New (1*R*,4*R*)-2-arylidene-*p*-menthan-3-ones with a bridging ester group in the arylidene fragment. Synthesis and behavior in liquid-crystalline systems

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(1*R*,4*R*)-2-(4-Hydroxybenzylidene)- and (1*R*,4*R*)-2-(4´-hydroxybiphenyl-4-yl)methylene-*p*-menthan-3-ones were synthesized by condensation of (−)-menthone with *O*-tetrahydropyran-2-yl derivatives of 4-hydroxybenzaldehyde and 4´-hydroxy-4-formylbiphenyl, respectively, in a DMSO—base medium followed by the removal of the protective group. The reactions of these hydroxy derivatives with 4-alkylbenzoic, 4-alkyloxybenzoic, *trans*-4-alkylcyclohexane-4-carboxylic, and 4´-alkylbiphenyl-4-carboxylic acids afforded three series of new chiral esters. Compounds containing the arylidene moiety with three benzene rings were found to exhibit liquid-crystalline properties. The characteristic features of these compounds are discussed based on the results of studies by polarizing microscopy, differential scanning calorimetry, and small-angle X-ray scattering. It was found that the mesomorphic compounds under study can form a smectic A mesophase, twist grain boundary mesophases (TGBA), and blue phases in a wide temperature range. Upon dissolution of certain of chiral compounds in 4´-cyano-4-pentylbiphenyl, a rather high twisting power and the thermal stabilizing effect on mesophases were observed.

Key words: (1*R*,4*R*)-2-(4-hydroxybenzylidene)- and (1*R*,4*R*)-2-(4´-hydroxybiphenyl-4-yl)methylene-*p*-menthan-3-ones, chiral esters, synthesis, mesomorphic properties, smectic A mesophase, twist grain boundary mesophase (TGBA), blue phases, helical twisting power.

Chiral compounds, *viz. p*-menthan-3-one derivatives, are used as additives for inducing cholesteric phases in nematic liquid-crystalline (LC) systems (see, for example, Refs. 1 and 2) and also as polar chiral components of ferroelectric LC composites.[3,4] The ability of nonmesogenic 2-arylidene-*p*-menthan-3-ones to induce a helical supramolecular structure with high efficiency upon introduction into nematic mesophases (twisting power) is associated with the characteristic features of their stereochemistry.[2] The axial orientation of the methyl substituent in the major chair-like conformation of the cyclohexanone ring and stereospecific twisting of the enone fragment are of importance for the manifestation of chiralization properties. At the same time, 2-arylidene-*p*-menthan-3-ones contain the chiral alicyclic fragment with the carbonyl group, whose large dipole moment is approximately perpendicular to the long molecular axis, which is responsible for their ability to induce not only a helical structure but also high spontaneous polarization, *i.e.*, to form ferroelectric liquid-crystalline systems, in tilted smectic phases. Both the twisting power and polarization power of these compounds increase as the length of the exocyclic 2-arylidene fragment increases (with increasing number of benzene rings).

The aim of the present study was to synthesize and investigate (1*R*,4*R*)-*p*-menthan-3-one derivatives, which contain fragments favorable for the appearance of mesomorphism (*i.e.*, the ability to form their own liquid-crystalline phases) with retention of the above-mentioned structural features responsible for the efficient chiralization in a mesophase. Compounds possessing such a combination of properties remain virtually unstudied.[5—7]

The above problem can be solved by performing a structural modification of (1*R*,4*R*)-2-arylidene-*p*-menthan-3-ones. The introduction of a bridging ester group between the benzene rings of the arylidene fragment (compounds **1—3**) is often favorable for the manifestation of mesomorphism.[8] It is also worthwhile to vary both the number of benzene rings in the arylidene fragment and the length of the terminal alkyl or alkoxy groups.

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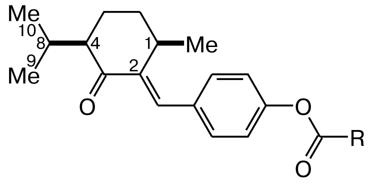
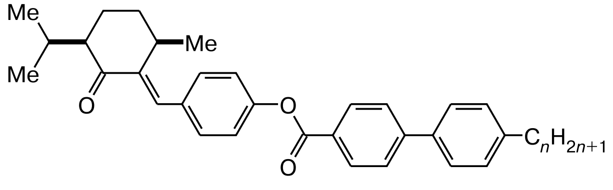
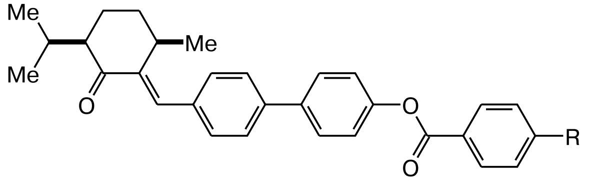


1a—j

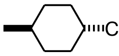


2a,b



3a—h

1: R = Ph (**a**), *p*-$C_6H_4OC_nH_{2n+1}$ (**b—g**),

p-C_6H_4Bu (**h**),  C_nH_{2n+1} (**i**, **j**);

n = 4 (**b**, **i**), 5 (**c**), 6 (**d**, **j**), 7 (**e**), 8 (**f**), 9 (**g**)

2: *n* = 6 (**a**), 8 (**b**)

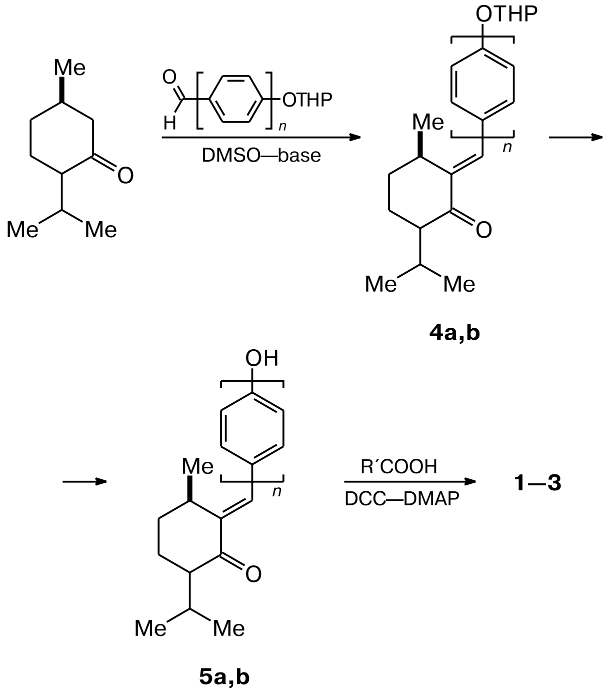
3: R = OC_nH_{2n+1} (**a—e**), C_nH_{2n+1} (**f—h**);
n = 6 (**a**), 7 (**b**), 8 (**c**), 9 (**d**, **f**), 10 (**g**), 16 (**e**, **h**)

The mesomorphic properties of compounds **1—3** were studied by differential scanning calorimetry (DSC) and thermal polarizing microscopy. In certain cases, the behavior of liquid-crystalline samples in electric field was examined, and the samples were studied by small-angle X-ray scattering. A high degree of molecular chirality of the compounds synthesized was confirmed by measuring the twisting power for particular representatives upon their introduction into a nematic liquid crystal, *viz.*, 4´-cyano-4-pentylbiphenyl.

The most convenient route to the target compounds **1—3** (Scheme 1) involves the synthesis of hydroxy derivatives **5a,b** as key intermediates using crotonization of protected 4-hydroxyarenealdehydes with (—)-menthone.

The reaction of 4-tetrahydropyran-2-yloxybenzaldehyde with (—)-menthone in a DMSO—KOH system performed earlier[9,10] afforded compound **5a** in very low yield (22 and 14% of the crude product, respectively). In the present study, we succeeded in increasing substantially the yield of phenol **5a**. We also synthesized its analog **5b** for the first time. Therefore, these phenols became readily accessible (for example, for the synthesis of chiral esters and liquid-crystalline polymers[10—13]).

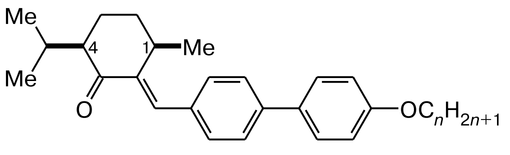
Scheme 1



n = 1 (**a**), 2 (**b**)

Results and Discussion

Most of (1*R*,4*R*)-2-arylidene-*p*-menthan-3-ones were successfully synthesized by crotonization of (—)-menthone with aromatic aldehydes in DMSO using KOH as the basic catalyst.[1,14] It was proved that this reaction was accompanied by the inversion of the chiral C(4) center to form predominantly (+)-isomenthone derivatives in the (1*R*,4*R*) configuration.[1,15] However, in some cases (in particular, in the synthesis of derivatives containing long terminal aliphatic substituents), the synthesis with the use of KOH gave rise to the reaction products in low yields. The use of bases with bulkier (softer) cations (Cs^+ or Bu_4N^+) instead of KOH and a decrease in the amount of the base (0.10—0.25 mol. equivalents of CsOH instead of 0.7—1.0 mol. equivalents of KOH) made it possible[16] to substantially increase the yields of compounds **6**.



