Properties of chiral liquid crystals with inner hydrogen bonds

Damian Pociecha,[a] Adam Krówczyński,[a] Jadwiga Szydłowska,[a] Ewa Górecka,[a] Milada Glogarova[b] and Jan Przedmojski[c]

[a]*Warsaw University, Department of Chemistry, Laboratory of Dielectrics and Magnetics, Al. Zwirki i Wigury 101, 02-089 Warsaw, Poland*

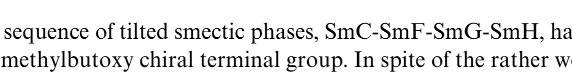
[b]*Academy of Sciences of the Czech Republic, Institute of Physics, Na Slovance 2, 180 40 Prague 8, Czech Republic*

[c]*Warsaw University of Technology, Department of Physics, 00-662 Warsaw, Poland*

A sequence of tilted smectic phases, SmC-SmF-SmG-SmH, has been observed in a series of enamino ketone derivatives with a 2-methylbutoxy chiral terminal group. In spite of the rather weak chiral centre, these compounds are characterized by high spontaneous polarization (*ca.* 0.5 μC cm^{-2}), which seems to be induced by the large molecular tilt (*ca.* 40°) observed in all mesophases. A memory effect in the switching process has been observed due to the formation of ion layers at electrodes. The high hydrogen ion concentration is a result of the dissociation of hydrogen bonded material under an applied electric field.

Compounds with inner hydrogen bonds forming thermotropic liquid crystalline phases have been studied because of their unique properties such as their chelating ability. Among them enamino ketone structures are the most extensively examined because simple synthetic procedures lead to a variety of molecular structures.[1–3]

Recently, several series of enamino ketone mesogens have been reported and it has been argued that their phase sequence can be controlled by molecular factors such as the electric dipole moment of the molecular structure or the electron donating and accepting properties of terminal groups, which affect the electron distribution within the mesogenic core.[4] In this paper, we present properties of a new chiral enamino ketone derivatives series denoted by (−)-**LAC*n***



which was designed to give a sequence of tilted smectic phases: liquid-like SmC, hexatic SmF and crystalline SmG, SmH. In order to obtain this phase sequence, strongly electron donating *n*-alkoxy and 2-methylbutoxy groups were attached to the three-ring phenyl–enamino ketone–phenyl core. For comparison the racemic counterparts (±)-LAC*n* were examined. Some other chiral three-ring enamino ketone derivatives have also been synthesized to establish the effect of molecular structure on liquid crystalline properties.

Experimental

The enamino ketone compounds were synthesized by reacting hydroxymethylene derivatives of 4-(2-methylbutoxy)phenylacetophenone with 4-alkoxyanilines and purifying by crystallization from toluene. A typical synthetic procedure is described for 1-(4-methoxyphenylamino)-3-[4-(2-methylbutoxy)phenyl]-prop-1-en-3-one: the sodium salt of 3-(4-methoxyphenyl)-3-oxopropanal was obtained by the Claisen formylation reaction by adding 4-(2-methylbutoxy)phenylacetophenone (15 mmol) and ethyl formate (5 ml) to sodium powder (0.4 g) dispersed in diethyl ether (25 ml) and stirring the mixture for 12 h. After the diethyl ether and excess ethyl formate had evaporated, the crude sodium salt (yield *ca.* 70%) was dissolved in methanol (20 ml). To this solution (*ca.* 10 mmol) anisidine (10 mmol) in methanol (20 ml) was added, then neutralized with acetic acid and left for 12 h. Yellow crystals of the product were filtered off and recrystallized. Yield 87%, mp 142.5 °C, clearing point 168 °C. The molecular structure was confirmed for the **LAC1** compound by ^{1}H NMR spectroscopy: δ_H 0.88–2.00 [m, 9H, $OCH_2CH(CH_3)CH_2CH_3$]; 3.70–3.92 (m, 5H, OCH_2, OCH_3); 5.93 (d, *J* 7.8, 1H, H^2); 6.80–7.10 (m, 7H, aromatic); 7.38 (dd, *J*1 7.8, *J*2 12.8, 1H, H^1); 7.90 (d, *J* 8.95, 1H, H$^{2''}$); 12.10 (d, *J* 12.8, 1H, N*H*).

