•	166.0 (7.88)	•
8	•	103.6 (21.39)	•	78.9 (0.004)	•	82.5 (0.02)	•	110.3 (2.85)	•	165.9 (7.94)	•
9	•	101.6 (12.89)					•	113.9 (1.73)	•	167.6 (7.94)	•

Table 5. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the ClTEPO*n* series.

n	Cr		B		SmB$_{Hex}$		SmA		N		I
1	•	121.6 (21.35)							•	137.4 (0.22)	•
2	•	129.4 (16.65)					•	165.1 (4.87)			•
4	•	108.8 (13.87)	•	102.6 (0.10)	•	105.9 (1.04)	•	181.7 (6.23)			•
5	•	74.3 (10.94)	•	96.0 (0.12)	•	102.8 (0.97)	•	182.5 (6.64)			•
6	•	68.6 (4.94)	•	96.8 (0.05)	•	104.3 (0.86)	•	185.2 (5.40)			•
7	•	69.3 (24.30)	•	96.5 (0.03)	•	105.5. (1.89)	•	184.9 (7.47)			•
8	•	65.5 (21.61)	•	95.63 (0.02)	•	105.8 (1.96)	•	184.6 (7.74)			•
10	•	71.5 (29.19)			•	105.0 (1.57)	•	182.3 (8.21)			•
11	•	75.1 (29.89)			•	104.3 (2.20)	•	180.3 (8.34)			•
12	•	79.5 (35.97)			•	104.2 (1.34)	•	178.2 (8.35)			•

Table 6. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the ITEPO*n* series.

n	Cr		G		SmF		SmC		SmA		I
5	•	140.4 (33.93)	•	104.4 (2.36)			•	125.6 (0.14)	•	146.2 (4.58)	•
6	•	129.5 (27.43)	•	96.7 (0.11)	•	102.1 (1.34)	•	107.5 (0.08)	•	152.3 (5.27)	•
8	•	96.9 (15.41)	•	90.2 (0.02)	•	103.4 (1.27)	•	106.2 (0.02)	•	157.8 (6.03)	•
9	•	66.7 (20.22)			•	101.4 (1.45)	•	103.8 (0.005)	•	158.8 (6.06)	•

Table 7. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the BrTEPO*n* series.

n	Cr		G		B		SmF		SmB$_{Hex}$		SmA		I
1	•	166.6 (34.90)											•
2	•	142.6 (20.60)									•	153.9 (4.60)	•
3	•	137.7 (17.16)									•	160.7 (5.04)	•
4	•	116.7 (15.10)	•	94.7 (0.07)	•	106.9 (0.02)			•	108.9 (1.21)	•	172.7 (5.81)	•
5	•	107.9 (28.80)	•	92.3 (0.04)	•		•	96.5 (0.004)	•	100.7 (0.94)	•	171.5 (6.26)	•
6	•	102.0 (25.68)			•	93.6 (0.04)			•	99.0 (1.09)	•	172.8 (7.67)	•
8	•	104.5 (1.79)			•	95.0 (0.02)			•	102.8 (1.52)	•	175.7 (7.29)	•
9	•	109.1 (4.56)			•	91.3 (0.004)			•	103.2 (0.80)	•	175.8 (7.63)	•
10	•	105.6 (27.54)								102.4 (0.87)	•	177.2 (7.69)	•

are shown in figure 1. For these series the mesophase temperature range increases on increasing the radius of the terminal halogen atom and within a series increases on increasing the length of the terminal alkyl chain attached to the thienyl ring. For the *n*TEPF, *n*TEPCl, and *n*TEPBr series only orthogonal phases (SmA and SmB$_{Hex}$) were observed while for the *n*TEPI series tilted phases appear. The phase transition between the liquid-like SmA and the hexatic SmB$_{Hex}$ phases is accompanied by strong heat capacity anomalies in both phases [7, 8] detected using DSC. Specifically, a broad peak with characteristic wings was observed (figure 2) in comparison with the usual very sharp peak observed for the SmA–B phase transition. This difference in the DSC

Table 8. Phase transition temperatures (°C) and associated enthalphy changes (in parentheses) (kJ mol^{-1}) for the CNTEPO*n* series.