6

n = 1—9

The use of this approach for condensation of (—)-menthone with 4-tetrahydropyranyloxybenzaldehyde

Table 1. Synthesis of 2-(4-hydroxybenzylidene)-*p*-menthan-3-one (**5a**)

Run	Base (number of equivalents)	Reaction time/h	Yield* (%)
1 [9]	KOH (0.2)	24	22
2 [10]	KOH (0.74)	12	14
3	KOH (1.1)	48	14
4	Bu_4NOH** (0.2)	144	26
5	$CsOH \cdot H_2O$ (0.5)	24	31
6	$CsOH \cdot H_2O$ (0.88)	24	36
7	$CsOH \cdot H_2O$ (1.1)	24	45

* The yields are given for products purified by crystallization (except for runs *1* and *2*).

** The reagent was used as a 30% aqueous solution.

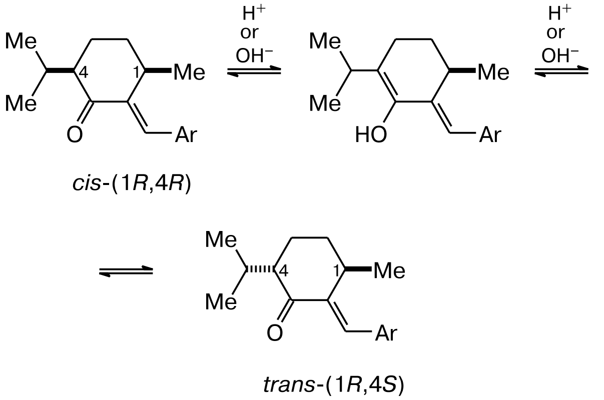
allowed us to prepare (after removal of the protective group from compound **4a**) hydroxy derivative **5a** (see Scheme 1) in higher yield than that obtained earlier.[9,10] As can be seen from Table 1, CsOH is the basic catalyst of choice in the synthesis of **5a** (*cf.* runs *1—4* and *5—7*). However, with the aim of achieving the maximum yield of the product, we increased the amount of CsOH to 1.1 mol. equiv. (runs *5—7*) compared to that used in the synthesis of compounds of type **6** (0.10—0.25 mol. equiv.[16]). Apparently, this is attributed to low reactivity of the starting aldehyde due to the stronger electron-donating effect of the 4-tetrahydropyran-2-yloxy substituent. It should be noted that this increase in the amount of KOH led even to a decrease in the yield of **5a** (see Table 1, runs *1—3*). Unlike the synthesis of compounds **6**, the use of Bu_4NOH as a 30% aqueous solution (0.2 mol. equiv.; see Table 1, run *4*) did not improve the result. An increase in the amount of this base seemed to be unreasonable because of attendant dilution of the reaction mixtures with water resulting in a decrease in the basicity of the medium.

The use of CsOH as the catalyst also allowed us to synthesize hydroxy derivative **5b** in 48% yield (see the Experimental section).

Products **5a,b** were isolated in the crystalline state. According to the HPLC data, they were prepared in the individual form. The structures of these products were confirmed by IR and ^{1}H NMR spectroscopy (see the Experimental section). The chemical shifts and multiplicities of the signals for the protons of the cyclohexanone ring in the spectra of hydroxy derivatives **5a,b** are analogous to those for 2-arylidene-*p*-menthan-3-ones studied earlier[17,18] (*cis*-*E*-(1*R*,4*R*) configuration). In addition, the stereochemical configuration has recently been established by X-ray diffraction analysis of compound **5a**.[19]

In the study,[9] it was assumed that the synthesis of **5a** afforded a mixture of the *E* and *Z* isomers in a ratio of 80 : 20. However, this assumption was not proved and, besides, the individual isomers were not isolated. Taking into account the results of the present investigation and our earlier studies, this assumption seems to be erroneous. Based on our data on the *E—Z* isomerization of 2-arylidene-*p*-menthan-3-ones[20,21] and their epimerization under mild conditions (both in basic and acidic media) resulting in an equilibrium mixture of the *E*-(1*R*,4*R*) (70—80%) and *E*-(1*R*,4*S*) diastereomers (30—20%) (Scheme 2),[22] crude product **5a** described earlier[9,10] was, most likely, a mixture of diastereomers rather than of the *E* and *Z* isomers.

Scheme 2



Recently, this epimerization of hydroxymenthanone **5a** has been carried out by heating with perchloric acid in dioxane.[23] This process can be promoted also by an acidic reagent used for removing the protective group from intermediate **4a** (pyridinium *p*-toluenesulfonate[9] or *p*-toluenesulfonic acid[10]). This accounts for the essential discrepancy between the physicochemical characteristics of compound **5a**. Thus, the melting point reported for **5a** [10] is lower, whereas $[\alpha]_D$ is higher than the corresponding values determined in the present study (see the Experimental section). The above explanation is indirectly confirmed by the fact that the specific rotations for the *trans*-(1*R*,4*S*) diastereomers of 2-(4-aroyloxymethylene)-*p*-menthan-3-ones prepared earlier are larger (approximately by a factor of 2) compared to those for the corresponding *cis*-(1*R*,4*R*)-diastereomeric compounds.[1]

Compounds **1—3** were synthesized by esterification of the corresponding hydroxy derivatives **5a,b** with various substituted carboxylic acids in the presence of a DCC—DMAP system[24,25] (see Scheme 1 and the Experimental section). Under these conditions, esterification was not accompanied by substantial *cis*-(1*R*,4*R*)→*trans*-(1*R*,4*S*) epimerization. According to the HPLC data, the reaction mixture produced in the synthesis of compound **1a** contained only ~6% of the *trans*-(1*R*,4*S*) diastereomer. The (1*R*,4*S*) diastereomer required for comparison has been prepared earlier by the directed aldol reaction of (−)-menthone with 4-benzoyloxybenzaldehyde followed by dehydration of the resulting ketol under mild conditions using a DCC—Cu_2Cl_2 system.[22]

According to the HPLC data, compounds **1—3** were isolated (after purification by crystallization) in the individual form. Their structures were confirmed by IR spectroscopy. Some compounds were also studied by mass spectrometry and ^{1}H NMR spectroscopy (Table 2, see the Experimental section).

Compounds **1—3** tend to undergo the *E*→*Z* photochemical transformation analogous to that observed for other (1*R*,4*R*)-2-arylidene-*p*-menthan-3-ones, including hydroxy derivative **5a**.[20,21,23] In addition, thermal *E*→*Z* and 4*R*→4*S* isomerizations are typical of the compounds synthesized, as evidenced by the results of studies by HPLC and ^{1}H NMR spectroscopy of compounds **2** and **3** before and after double heating to isotropic states under the DSC experimental conditions. Compounds **2** are most prone to thermal transformations. According to the data from ^{1}H NMR spectroscopy based on analysis of the signals of the arylidene protons,[21] two cycles of thermal treatment of compound **2b** afforded a mixture containing 22% of the *E*-(1*R*,4*S*)-*trans* diastereomer (s, $\delta_{=CH}$ 7.02) and 5% of each of the *Z* isomers with the 4*R* and 4*S* configurations (s at $\delta_{=CH}$ 6.32 and d at $\delta_{=CH}$ 6.23, respectively, ^4J = 2 Hz). Similar results were obtained by HPLC. The observed thermal behavior of compounds **2** is consistent with the results of the study,[26] which demonstrated that thermal treatment of any one of the *E* diastereomers (1*R*,4*R* and 1*R*,4*S*) or the *Z*-(1*R*,4*R*) isomer of 2-(4-phenylbenzylidene)-*p*-menthan-3-one afforded a mixture of all isomerization products with virtually the same composition.

Esters **3** are much more thermally stable than compounds **2**. After thermal treatment under the DSC experimental conditions, samples of esters **3** contained only from 2 to 6% of impurities.

Possible photochemical and thermal transformations of compounds **2**, **3**, and, presumably, **1** (which should be taken into account in studies of their mesomorphic behavior) can be represented by Scheme 3.

