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Synthesis of New Liquid Crystalline Compounds Containing an α,β-Unsaturated Ketone and β-Chloroketone Groups in the Side Chain

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Abstract—A number of new liquid crystalline compounds containing an α,β-unsaturated ketone or β-chloro ketone moiety in the side chain were synthesized. The key intermediates in the synthesis were 1-(4-hydroxyphenyl)-2-octen-1-one and 3-chloro-1-(4-hydroxyphenyl)octan-1-one which were prepared from 5-(4-hydroxyphenyl)-3-pentyl-4,5-dihydroisoxazole and 3-hydroxy-1-(4-hydroxyphenyl)octan-1-one, respectively.

We previously [1] synthesized a series of new liquid crystalline compounds which contained a β-hydroxy ketone moiety in the side chain. The key intermediate product in these syntheses was β-hydroxy ketone **IV** which was prepared from 4-hydroxybenzaldehyde (**I**) through oxime **II** and 4,5-dihydroisoxazole **III** (Scheme 1). It was presumed that compound **IV** can also be used to prepare new liquid crystalline compounds having an α,β-unsaturated ketone fragment in the side chain. For this purpose we examined dehydration of compound **IV**.

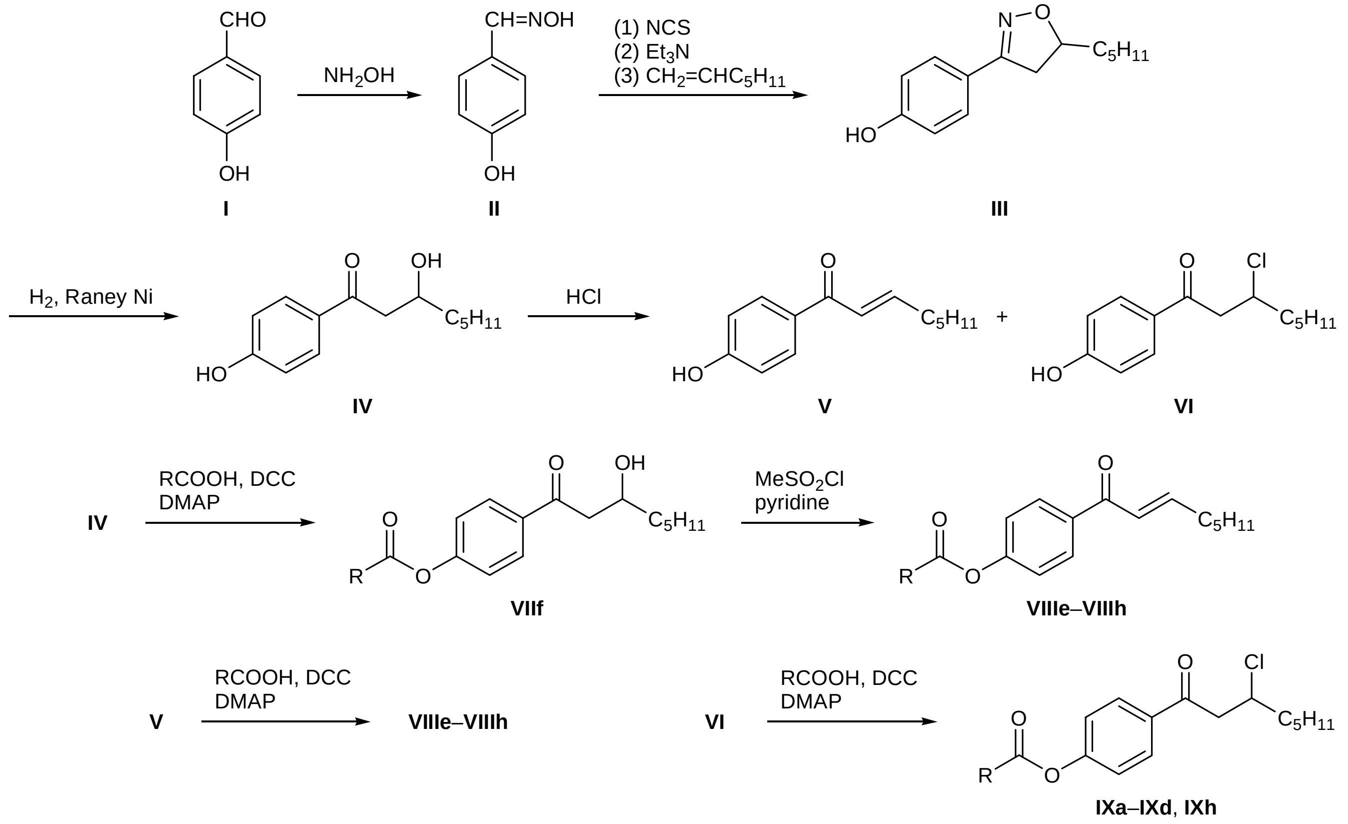
Various procedures for dehydration of compound **IV** by the action of both acids and bases were studied. Heating of compound **IV** in 2-propanol with excess triethylamine gave 15% of α,β-unsaturated ketone **V**, while the most part of initial β-hydroxy ketone **IV** was recovered from the reaction mixture. By heating of compound **IV** in toluene in the presence of alkaline aluminum oxide, enone **V** was obtained in 20% yield. Much better results were obtained by dehydration of **IV** in the presence of acid catalysts. Treatment of **IV** with concentrated hydrochloric acid afforded two products in approximately equal amounts. According to the spectral data, these products were assigned the structures of α,β-unsaturated ketone **V** and β-chloro ketone **VI** (Scheme 1). When the reaction of β-hydroxy ketone **IV** with hydrochloric acid was prolonged, the major product was β-chloro ketone **VI** which was isolated in 70% yield. When perchloric acid was used for dehydration of β-hydroxy ketone **IV**, α,β-unsaturated ketone **V** was isolated in 65% yield.