n	Cr		SmA$_d$		I
5	•	131.0 (8.40)	•	182.0 (4.49)	•
6	•	125.8 (9.47)	•	183.6 (5.13)	•
7	•	124.2 (11.18)	•	186.3 (5.65)	•
8	•	118.6 (14.69)	•	183.4 (5.85)	•
9	•	122.0 (14.42)	•	185.8 (6.59)	•
10	•	113.5 (7.11)	•	187.9 (7.03)	•
11	•	116.4 (27.52)	•	186.2 (7.26)	•
12	•	105.2 (7.74)	•	182.4 (7.17)	•
13	•	121.4 (3.65)	•	184.4 (8.01)	•
14	•	106.6 (7.70)	•	184.0 (7.70)	•

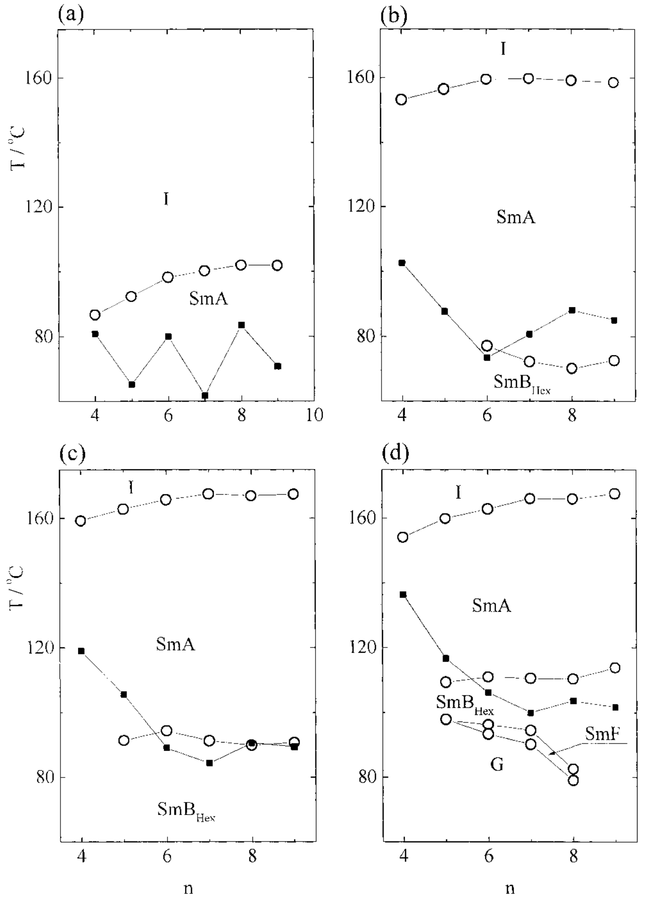

Figure 1. Dependence of the transition temperatures on the number of carbon atoms in the alkyl chain for the (*a*) *n*TEPF, (*b*) *n*TEPCl, (*c*) *n*TEPBr and (*d*) *n*TEPI series. Filled squares represent the crystal melting temperature.

signal prevents the misidentification of crystalline or hexatic B phases based only on the observation of optical textures. The assignment of the hexatic SmB phase is further supported by the X-ray measurements. At the SmA–SmB$_{Hex}$ phase transition a continuous increase in the layer spacing, without any detectable jump, was observed, which originates from changes in the extent of molecular interdigitation between the smectic layers as well as changes in the orientational order of the long molecular axes [5]. In the *n*TEPI series, compounds with $n = 6, 7, 8$ exhibit the rare phase sequence, SmB$_{Hex}$–SmF. It has been shown already [9] that at this transition the molecular tilt with respect to the layer normal, which is the primary order parameter, changes continuously with temperature for 6TEPI and 7TEPI but exhibits a jump for 8TEPI. On the SmB$_{Hex}$–SmF phase transition line, the tricritical point, at which the phase transition changes from being first to second order, was found at $n = 7.3$, as detected for binary mixtures of $n = 7$ and $n = 8$. The change of the order at the phase transition is probably caused by crystalline fluctuations arising from the proximity of the crystal G phase that is formed below the SmF phase.