Mesomorphic behavior of new chiral esters

Study of mesomorphism of chiral esters by polarizing microscopy and DSC. All compounds **1** are nonmesogenic (see Table 2), whereas esters **2** and **3** with the more extended π-electron 2-arylidene fragments consisting of

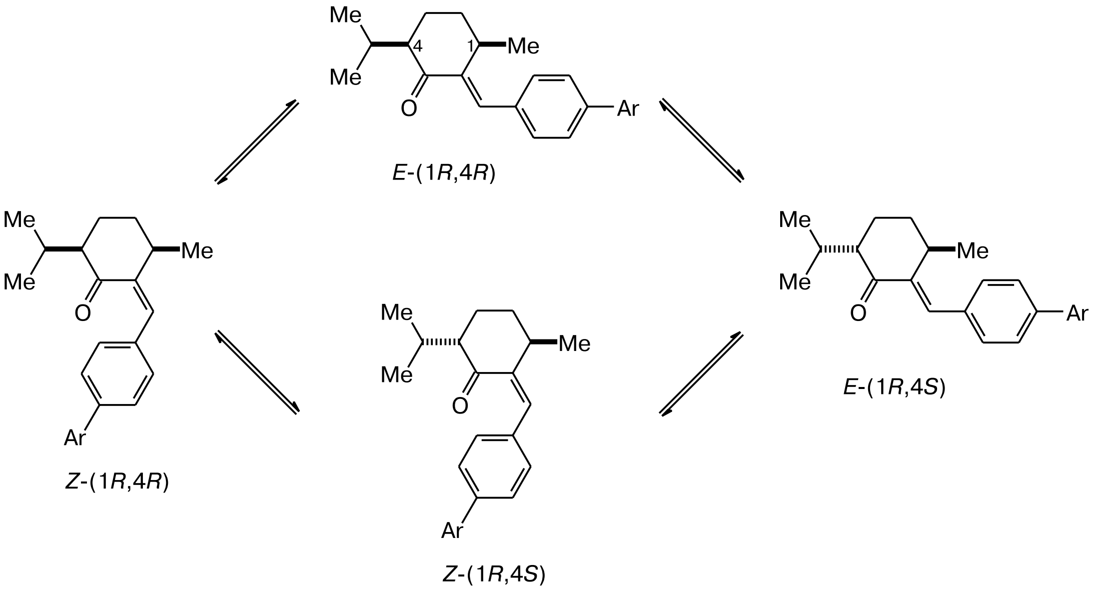
Table 2. Yields and selected physicochemical and spectroscopic characteristics of nonmesomorphic 4-(3-isopropyl-6-methyl-2-oxocyclohexylidenemethyl)phenyl benzoates (compounds **1a—h**) and *trans*-4-alkylcyclohexanecarboxylates (compounds **1i,j**)

Compound	*n*	Yield (%)	M.p. /°C	$[\alpha]_D^{20}$ ($CHCl_3$)	Found / Calculated (%)		Molecular formula	IR (KBr), ν/cm^{-1}	
					C	H		ν(C=O)	ν(C=C), ν(Ar)
1a	—	57	78	—	79.38 79.53	7.16 7.23	$C_{24}H_{26}O_3$	1731, 1672	1594
1b	4	87	139	−177	77.50 77.39	7.99 7.89	$C_{28}H_{34}O_4$	1727, 1670	1599
1c	5	77	106	−152	77.81 77.65	8.18 8.09	$C_{29}H_{36}O_4$	1730, 1673	1600
1d*	6	83	101	−135	78.06 77.89	8.34 8.28	$C_{30}H_{38}O_4$	1734, 1676	1604
1e	7	83	102	−145	78.01 78.12	8.29 8.46	$C_{31}H_{40}O_4$	1734, 1675	1603
1f	8	80	98	−137	78.19 78.33	8.54 8.63	$C_{32}H_{42}O_4$	1735, 1676	1603
1g**	9	82	79	−162	78.11 78.53	8.96 8.79	$C_{33}H_{44}O_4$	1726, 1670	1603
1h	4	64	102	−157	80.27 80.35	8.04 8.19	$C_{28}H_{34}O_3$	1734, 1680	1604
1i	4	51	109	−192	79.36 79.20	9.62 9.50	$C_{28}H_{40}O_3$	1745, 1683	1602
1j	6	51	89	−163	79.84 79.60	9.96 9.80	$C_{30}H_{44}O_3$	1741, 1675	1602

* MS, *m/z*: 462 $[M]^+$, 247, 205, 131, 121, 107.

** MS, *m/z*: 504 $[M]^+$, 248, 247, 233, 122, 121, 107.

Scheme 3



three rings exhibit the mesomorphic behavior. Their phase states and transition temperatures are given in Table 3.

Compounds **3** are most suitable for a detailed examination of their mesomorphic properties, as evidenced by the above-given data on their thermal and photochemical transformations. Nevertheless, the studies were carried out on handling with samples at elevated temperatures (>150 °C) over a period of time as short as possible and using a reduced power of a microscope condenser. Under these conditions, the results of observations and measurements are well-reproducible, and it is reasonable to assume that the texture features and other properties of the mesophases formed by compounds of this series correspond to the individual compounds rather than to their mixtures with isomerization products. However, in some cases, limitations on the time of heating and the light power did not allow us to carry out a detailed study of the region in the vicinity of the isotropic liquid (Iso) → mesophase transition, where low-contrast colorless textures corresponding to blue phases (BP) can be observed between crossed polarizers. Because of thermal instability of compounds **2**, the observed mesophases (quite identifiable) cannot be assigned to individual compounds (see Table 3, compound **2b**). Therefore, the mesomorphic properties of these compounds are not discussed in the present study.

All compounds **3** exhibit a similar mesomorphic behavior. Their thermograms (Fig. 1) are characterized by the presence of a broad peak at a temperature higher than that of the isotropic liquid → mesophase transition, which was determined by polarizing microscopy. The appearance of this peak is characteristic of chiral compounds that form twist grain boundary (TGB) mesophases (see, for example, Refs. 27—30). Several (two or, sometimes, three) closely spaced (in some cases, overlapping) peaks are observed in the vicinity of the isotropic phase transition. Apparently, this corresponds to the presence of blue phases typical of highly chiral mesogenic compounds. In addition, most of the thermograms have a low-energy peak (ΔH = 0.01—0.06 kJ mol^{-1}) in the middle of the mesomorphic range, the latter being divided into two broad regions (mesophases S1 and S2).

According to the data from polarizing microscopy, the higher-temperature mesophase (S1) forms a focal-conic (FAN) texture typical of the smectic A (SmA) phase[31] upon cooling between untreated glass plates. The texture of the lower-temperature phase (S2) differs from that of the S1 mesophase by the appearance of thin lines crossing the domain surfaces, as can be seen from Fig. 2 presenting data for compound **3d**. Samples of compounds **3** cooled from the isotropic liquid state under planar boundary con-

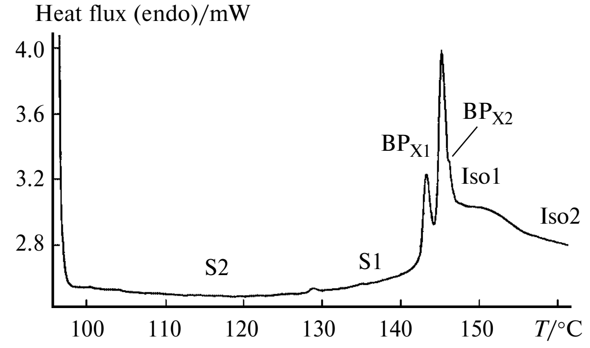


Fig. 1. Thermogram of mesogenic compound **3h** measured in the heating mode at a rate of 10 °C min^{-1}.