Liquid crystalline properties were examined using polarizing microscopy (Nikon Optiphot2-Pol equipped with P101 photometer and Mettler FP82HT hot stage) and by differential scanning calorimetry (Perkin-Elmer DSC7). Thermograms were taken at several scanning rates, and temperatures and thermal effects were recalculated at 5 °C min^{-1} if necessary. Layer spacing data were obtained from X-ray scattering in reflection mode for homotropically aligned samples placed in a double oven. The measurements were taken with a modified DRON spectrometer. The wave vector was determined to within 10^{-3} Å^{-1}. Dielectric properties were studied using a Wayne Kerr Precision Component Analyzer 6425. Measurements of spontaneous polarization, P_s, and apparent tilt, θ, were recorded. The spontaneous polarization was obtained from the $P_s(E)$ hysteresis loop detected during the P_s switching. The apparent tilt was determined from an angle difference between minimum transmission positions of a planar sample placed between crossed polarizers under opposite DC fields. Molecular dimensions were estimated by molecular modelling (HYPERCHEM 3.0).

Results and Discussion

The phase diagram for the (−)-**LAC*n*** series is presented in Fig. 1. Phase transition temperatures and thermal effects are collected in Table 1. In materials studied there is no pronounced chiral discrimination effect;[5,6] the phase transition temperatures and enthalpies are almost equal for the chiral and racemic materials.

In the compounds studied exclusively tilted smectic phases were detected. This is in agreement with our predictions, since the strongly electron donating alkoxy groups (Hammett constant σ *ca.* −0.3) used as the terminal chains promote tilted phases for three-ring enamino ketone molecules.[4] The nematic phase was observed only for short homologues.

The compounds studied have distinctly lower clearing and melting temperatures compared to materials with non-branched *n*-butoxy terminal chains.[7] The difference is of the

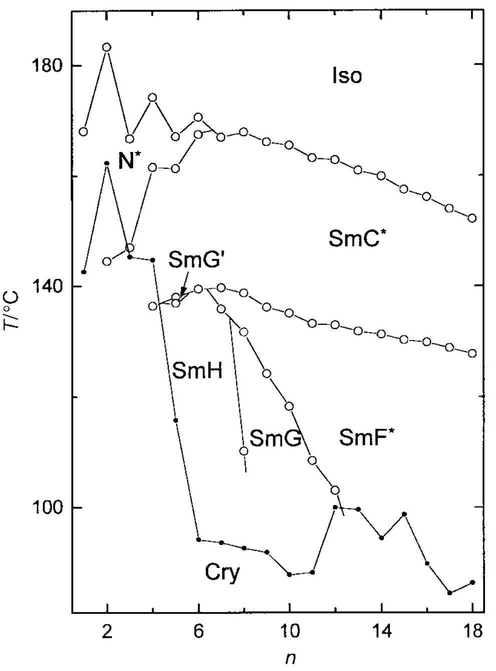


Fig. 1 Phase diagram for the (−)-**LAC*n*** homologues series

order of 30 °C. This behaviour is typical since non-linear terminal groups do not allow close molecular packing.

As with previously reported series,[2,7] one can observe that the liquid-like SmC to hexatic SmF phase transition temperatures and enthalpy changes depend slightly on terminal chain length. The SmC–SmF phase transition, which theoretically should be of the first order,[8] is always accompanied by strong both-side heat capacity anomalies seen as very broad peaks on DSC thermograms.[9] In contrast, enthalpy changes at the strongly first order, as detected by X-ray measurements, hexatic–crystalline smectic (SmF–SmG) phase transition are small and rapidly decrease with increasing terminal chain length. In the LAC*n* series the SmF–SmG phase transition enthalpy changes become undetectable ($\Delta H < 0.01$ J g^{-1}) for homologues $n > 12$ [series (−)-**LAC*n***] or $n > 11$ [series (±)-**LAC*n***]. Moreover, while the stability of the hexatic phase is almost independent in the homologous series, the crystalline SmG phase is strongly destabilized with increasing length of the alkoxy terminal group. For short homologues the hexatic–crystalline phase transition is accompanied by freezing of the schlieren texture leading to the paramorphic mosaic texture retaining schlieren characteristics;[10] for higher homologues the texture changes are small and difficult to detect. The SmG–SmH phase transition is detectable using calorimetric and microscopic methods.