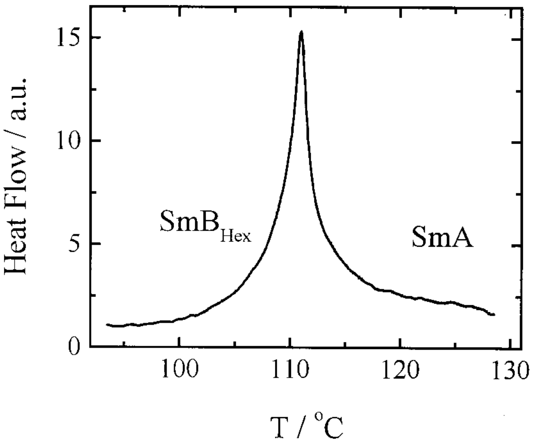

Figure 2. DSC trace showing the SmB$_{Hex}$–SmA phase transition in 6TEPI.

A similar tendency for stabilizing orthogonal phases was also observed when the halogen atom was attached to the thienyl ring giving the XTEPO*n* series (figure 3). For the ClTEPO*n* series, only orthogonal phases were observed, while for the ITEPO*n* series the tilted phase sequence SmC–SmF–G appeared below the SmA phase. For the BrTEPO*n* series, the observed phase behaviour is more complicated. Only one homologue ($n = 5$) reveals a tilted phase sequence involving the SmF and G phases below the orthogonal SmA and SmB$_{Hex}$ phases. Due to reasons of phase symmetry, multicritical points can appear at the ends of the B–SmF phase transition line, see figure 3 (*d*). However, DSC measurements of binary mixtures containing $n = 5$ and 6 homologues did not show a decreasing enthalpy change along the first order SmB$_{Hex}$–SmF and SmF–G transition lines. Moreover, the B–SmF phase transition line has a very steep negative gradient, which suggests a reentrant B–SmF phase sequence. The topology of the phase diagram for binary mixtures of $n = 4$ and 5 homologues was very difficult

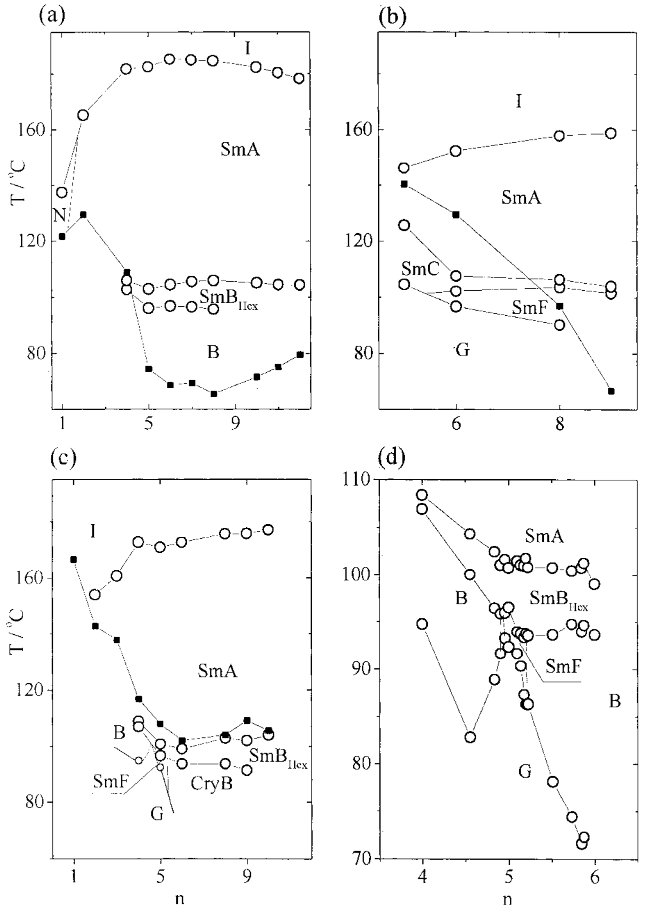

Figure 3. Dependence of the transition temperatures on the number of carbon atoms in the alkyl chain for the (*a*) ClTEPO*n*, (*b*) ITEPO*n*, (*c*) BrTEPO*n* series, and (*d*) for mixtures of BrTEPO4–BrTEPO5 and BrTEPO5–BrTEPO6. Filled squares represent crystalline melting temperatures.

to establish. The B–G and SmF–G phase transition lines are steep and it appears that two triple points, SmB$_{Hex}$–B–G and SmB$_{Hex}$–SmF–G, are located very close to each other. This proposed topology does not assume reentrant phase sequences. In binary mixtures of homologues with $n = 4$ and 6 the tilted SmF phase was not detected.