Table 3. Phase transitions (PT) for compounds **2b** and **3b—h**

Compound	*n*	Type of PT	Temperature of PT/°C	Heat of PT /kJ mol^{-1}
2b	8	Cr→S1	131.5	—
		S1→Iso1	158.5	—
		Iso1→Iso2	163.5	—
3b	7	Cr→S1	114.3	29.93
		S1→BP$_{X1}$	200.4	0.046
		BP$_{X1}$→Iso1	202.1	0.143
		Iso1→Iso2	209.2	0.521
3c	8	Cr→S2	122.5	28.43
		S2→S1	159.5	0.014
		S1→BP$_{X1}$	199.0	0.003
		BP$_{X1}$→Iso1	200.8	0.177
		Iso1→Iso2	208.9	0.723
3d	9	Cr→S2	113.2	21.54
		S2→S1	136.9	0.062
		S1→BP$_{X1}$	192.0	0.009
		BP$_{X1}$→Iso1	193.1	0.267
		Iso1→Iso2	204.0	1.086
3e	16	Cr→S2	103.5	38.03
		S2→S1	126.0	—
		S1→BP$_{X1}$	164.0	0.039
		BP$_{X1}$→BP$_{X2}$	166.8	0.502
		BP$_{X2}$→Iso1	167.7	0.102
		Iso1→Iso2	173.4	0.191
3f	9	Cr→S2	108.5	29.81
		S2→S1	119.8	0.018
		S1→BP$_{X1}$	165.4	0.007
		BP$_{X1}$→Iso1	168.1	0.149
		Iso1→Iso2	181.0	0.682
3g	10	Cr→S2	102.3	16.93
		S2→S1	128.9	0.041
		S1→BP$_{X1}$	157.0	0.003
		BP$_{X1}$→Iso1	158.6	0.178
		Iso1→Iso2	173.0	0.515
3h	16	Cr→S2	94.9	34.22
		S2→S1	128.7	0.009
		S1→BP$_{X1}$	142.9	0.140
		BP$_{X1}$→BP$_{X2}$	145.2	0.540
		BP$_{X2}$→Iso1	146.0	0.200
		Iso1→Iso2	151.6	0.101

Note. The transition temperatures were determined by DSC in the heating mode (except for the S1→S2 transition for compound **3e**, for which the transition temperature was determined based on the results of texture study). For most of the compounds, at least one blue phase (BP$_{X1}$) occurring in the narrow temperature range was revealed. In the thermograms, blue phases generally appeared as overlapping peaks. The Iso1→Iso2 transition was observed in the thermograms as a broad and relatively high-energy peak analogous to that described earlier.[27]

ditions (Lincam cells with the thickness of the liquid-crystalline layer of 5 μm) in the temperature range of the S1 phase appeared as a black field between crossed polarizers and did not exhibit any birefringence upon rotation of the sample. Only for compound **3b** containing the shortest terminal alkoxy substituent (seven C atoms), no separation of the mesomorphic range into the S1 and S2 phases was observed by both DSC and polarizing microscopy. The textures of compound **3b** prepared both on untreated glasses and under planar boundary conditions are identical to those for the S1 phase of other homologs of this series.

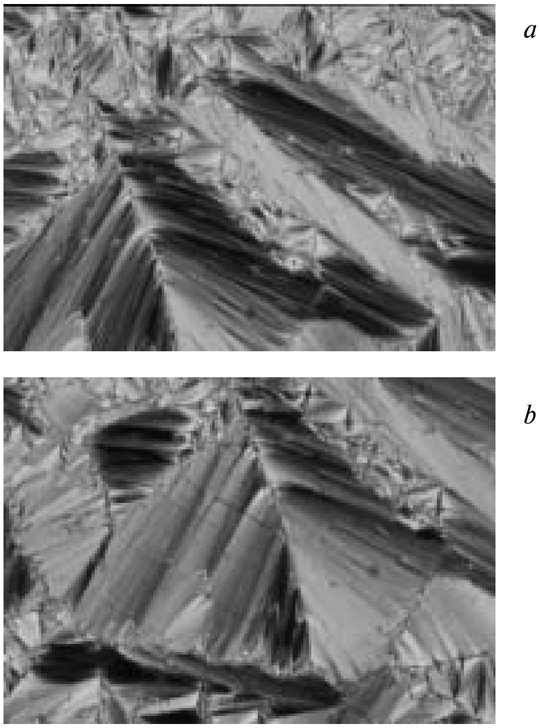


Fig. 2. Optical photomicrographs of a sample of compound **3d** in a cell with untreated surfaces at 178 (*a*) and 135 °C (*b*).

The mesomorphic properties of compounds **3e,h** containing the longest terminal groups ($OC_{16}H_{33}$ and $C_{16}H_{33}$) were studied in most detail due, in part, to a substantial shift of their mesomorphic ranges to a lower-temperature region compared to those of homologs **3b—d** with the shorter terminal groups (see Table 3). In addition, we intended to reveal in detail the possible effect of the large difference in the length of the terminal substituents on the mesomorphic behavior of compounds of this type.

Although the thermogram of alkyl-substituted compound **3h** (R = $C_{16}H_{33}$) has a sequence of peaks analogous to those observed for compounds **3c,d,f,g**, the textures of the S1 and S2 phases obtained for samples between untreated glass plates change substantially (particularly, for the S2 phase) (*cf.* Figs. 2 and 3). On cooling of a sample of compound **3h** under homeotropic boundary conditions, the distinct transition from the blue phase (Fig. 4, *a*, colorless crystals characterized by low birefringence) to the S1 phase (Fig. 4, *b*, FAN texture) was observed. The latter phase was transformed through a filament-type texture into the orthogonal smectic phase S2

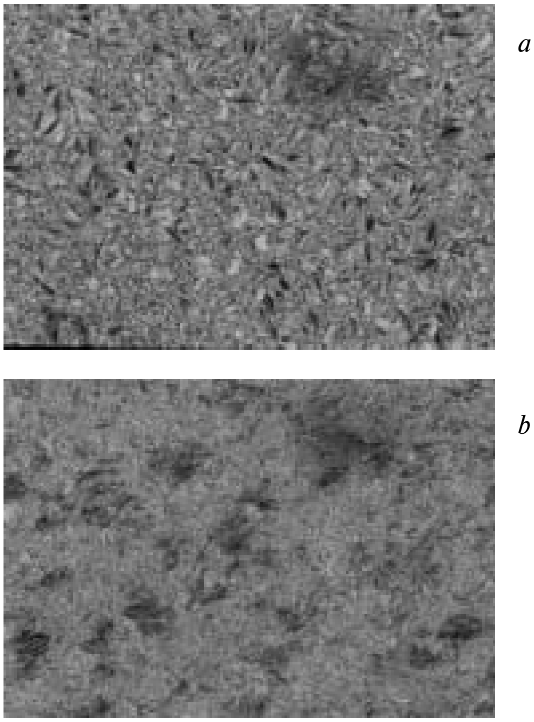


Fig. 3. Optical photomicrographs of a sample of compound **3h** in a cell with untreated surfaces at 133 (*a*) and 114 °C (*b*).

(Fig. 4, *c*), which appeared as a black field on examination between crossed polarizers. The inverse sequence of textures was observed on heating of the sample.

Under homogeneous planar boundary conditions, compound **3h** showed at least one high-temperature phase existing in the narrow temperature range (apparently, of the BP type; Fig. 5, *a*), which was transformed into a blue texture with Grandjean—Cano walls (Fig. 5, *b*). Under such boundary conditions, this fact corresponds to a strongly twisted helical ordering with the axis perpendicular to the boundary surfaces. At 127 °C, the vertical helicoid was unwound as a result of approach to the transition to a smectic phase, and the color rapidly changed from blue to red. At 125 °C, the texture was transformed into a brightly colored form (Fig. 5, *c*) typical of the SmA phase under these boundary conditions.[31]

A combination of the texture changes observed under different boundary conditions,[27,32—34] most likely, characterizes the following sequence of phase transitions on cooling of a sample: Iso → BP → TGB → SmA* → Cr (Cr is a crystal).

The mesomorphic behavior of compound **3e** containing the terminal $OC_{16}H_{33}$ group resembles the behavior of its alkyl analog (**3h**). For a sample between two untreated plates, at least two blue phases and one texture transition in the middle of the broad mesomorphic range are observed with a polarizing microscope. As in the case of compound **3h**, the latter transition divides the mesomorphic temperature range into regions of the S1 and S2 phases (see Table 3). Mesogens **3e,h** under study differ in that the S1 → S2 transition for mesogen **3e** was detected only by polarizing microscopy, whereas this transition was unobservable in the thermogram.