For all chiral substances textures with dechiralization lines could be observed in the SmC and SmF phases which indicates the existence of a helical structure of the director.[11,12] The helical pitch calculated from dechiralization line spacing is of the order of 1 µm, which points to a rather weak twisting power of the molecular chiral centre.

X-Ray

All compounds studied show interlayer distances (*d*) markedly smaller than the fully extended molecular length (*L*) calculated from molecular modelling. The d/L ratio is 0.75–0.82. This indicates a strong molecular tilt within the smectic layers—the tilt angle calculated from the d/L ratio is *ca.* 40–45°. This value is in agreement with data obtained from electrooptic switching measurements in the SmC and SmF phase. In the higher ordered phases the electrooptic measurements with a DC electric field could not be carried out because of the high threshold switching field and conductivity of the material. The tilt angle is nearly constant in the temperature range of the SmC and SmF phases. However, the layer spacing was found to exhibit a critical anomaly at the SmC–SmF phase transition (Fig. 2). For short homologues the layer spacing decreases with decreasing temperature while for long homologues the layer spacing changes are inverted—increase of layer thickness with decreasing temperature is observed, the magnitude of changes being smaller for long homologues. For materials with intermediate terminal chain length the changes are less pronounced. The layer spacing changes at the SmC–SmF phase transition seem to be caused by two opposing factors—small tilt angle changes (*ca.* 1–2°) and the chain melting phenomenon. For compounds with short terminal groups the chain melting effect is weak so one can correlate the decreasing d/L ratio at the SmC–SmF phase transition with the small increase in the tilt angle. For the long homologues the chain melting affects the layer spacing more strongly than the tilt angle changes, so a lower interlayer distance in the SmC phase than in the SmF phase is observed.

Table 1 Temperatures and, in parentheses, enthalpies of the phase transitions for the compounds of the LAC*n* series

n	Cry	*T*/°C (ΔH/J g^{-1})	SmH	*T*/°C (ΔH/J g^{-1})	SmG	*T*/°C (ΔH/J g^{-1})	SmF	*T*/°C (ΔH/J g^{-1})	SmC	*T*/°C (ΔH/J g^{-1})	N	*T*/°C (ΔH/J g^{-1})	Iso
1	•	142.6 (97.4)									•	168.1 (2.2)	•
2	•	162.4 (92.4)								144.6 (4.9)	•	183.4 (3.9)	•
3	•	145.4 (46.4)								147.0 (5.8)	•	166.7 (3.4)	•
4	•	144.7 (37.4)	•	136.4 (8.6)						161.6 (6.5)	•	174.2 (4.4)	•
5	•	115.7 (26.4)	•	136.9 (0.5)	•[a]	138.0 (7.1)				161.3 (9.8)	•	167.1 (4.6)	•
6	•	94.2 (20.8)	•	139.5 (10.3)						167.5 (10.0)	•	170.6 (5.2)	•
7	•	93.6 (27.5)	•	135.8 (3.1)			•	139.7 (6.8)	•	167.0 (18.6)			•
8	•	92.6 (29.1)	•	110.1 (0.3)	•	131.7 (1.6)	•	138.7 (7.8)	•	167.9 (19.0)			•
9	•	91.9 (32.0)			•	124.2 (0.8)	•	136.2 (7.8)	•	166.1 (18.2)			•
10	•	87.8 (32.0)			•	118.2 (0.4)	•	135.1 (5.0)	•	165.5 (17.7)			•
11	•	88.2 (77.0)			•	108.4 (0.4)	•	133.2 (7.1)	•	163.2 (16.9)			•
12	•	99.9 (75.0)			•	103.0 (0.1)	•	132.9 (5.6)	•	162.9 (16.4)			•
13	•	99.6 (70.4)					•	131.8 (2.4)	•	161.0 (16.1)			•
14	•	94.4 (62.6)					•	131.2 (3.3)	•	159.9 (16.0)			•
15	•	86.1 (75.4)					•	130.2 (4.0)	•	157.5 (15.7)			•
16	•	89.8 (72.4)					•	129.8 (5.1)	•	156.2 (15.7)			•
17	•	84.5 (71.0)					•	128.8 (3.9)	•	154.0 (15.6)			•
18	•	86.4 (84.0)					•	127.7 (3.9)	•	152.2 (15.0)			•

[a] SmG′.