Comparing the phase transition temperatures within the *X*TEPO*n* series, it can be seen that a big, bulky substituent close to the bent part of the molecule destroys the stability of the mesophases. For medium size halogen atoms, chlorine or bromine, one can observe that changing the halogen atom position from the thienyl to phenyl ring decreases the stability of the mesophases by ~20 K. However, this does not apply to the bulky iodine atom substituent.

For materials with the cyano group (which possesses strong electron-accepting properties) substituted on the thienyl ring, only the partial bilayer SmA$_d$ phase [10] was observed and over a broad temperature range (figure 4). The ratio of the smectic layer spacing, *d*, measured by X-ray scattering, to the fully extended molecule length, *L*, estimated by molecular modelling, was found to be 1.28 for CNTEPO5 at 150°C. The type of phase formed by the cyano derivatives is in agreement with the general rule that substituents which decrease electron density in the mesogenic core promote orthogonal phases of low order within the smectic layer. The observation of the partial bilayer SmA$_d$ phase for the CNTEPO*n* series also proves that in order to obtain the molecular dimers responsible for the formation of the SmA$_d$ phase it is not necessary that the molecule possesses a strong dipole moment exactly along the long molecular axis.

4. Conclusions

Our results show that compounds possessing a slightly bent molecular structure when substituted by moderately electron-accepting terminal groups have a strong tendency towards the formation of orthogonal phases. In the majority of the series, the phase sequence SmA–SmB$_{Hex}$–B was observed. Tilted phases appeared only for the iodine (*n*TEPOI and ITEPO*n*) and bromine (BrTEPO*n*) substituted series, as the electron donating properties and the polarizabilities are greater for the larger halogen atoms. The competing interactions between the bent molecular shape and the electron-accepting properties leads to the

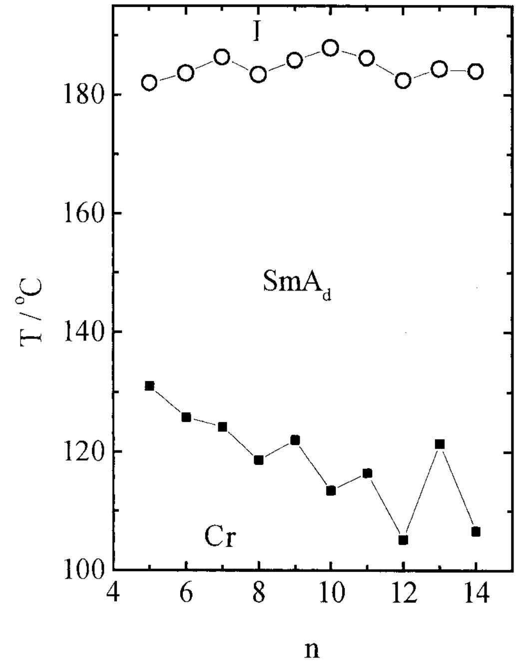

Figure 4. Dependence of the transition temperatures on the number of carbon atoms in the alkyl chain for the CNTEPO*n* series. Filled squares represent crystalline melting temperatures.

rarely observed phase transition between the orthogonal and tilted hexatic smectic phases, SmB_{Hex}–SmF (BrTEPO*n* and *n*TEPOI series). Substituting the strongly electron-accepting cyano group in the terminal position of the thienyl-enaminoketone-phenyl core, which introduces a large longitudinal component of the dipole moment, results in the formation of the orthogonal, partial bilayer SmA_d phase and an increase in the clearing temperatures in comparison with those of the halogen-substituted series. The higher clearing temperatures most probably result from the substitution of the CN group which has two unsaturated bonds, thus extending the conjugated π-bond system of the mesogenic core and thus, increasing its polarizability.

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