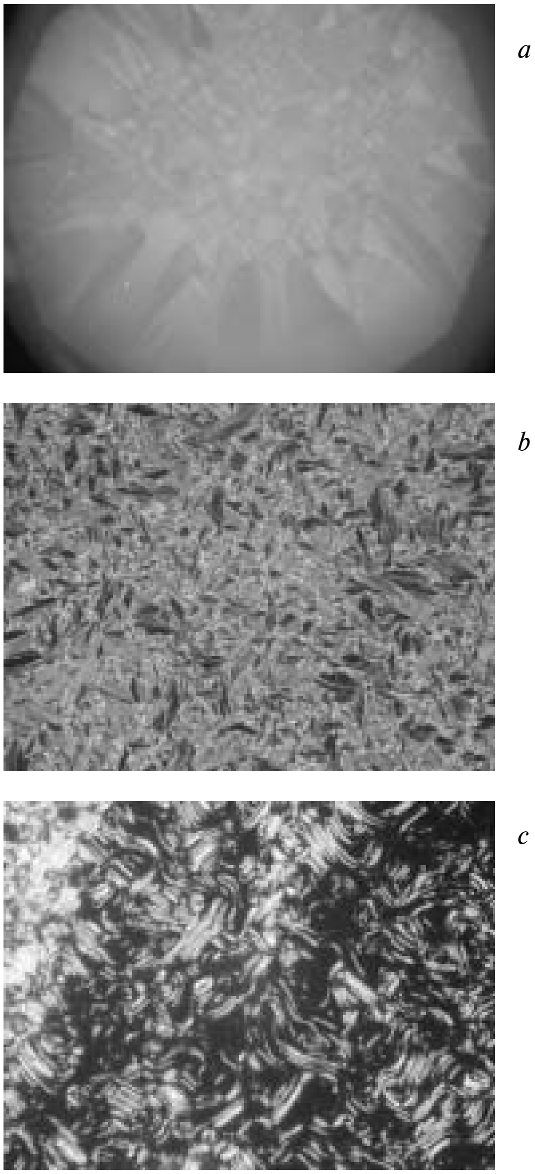


Fig. 4. Optical photomicrographs of a sample of compound **3h** under homeotropic boundary conditions at 146 (*a*), 135 (*b*), and 125 °C (*c*).

Microscopic study of a sample of **3e** under homeotropic boundary conditions on cooling revealed the presence (after two blue phases occurring in narrow temperature ranges) of the S1 phase, which appeared as a fine FAN texture. Thin lines across the domain surfaces became visible after the phase transition at 126 °C. Under homogeneous planar boundary conditions, a sample of this compound did not exhibit birefringence and remained

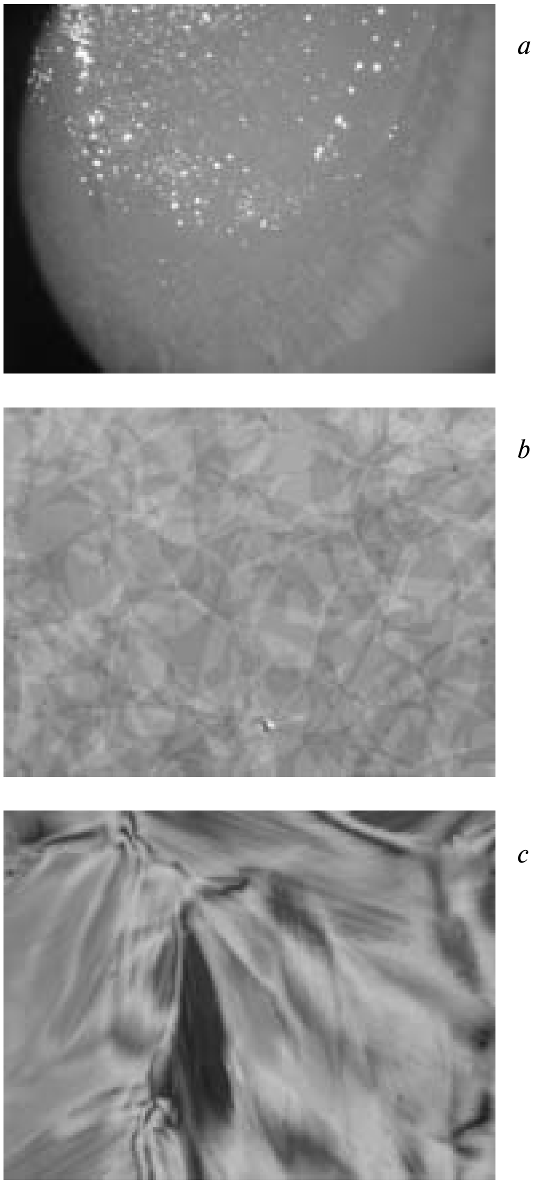


Fig. 5. Optical photomicrographs of a sample of compound **3h** under planar boundary conditions at 146 (*a*), 135 (*b*), and 125 °C (*c*).

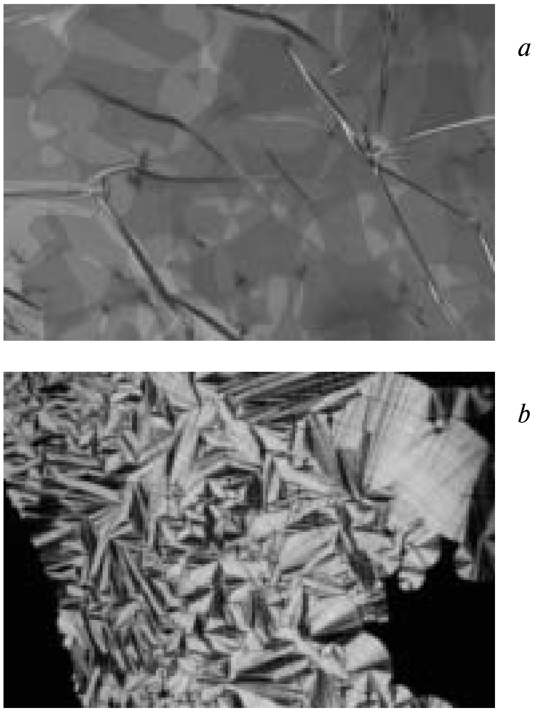


Fig. 6. Optical photomicrographs of a sample of compound **3e** under planar boundary conditions at 121.1 °C (*a*) and of the same sample at 130 °C in AC electric field (rectangular pulses, field strength was 7 V μm^{-1}, frequency was 32 Hz) (*b*).

black on examination of the high-temperature region of the S1 phase between crossed polarizers. Upon further cooling (below 144 °C), the violet Grandjean—Cano texture was clearly seen. The phase transition at 126.5 °C was accompanied by the appearance of defects as cracks in this texture (Fig. 6, *a*), after which the texture remained unchanged up to crystallization.

The AC electric field with a strength of higher than 7 V μm^{-1} applied to planar-oriented samples of compounds **3d,e,g,h** in the temperature range of the S1 phase induced the transformation of its texture (black field) into a FAN-like texture (Fig. 6, *b*). No induction of a focal-conic texture was found for the S2 phase using compound **3e** as an example. Besides, the application of the triangular or rectangular AC electric field (up to 11 V μm^{-1}, 0.1—1000 Hz) did not cause electrooptical switching throughout the mesomorphic temperature range. This behavior provides evidence for the existence of orthogonal smectic phases rather than tilted smectic phases (SmC*) of the compounds under study.

Apparently, strongly twisted TGB-like phase states are typical of all compounds of type **3** (S1 phase), although characteristic filament textures[32] were not observed for some of these compounds. The fact that the thermograms of these compounds have a broad peak at a higher temperature compared to that observed for the isotropic liquid—mesophase transition (data from polarizing microscopy) is strong evidence in favor of the above-given assignment of the S1 phase. Analogous peaks attendant on TGB states have also been found earlier,[27—30] although the interpretation of the reasons for their appearance is ambiguous. Based on this criterion, the TGBA-type supramolecular ordering can be assigned to the only S1 mesophase of compound **3b** as well.

For most of the compounds under study, the lowest-temperature S2 phase is a smectic A*. However, in some cases (compound **3e**), the TGB → SmA* phase transition was undetectable by DSC due, apparently, to low ΔH.

Therefore, the texture studies demonstrated with high probability that the compounds under study form TGB phases with a short pitch of helix corresponding to selective reflection of light in the near-UV region (black textures of samples with a planar homogeneous orientation). Noteworthy are broad temperature ranges of the observed TGB phases (from 14.5 °C for **3h** to 86 °C for **3b**).

Study of mesogenic esters by small-angle X-ray scattering. To unambiguously determine the type of the mesophases formed (orthogonal or tilted), compounds **3g** (R = $C_{10}H_{21}$) and **3h** (R = $C_{16}H_{33}$) were studied by small-angle X-ray scattering. Based on the results of these studies, we also intended to reveal possible difference in the mesomorphic behavior of compounds **3** containing relatively short (7—10 C atoms) and long (16 C atoms) terminal alkyl chains.

As can be seen from Fig. 7, the interlayer distance (*d*) in the mesophases under study, which was determined from the angular positions of X-ray scattering peaks, varies only slightly throughout almost the entire mesomorphic temperature range for both compounds. For **3h**, a rapid decrease in *d* is observed only at temperatures higher than 142 °C. The temperature dependences of the scattering parameters (see Fig. 7) for mesophases of compounds **3g,h** have two bends. A weak bend at 129 °C for compound **3g** (see Fig. 7, *a*) or at 125 °C for **3h** (see Fig. 7, *b*) is indicative of the transition between mesophases with similar ordering. The character of the observed dependences (a weak decrease in the interlayer distance with increasing temperature) along with the above-described results of the texture and electrooptical studies are, most likely, indicative of the orthogonal layer ordering (SmA* and TGBA) in the major mesomorphic range rather than of the tilted ordering (for example, SmC*).