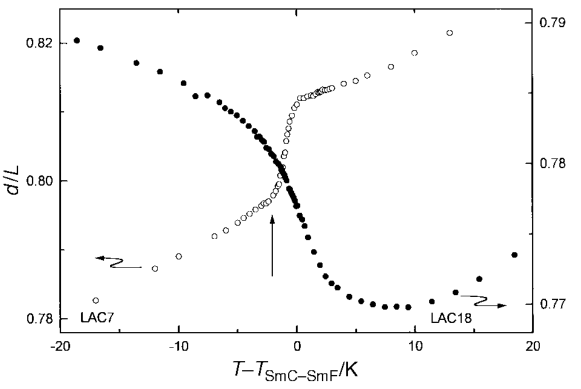


Fig. 2 Temperature dependence of the ratio of smectic layer thickness (*d*) to molecular length (*L*) for (–)-**LAC7** (○, left axis) and (–)-**LAC18** (●, right axis) compounds. The arrow indicates the SmF–SmG phase transition temperature for (–)-**LAC7**.

Electric Properties

Although having a weak electric dipole moment at the chiral centre, the materials of the (–)-**LAC*n*** series are characterized by spontaneous polarization as high as 600 nC cm^{-2} for (–)-**LAC8** in the SmC phase. It seems that the result of the strong molecular tilt observed in the smectic phases is pronounced hindrance of molecular rotation around the long molecular axis.[13] Measurements of spontaneous polarization wererather difficult for (–)-**LAC*n*** compounds due to high electric conductivity of enamino ketone substances that appears as strong ionic currents in the sample. While the tilt angle is almost temperature independent, the spontaneous polarization depends strongly on temperature (Fig. 3). However, decrease in the spontaneous polarization with decreasing temperature may result from non-complete polarization reversal because of insufficient applied electric field intensity since rather high coercive fields were found in ordered smectics. The switching current peaks are relatively broad, which indicates that the compounds studied are characterized by long switching times. Unfortunately, the enamino ketone derivatives studied are not stable under high electric fields. Under the fields, dissociation of hydrogen atoms takes place, which breaks the hydrogen bond and destroys the molecular core. The high hydrogen ion concentration then leads to the relatively high conductivity of the material, which precludes detection of the Goldstone mode in the dielectric measurements.

A non-typical optical switching with memory effect was found when applying a DC electric field in the studied materials near the SmC–SmF phase transition, in both phases (Fig. 4). A planar sample was placed between crossed polarizers in a position which gives the minimum transmission in one of the uniform states. After full switching to the other uniform state minimum transmission was also observed because the tilt angle value is close to 45°. The uniform states are separated by the twisted state, in which the director has opposite orientations on sample surfaces so that the director projection onto the surface has to twist along the surface normal.[14] This director configuration within the sample gives maximum transmission. An observed hysteresis of switching through the twisted state is probably caused by screening of one electrode by a layer of heavy non-mobile ions,[15] which makes absolute values of the electric field different at cathode and anode. The screening effect results in switching of spontaneous polarization direction first at one electrode when the applied field is increased and thus forces the twisted state to be formed.

Modifications in Molecular Structure

In order to establish the effect of the molecular structure on the liquid crystalline properties some other chiral three-ring enamino ketone derivatives have also been synthesized; their structures as well as phase transition temperatures and thermal effects are collected in Table 2. It was found that exchanging of the terminal group positions in (–)-**LAC6** resulting in compound **I** had no influence on the phase sequence and only weakly suppressed the temperature range of the mesophases. In compound **II** the 2-methylbutoxy chiral group was replaced with the 2-methylbutoxycarbonyl group. The change resulted in an increase in the melting and clearing temperatures by more than 60 and 10 °C, respectively, in comparison with (–)-**LAC6**. This seems to be an effect of lengthening the rigid part of the molecule as the carbonyl group is stiff enough to be considered as a part of the molecular mesogenic core. In this case the phase sequence was also affected; the orthogonal SmA phase was formed above the SmC phase. The occurrence of the orthogonal phase is most probably due to the electron