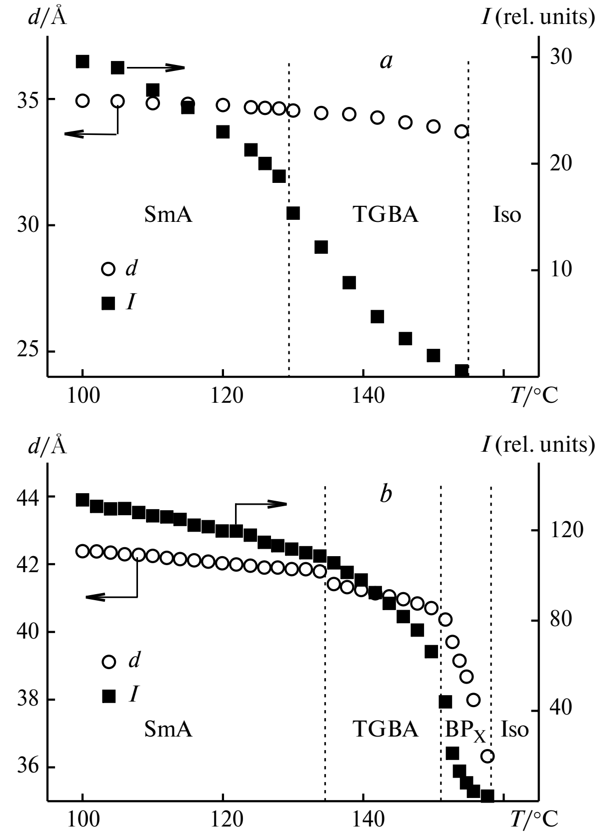


Fig. 7. Temperature dependences of the interlayer distance (*d*) and the scattering intensity (*I*) for samples of compounds **3g** (*a*) and **3h** (*b*).

In the case of compound **3g**, the scattering intensity is much weaker than that observed for **3h**, and the bend at 129 °C in the plot *d*(*T*) (see Fig. 7, *a*) is hardly observable. This bend is more pronounced in the plot of the scattering intensity *vs*. the temperature. This is associated with the larger correlation length of smectic layer ordering for compound **3h** compared to that for **3g**.

As can be seen from Fig. 7, the smectic ordering is retained in both compounds up to the transition into the isotropic liquid. However, there is a difference in the behavior of the interlayer distance *d* in the vicinity of the isotropic transition. This parameter remains virtually unchanged for compound **3g** (see Fig. 7, *a*), whereas this parameter for **3h** sharply decreases at temperatures higher than 142 °C (see Fig. 7, *b*). The change in the interlayer distance with changing temperature in the pre-isotropic region observed for **3h** is analogous to that observed recently for the layered blue phases (such as BP_{Sm}).[30]

The above-described results show that the mesomorphic behavior of the chiral esters of the homologous series under study is virtually independent of the length of the terminal alkyl chain. The character of the supramolecular organization of the S1 and S2 mesophases (TGBA and SmA*) in the major mesomorphic range is analogous for homologs containing both the long ($C_{16}H_{33}$ and $OC_{16}H_{33}$) and medium-length (C_8H_{17}—$C_{10}H_{21}$) alkyl chains. For the shortest seventh homolog in the series under study, the SmA* phase is suppressed.

It can be stated that the mesogens containing terminal substituents of substantially different lengths differ only by the phase behavior in the vicinity of the isotropic liquid—mesophase transition. Thus, both the texture studies and DSC revealed two blue phases, *viz*., BP_{X1} and BP_{X2}, in higher homologs (compounds **3e,h**) (see Table 3 and Fig. 1) rather than one blue phase observed for lower homologs.

Very wide temperature ranges for the TGB states and the absence of a less ordered cholesteric phase are associated with the characteristic features of the molecular structures of the compounds under study. Apparently, the presence of only one terminal *n*-alkyl chain, the branched isopropyl group as the second terminal substituent, and, particularly, the axial methyl group are responsible for a decrease in the terminal lability (migration of the molecules along their long axes), thus hindering the transformation of the TGB phase into the cholesteric phase.

Induced cholesteric systems containing new chiral esters

The efficiency of induction of a helical supramolecular structure in liquid crystals by chiral compounds is quantitatively characterized by the twisting power (β) determined by the equation[2]

$$P^{-1} = \beta r C,$$

where *P* is the pitch of the induced helix, *C* is the concentration of the chiral additive in mole fractions, and *r* is the enantiomeric purity (for the compounds, under study, *r* is equal to unity).

Using two compounds, **1d** and **3f**, as examples, we measured the twisting powers of the chiral esters in a nematic solvent, *viz.*, 4´-cyano-4-pentylbiphenyl. As can be seen from Table 4, these compounds exhibit strong chiralization properties in the mesophase (large absolute values of β), although their twisting power is only slightly higher than that of analogous compounds of type **6**. Consequently, the introduction of the bridging OCO group between the benzene rings (*cf.* **1d** and **6** for $n = 6$) or the introduction of the additional benzene ring into the arylidene fragment of chiral additive **1d** (*cf.* **1d** and **3f**) has only a slight effect on the twisting properties in the mesophase. This indicates that an increase in β of chiral compounds containing an extended molecular core is damped out as this core is elongated. Thus, the absolute value of β increases substantially on going from the simplest chiral additive of this type containing the 2-arylidene fragment with only one benzene ring and the terminal OMe group ($|\beta| = 30.5$ μm^{-1} (mole fraction)$^{-1}$ in an eutectic mixture of 4-cyanobiphenyl derivatives[1]) to compounds **6** (see Table 4). In the case of esters **1** and **3**, a subsequent increase in the length of the molecular core is of less importance. Apparently, this reflects the slowly damping increase in the degree of molecular chirality as the achiral 2-arylidene fragment is elongated.[2]

The high twisting power of the new chiral compounds allows one to prepare induced cholesteric composites, which selectively reflect light in the visible spectral range at a relatively low concentration of a chiral additive. The temperature dependence of λ_{max} for the band of selective reflection of light (Fig. 8) for a composition containing chiral additive **3f** (12.9 wt.%) in 4´-cyano-4-pentylbiphenyl shows that λ_{max} for this system is shifted to a short-wavelength region with increasing temperature, which corresponds to an increase in twisting of the cholesteric helix. This type of the temperature dependence is characteristic of induced cholesteric systems involving chiral additives with the anisometric molecular core and long terminal aliphatic substituents (see, for example, Ref. 35).

Table 4. Twisting power (|β|) of the compounds under study in 4´-cyano-4-pentylbiphenyl

Compound	R	|β| /μm^{-1} (mole fraction)$^{-1}$
1d	$C_6H_4OC_6H_{13}$	48.0±0.6
3f	C_9H_{19}	48.7±1.4
6	OMe	40.1±1.4 [22]
6	OC_6H_{13}	42.4 [22]

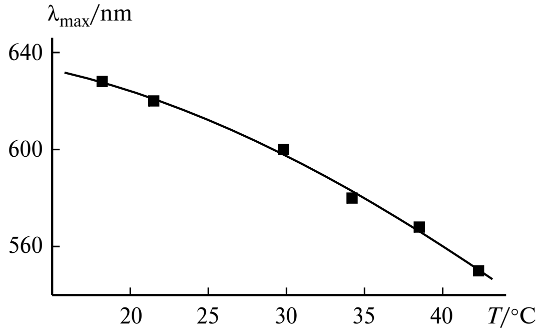


Fig. 8. Temperature dependence of λ_{max} for the band of selective reflection of light for a liquid-crystalline composite based on 4´-cyano-4-pentylbiphenyl with chiral additive **3f** (12.9 wt.%).

In addition, the chiral additives synthesized in the present study are characterized by the thermal stabilizing effect on the mesophase of 4´-cyano-4-pentylbiphenyl. Thus, the clearing temperature (transformation into an isotropic liquid) increases from 35 (for individual 4´-cyano-4-pentylbiphenyl) to 55.4 °C (for the above-mentioned composition containing compound **3f**). This is associated with high molecular anisometry and, correspondingly, high anisotropy of molecular polarizability of the chiral additive, which, to a certain extent, are responsible for its mesomorphic properties. An analogous thermal stabilizing effect was observed also in some other series of chiral additives containing a highly polarizable molecular core,[5,6] as opposed to a decrease in the clearing temperature for most of the additives studied earlier,[1] which are also based on *p*-menthan-3-one with the difference that they have low molecular anisometry.

Therefore, an unusual combination of the pronounced molecular chirality, which manifests itself in the high twisting power of the compounds under consideration, with the tendency to form layered supramolecular structures, which is associated with high anisotropy of molecular polarizability, is responsible for the observed characteristic features of the phase behavior of the liquid-crystalline compounds under study in the presence of even only one long terminal alkyl chain. These compounds exhibit the unique ability to form wide-range TGB phases combining the layered ordering with the helical twisting of smectic blocks.[27]

Experimental

The compounds synthesized were analyzed by HPLC on a Milikhrom 5 microcolumn chromatograph equipped with a Silasorb 600 C18 reverse-phase column (a MeCN—H_2O or MeCN—$CHCl_3$ mixture as the eluent, detection using absorption at $\lambda = 260$ nm). The ^1H NMR spectra were recorded on a Jeol JNM-LA 400 FT spectrometer (400 MHz) in $CDCl_3$ with Me_4Si as the internal standard. The IR spectra were measured on a Specord M82 spectrophotometer. The mass spectra were obtained on an automated Finnigan-MAT 1020 GC/MS spectrometer (energy of ionizing electrons was 70 eV, direct inlet of the sample into the ion source). The specific rotation of the chiral compounds (in (deg mL) (g dm)$^{-1}$) was measured on SU-4 or automated AA-10 polarimeters in $CHCl_3$ using a Na D line ($\lambda = 589$ nm) at a concentration of the sample of 1.0—1.5 g (100 mL)$^{-1}$. The melting points were measured and texture studies of compounds **1—3** were carried out by polythermal polarizing microscopy on an Olympus BDSP 753 polarizing microscope equipped with a Mettler FP 52 heating stage; the temperature was stabilized with an accuracy of 0.1 °C. Planar oriented liquid-crystalline samples were prepared between glasses coated with polyvinyl alcohol or in polyimide-coated Lincam cells (layer thickness was 5 μm). Homeotropically oriented liquid-crystalline samples were prepared between lecitin-coated glasses or in Lincam cells (layer thickness was 5 μm). The DSC studies of compounds **1—3** were carried out on a Perkin—Elmer DSC 7 calorimeter; the temperature was changed a rate of 10 and 2 K min^{-1}. The twisting power of compounds **1d** and **3f** was measured using the Grandjean—Cano method.[36] The temperature dependences of the spectra of selective reflection of light for planar oriented samples (thickness of the liquid-crystalline layer was 10 μm) were obtained on a Hitachi 330 spectrometer equipped with a temperature-controlled cell; the temperature was stabilized with an accuracy of 0.3 °C.

4-(Tetrahydropyran-2-yloxy)benzaldehyde was prepared according to a known procedure.[9]

4´-(Tetrahydropyran-2-yloxy)biphenyl-4-carbaldehyde was prepared analogously from 4´-hydroxybiphenyl-4-carbaldehyde.[22] The yield was 53%, m.p. 113—114 °C (from MeOH). IR (KBr), ν/cm^{-1}: 1695, 1599. Found (%): C, 76.92; H, 6.39. $C_{18}H_{18}O_3$. Calculated (%): C, 76.57; H, 6.43.

(1*R*,4*R*)-2-(4-Hydroxybenzylidene)-*p*-menthan-3-one (5a). The required amount of a base (see Table 1) was added to a predegassed solution of 4-(tetrahydropyran-2-yloxy)benzaldehyde (6.4 g, 31 mmol) and (–)-menthone (5.6 mL, 32 mmol) in DMSO (15 mL) under argon at 18—20 °C. The reaction mixture was stirred at this temperature until the reaction was completed (TLC control), diluted with a 2% AcOH solution (200 mL), and extracted with CH_2Cl_2. The organic extracts were washed with water and concentrated to dryness. A crude mixture of diastereomeric 2-(4-tetrahydropyran-2-yloxybenzylidene)-*p*-menthan-3-ones was prepared as a yellowish oil. The protective tetrahydropyranyl group was removed according to method ***A*** or ***B*** (the total yield for two steps of the synthesis is given in Table 1).

A. A mixture of diastereomeric 2-(4-tetrahydropyran-2-yloxybenzylidene)-*p*-menthan-3-ones (see above) was dissolved in 96% EtOH (80 mL) and then pyridinium *p*-toluenesulfonate (0.8 g) was added. The reaction mixture was heated to 50 °C and stirred until the reaction was completed (TLC control). Then the reaction mixture was diluted with water (200 mL), extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated to dryness. The residue was purified by flash chromatography on silica gel (hot CCl_4 as the eluent). The solution of the product in CCl_4 was concentrated to 35—40 mL. After cooling, 2-(4-hydroxybenzylidene)-*p*-menthan-3-one was obtained as colorless crystals.

B. A mixture of diastereomeric 2-(4-tetrahydropyran-2-yloxybenzylidene)-*p*-menthan-3-ones (see above) was dissolved in 90% aqueous MeCN (40 mL) and then pyridinium *p*-toluenesulfonate (0.8 g) was added. The reaction mixture was heated to 50 °C and stirred until the reaction was completed (TLC control), generally, for 3—4 h. After cooling to 0 °C, the crystals that formed were filtered off, washed with cold MeCN and dried.

Samples of compound **5a** (m.p. 153—155 °C) prepared by methods ***A*** or ***B*** were rather pure (HPLC data) and can be used for subsequent syntheses without additional purification. An analytically pure sample of compound **5a** was prepared by recrystallization from MeCN, m.p. 154—155 °C (*cf.* lit. data[10]: 140—141 °C), $[\alpha]_D^{28}$ –173.9 ($CHCl_3$) (*cf.* lit. data[10]: $[\alpha]_D^{22}$ –289.8 ($C_2H_2Cl_2$)). IR (KBr), ν/cm^{-1}: 3460, 3250, 3023, 2952, 2922, 2868, 1684, 1603, 1232. MS, *m/z*: 258 $[M]^+$, 243, 216, 187, 160, 145. ^1H NMR, δ: 0.90, 0.96, and 1.20 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, $J = 7.0$ Hz); 1.80, 1.90 (both m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.24 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.42 (m, 1 H, H(1)); 6.10 (br.s, 1 H, OH); 7.12 (s, 1 H, =CH); 6.86 and 7.28 (both d, 2 H each, 1,4-substituted benzene ring, $J = 8.6$ Hz).

(1*R*,4*R*)-2-(4´-Hydroxybiphenyl-4-yl)methylene-*p*-menthan-3-one (5b) was prepared analogously to **5a** (removal of the protective group according to method ***B***). The yield was 48%, m.p. 188—189 °C (from MeCN), $[\alpha]_D^{25}$ –223.8 ($CHCl_3$). IR (KBr), ν/cm^{-1}: 3337, 3034, 2962, 2896, 2870, 1648, 1599, 1583. MS, *m/z*: 334 $[M]^+$, 292, 263, 236, 221, 207, 183. ^1H NMR, δ: 0.91, 0.98, and 1.23 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, $J =$ 6.9 Hz); 1.80 and 1.90 (both m, 4 H each, $C(5)H_2$, $C(6)H_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.48 (m, 1 H, H(1)); 5.24 (br.s, 1 H, OH); 7.16 (s, 1 H, =CH); 6.93, 7.42, 7.49, and 7.55 (all d, 2 H each, 1,4-substituted benzene rings, $J = 8.3$—8.7 Hz).

Synthesis of esters 1—3 (general procedure). A 20% molar excess of DCC was added with stirring and cooling with ice water to a mixture of equimolar amounts of phenol (**5a** or **5b**) and the corresponding aromatic acid and several milligrams of DMAP. The reaction mixture was heated to ~20 °C and stirred for 10—12 h. Then the reaction solution was filtered through a short plug of silica gel, washed with CH_2Cl_2, concentrated to dryness, and recrystallized from hexane or MeCN. The yields, melting points, spectroscopic characteristics, and elemental analysis data for nonmesogenic compounds **1** are listed in Table 2. The corresponding characteristics for compounds **2** and **3** are given below. The transition temperatures for mesogenic compounds **2** and **3** are given in Table 3.