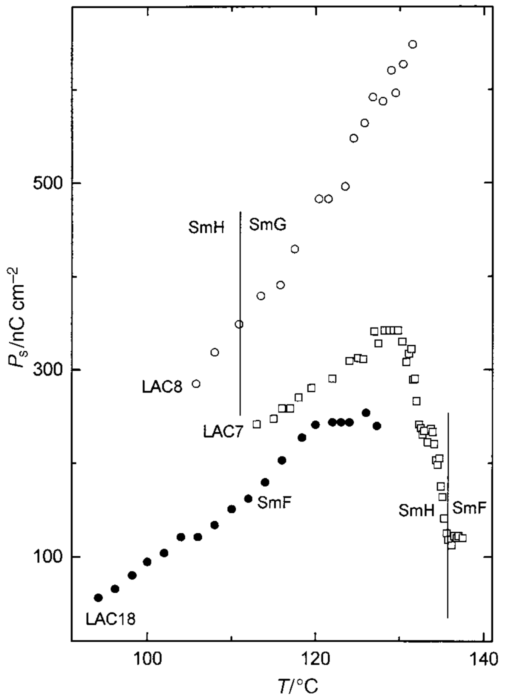


Fig. 3 Temperature dependence of spontaneous polarization for (–)-**LAC7** (□), (–)-**LAC8** (○) and (–)-**LAC18** (●) compounds

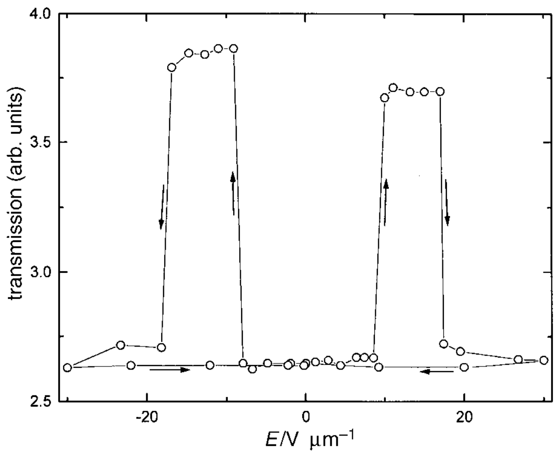
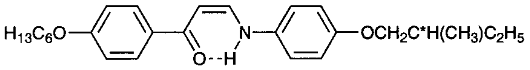
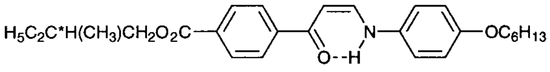
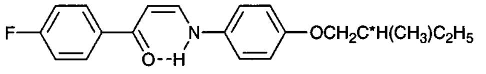


Fig. 4 Light transmission through a planar sample of (–)-**LAC6** compound in the SmC phase *vs.* applied DC electric field

Table 2 Temperatures and, in parentheses, enthalpies of the phase transitions for the compounds **I–III**

	Cry	T/°C (ΔH/J g^{-1})	SmH	T/°C (ΔH/J g^{-1})	SmC	T/°C (ΔH/J g^{-1})	SmA	T/°C (ΔH/J g^{-1})	N	T/°C (ΔH/J g^{-1})	Iso
I											
	•	116.4 (20.7)	•	138.6 (7.9)	•	164.7 (15.2)			•	168.6 (3.9)	•
II											
	•	156.0 (65.3)				159.5 (0.9)	•	179.0 (9.4)			•
III											
	•	128.0 (48.1)					•	166.2 (19.7)			•

accepting (Hammet constant σ *ca.* 0.5) properties of the 2-methylbutoxycarbonyl terminal group. The same effect was observed for compound **III** with fluorine (Hammet constant $\sigma = 0.06$) attached to the mesogenic core instead of the *n*-alkoxy chain. This material was found to exclusively form the SmA phase. The tendency towards formation of the orthogonal phase is enhanced by another molecular factor—the more linear shape of **III** compared to **II**.

Conclusion

A novel series of chiral enamino ketone derivatives, designed to obtain the sequence of tilted smectic phases, was synthesized and examined for liquid crystalline and electric properties. According to our predictions all compounds studied exclusively form strongly tilted phases. The high tilt angle values might be responsible for the rather high spontaneous polarization (*ca.* 0.5 μC cm^{-2}) observed in the liquid-like and hexatic smectic phases. The memory effect was found during electrooptic switching, which is most probably caused by hydrogen ion layers at the electrodes. The relatively high concentration of hydrogen ions results from dissociation under an applied electric field. The liquid crystalline properties of other enamino ketone derivatives confirm the effect of molecular factors such as electron distribution within the mesogenic core or molecular shape on phase sequence as well as on mesophase stability.

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