(3*R*,6*R*)-4-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)phenyl 4´-hexylbiphenyl-4-carboxylate (2a). The yield was 80%, $[\alpha]_D^{26.5}$ –100.3 (*c* 2.7, $CHCl_3$). Found (%): C, 82.49; H, 8.24. $C_{36}H_{42}O_3$. Calculated (%): C, 82.72; H, 8.10. MS, *m/z*: 522 $[M]^+$, 428, 386, 265, 194, 166, 152. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, $J = 6.6$ Hz); 0.91, 0.98, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, $J = 7.0$ Hz); 1.30 (m, 6 H, $C_{Alk}H_2$);

1.66 (q, 2 H, $ArCH_2C\underline{H}_2$); 1.80 and 1.90 (both m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.25 (m, 1 H, H(4)); 2.57 (sept.d, 1 H, H(8)); 2.67 (t, 2 H, $ArC\underline{H}_2$, *J* = 7.6 Hz); 3.44 (m, 1 H, H(1)); 7.12 (s, 1 H, =CH); 7.25, 7.30, 7.43, 7.58, 7.73, and 8.25 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)phenyl 4´-octylbiphenyl-4-carboxylate (2b). The yield was 68%, $[\alpha]_D^{26.5}$ –95.1 (*c* 3.3, $CHCl_3$). Found (%): C, 82.81; H, 8.49. $C_{38}H_{46}O_3$. Calculated (%): C, 82.87; H, 8.42. MS, *m/z*: 550 $[M]^+$, 522, 386, 293, 265, 194, 166, 152. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.6 Hz); 0.91, 0.98, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.0 Hz); 1.29, 1.34 (both m, 10 H, $C_{Alk}H_2$); 1.66 (q, 2 H, $ArCH_2C\underline{H}_2$); 1.80, 1.90 (both m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.25 (m, 1 H, H(4)); 2.57 (sept.d, 1 H, H(8)); 2.67 (t, 2 H, $ArC\underline{H}_2$, *J* = 7.6 Hz); 3.44 (m, 1 H, H(1)); 7.12 (s, 1 H, =CH); 7.25, 7.30, 7.43, 7.58, 7.73, and 8.25 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-hexyloxybenzoate (3a). The yield was 74%. Found (%): C, 80.20; H, 7.88. $C_{36}H_{42}O_4$. Calculated (%): C, 80.26; H, 7.86. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.6 Hz); 0.91, 0.97, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.0 Hz); 1.27 and 1.48 (both m, 6 H, $C_{Alk}H_2$); 1.79—1.94 (m, 6 H, $C(5)H_2$, $C(6)H_2$, $OCH_2C\underline{H}_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.49 (m, 1 H, H(1)); 4.05 (t, 2 H, OCH_2, *J* = 6.5 Hz); 7.15 (s, 1 H, =CH); 6.97, 7.29, 7.45, 7.60, 7.65, and 8.16 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-heptyloxybenzoate (3b). The yield was 65%. Found (%): C, 80.52; H, 8.12. $C_{37}H_{44}O_4$. Calculated (%): C, 80.40; H, 8.02. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.6 Hz); 0.91, 0.97, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.0 Hz); 1.27 and 1.48 (both m, 8 H, $C_{Alk}H_2$); 1.79—1.94 (m, 6 H, $C(5)H_2$, $C(6)H_2$, $OCH_2C\underline{H}_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.49 (m, 1 H, H(1)); 4.05 (t, 2 H, OCH_2, *J* = 6.5 Hz); 7.15 (s, 1 H, =CH); 6.97, 7.29, 7.45, 7.60, 7.65, and 8.16 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-octyloxybenzoate (3c). The yield was 74%, $[\alpha]_D^{26.5}$ –116 (*c* 2.0, $CHCl_3$). Found (%): C, 80.66; H, 8.19. $C_{38}H_{46}O_4$. Calculated (%): C, 80.53; H, 8.18. MS, *m/z*: 567 $[M]^+$, 386, 333, 233, 121. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.8 Hz); 0.91, 0.97, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.0 Hz); 1.27—1.52 (m, 10 H, $C_{Alk}H_2$); 1.79—1.94 (m, 6 H, $C(5)H_2$, $C(6)H_2$, $OCH_2C\underline{H}_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.49 (m, 1 H, H(1)); 4.05 (t, 2 H, OCH_2, *J* = 6.5 Hz); 7.15 (s, 1 H, =CH); 6.97, 7.29, 7.45, 7.60, 7.65, and 8.16 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-nonyloxybenzoate (3d). The yield was 80%. Found (%): C, 80.50; H, 8.27. $C_{39}H_{48}O_4$. Calculated (%): C, 80.65; H, 8.33. MS, *m/z*: 580 $[M]^+$, 333, 247, 121. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.7 Hz); 0.91, 0.97, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.0 Hz); 1.25—1.51 (m, 12 H, $C_{Alk}H_2$); 1.79—1.94 (m, 6 H, $C(5)H_2$, $C(6)H_2$, $OCH_2C\underline{H}_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.49 (m, 1 H, H(1)); 4.05 (t, 2 H, OCH_2, *J* = 6.5 Hz); 7.15 (s, 1 H, =CH); 6.98, 7.29, 7.45, 7.60, 7.65, and 8.16 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-hexadecyloxybenzoate (3e). The yield was 75%. Found (%): C, 81.55; H, 9.19. $C_{46}H_{62}O_4$. Calculated (%): C, 81.37; H, 9.20. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.7 Hz); 0.91 and 0.97 (both d, 3 H each, $C(9)H_3$, $C(10)H_3$, *J* = 7.1 Hz); 1.25—1.51 (m, 29 H, $C_{Alk}H_2$, $C(7)H_3$); 1.79—1.94 (m, 6 H, $C(5)H_2$, $C(6)H_2$, $OCH_2C\underline{H}_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 3.49 (m, 1 H, H(1)); 4.05 (t, 2 H, OCH_2, *J* = 6.5 Hz); 7.15 (s, 1 H, =CH); 6.98, 7.29, 7.45, 7.60, 7.65, and 8.16 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-nonylbenzoate (3f). The yield was 84%. Found (%): C, 83.06; H, 8.66. $C_{39}H_{48}O_3$. Calculated (%): C, 82.94; H, 8.57. MS, *m/z*: 564 $[M]^+$, 333, 231, 131, 91. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.9 Hz); 0.91, 0.98, and 1.23 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.2 Hz); 1.25—1.35 (m, 12 H, $C_{Alk}H_2$); 1.66 (q, 2 H, $ArCH_2C\underline{H}_2$); 1.75—2.00 (m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.26 (m, 1 H, H(4)); 2.57 (sept.d, 1 H, H(8)); 2.71 (t, 2 H, $ArC\underline{H}_2$, *J* = 7.6 Hz); 3.49 (m, 1 H, H(1)); 7.16 (s, 1 H, =CH); 7.29, 7.33, 7.45, 7.61, 7.65, and 8.13 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-decylbenzoate (3g). The yield was 85%. Found (%): C, 83.14; H, 8.81. $C_{40}H_{50}O_3$. Calculated (%): C, 83.00; H, 8.71. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.9 Hz); 0.91, 0.98, and 1.24 (all d, 3 H each, $C(10)H_3$, $C(9)H_3$, $C(7)H_3$, *J* = 7.2 Hz); 1.25—1.33 (m, 14 H, $C_{Alk}H_2$); 1.66 (q, 2 H, $ArCH_2C\underline{H}_2$); 1.75—2.00 (m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 2.70 (t, 2 H, $ArC\underline{H}_2$, *J* = 7.6 Hz); 3.48 (m, 1 H, H(1)); 7.16 (s, 1 H, =CH); 7.29, 7.33, 7.45, 7.61, 7.65, and 8.13 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

(3*R*,6*R*)-4´-(3-Isopropyl-6-methyl-2-oxocyclohexylidenemethyl)biphenyl-4-yl 4-hexadecylbenzoate (3h). The yield was 75%. Found (%): C, 83.40; H, 9.31. $C_{46}H_{62}O_3$. Calculated (%): C, 83.33; H, 9.43. ^1H NMR, δ: 0.89 (t, 3 H, $C_{Alk}H_3$, *J* = 6.9 Hz); 0.91 and 0.98 (both d, 3 H each, $C(9)H_3$, $C(10)H_3$, *J* = 7.2 Hz); 1.24—1.32 (m, 29 H, $C_{Alk}H_2$, $C(7)H_3$); 1.66 (q, 2 H, $ArCH_2C\underline{H}_2$); 1.75—2.00 (m, 4 H, $C(5)H_2$, $C(6)H_2$); 2.26 (m, 1 H, H(4)); 2.58 (sept.d, 1 H, H(8)); 2.70 (t, 2 H, $ArC\underline{H}_2$, *J* = 7.6 Hz); 3.48 (m, 1 H, H(1)); 7.16 (s, 1 H, =CH); 7.29, 7.33, 7.45, 7.61, 7.65, and 8.13 (all d, 2 H each, 1,4-substituted benzene rings, *J* = 8.3—8.6 Hz).

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