Compounds **V** and **VI** can be regarded as starting materials for the synthesis of liquid crystalline substances. The structure of **V** and **VI** was proved by analysis of their UV, IR, and ^{1}H NMR spectra. The IR spectrum of **V** contained an absorption band at 1662 cm^{-1} due to carbonyl stretching vibrations and a band at 1618 cm^{-1} belonging to stretching vibrations of the double bond. In the ^{1}H NMR spectrum of **V**, the vinyl proton on C^3 gave a triplet of doublets at δ 7.05 ppm with coupling constants *J* of 7 Hz (with the methylene protons on C^4) and 15 Hz (with the vinyl proton on C^2). The signal from 2-H was partially overlapped by the multiplet signal from the hydroxy proton at δ 6.82–6.98 ppm. The downfield position of the 3-H signal relative to 2-H results from deshielding effect of the carbonyl group, which is typical of conjugated enone systems. The coupling constant for the vinyl protons 2-H and 3-H, *J* = 15 Hz, indicates *trans* configuration of the double bond.

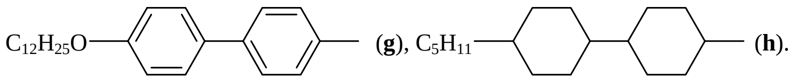
In the IR spectrum of β-chloro ketone **VI**, stretching vibrations of the carbonyl group appeared at 1675 cm^{-1}. The ^{1}H NMR spectrum of **VI** is characterized by downfield shifts of the multiplet signals from 2-H and 3-H (Δδ = 0.23–0.39 ppm) relative to the corresponding signals of initial ketone **IV**.

Liquid crystalline compounds having an α,β-unsaturated and β-chloro ketone fragments in the side

Scheme 1.



R = 4-FC_6H_4 (**a**), 4-NCC_6H_4 (**b**), 4-$C_3H_7OC_6H_4$ (**c**), 4-$C_6H_{13}OC_6H_4$ (**d**), 4-$C_5H_{11}OC_6H_4$ (**e**), 4-$C_{12}H_{25}OC_6H_4$ (**f**),



chain were synthesized by esterification of phenols **V** and **VI** with various mesogenic carboxylic acids. Reactions of compound **V** with carboxylic acids in the presence of *N*,*N'*-dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine gave 60–90% of esters **VIIIe**, **VIIIg**, and **VIIIh**. Likewise, from phenol **VI** we obtained esters **IXa**–**IXd** and **IXh** in 70–80% yield. Esters **VIII** were also synthesized by an alternative procedure from β-hydroxy ketone **IV**, i.e., the first stage in the synthesis was esterification, and the second, dehydration. The reaction of **IV** with 4-dodecyloxybenzoic acid according to the procedure reported in [1] afforded ester **VIIf** which was treated with methanesulfonyl chloride in pyridine; as a result, ester **VIIIf** was isolated in ~60% yield.

The structure of esters **VIIIe**–**VIIIh**, **IXa**–**IXd**, and **IXh** was confirmed by the UV, IR, and ^{1}H NMR spectra. The IR spectra of these compounds contained strong absorption bands from the ester carbonyl group at 1750–1735 cm^{-1}, while bands assignable to phenolic hydroxy group were absent. Compounds **VIIIe**–**VIIIh** showed in the IR spectra absorption bands due to stretching vibrations of the double bond at 1618–1625 cm^{-1}, as well as of the conjugated carbonyl group at 1668 cm^{-1} for the *s-cis* conformers and 1648 cm^{-1} for the *s-trans* conformers. The carbonyl stretching vibration frequency in the spectra of **IXa**–**IXd** and **IXh** ranges from 1675 to 1690 cm^{-1}. In the ^{1}H NMR spectra of esters **VIIId**–**VIIIh**, **IXa**–**IXd**, and **IXh** we observed multiplet signals from the vinyl protons or CHCl protons, which indicated conservation of the enone and β-chloro ketone moieties in the esterification of phenols **V** and **VI**, respectively.

Among the nine newly synthesized esters, five compounds were found to exhibit mesomorphic properties. Comparison of the phase transition temperatures for esters **VIIIe**–**VIIIh**, **IXa**–**IXd**, and **IXh** with those of the previously reported liquid crystalline compounds having a β-hydroxy ketone fragment in the side chain [1] allowed us to estimate the effect of side-

Phase transition temperatures of compounds **VIIIe–VIIIh**, **IXa–IXd**, and **IXh**

Compound no.	mp, °C	Smecic phase C	Smectic phase B	Transition temperature, °C	Smectic phase A	Nematic phase	Clarification temperature, °C
VIIIe	90.5–91	–	–	–	–	–	–
VIIIf	107–107.5	–	–	–	–	–	–
VIIIg	125	●	–	–	–	–	205.5
VIIIh	98	●	–	183	●	–	191
IXa	93–94	–	–	–	–	–	–
IXb	95–94	–	–	–	–	–	–
IXc	85	–	–	(74)	●	–	(77)
IXd	86	–	●	92.5	●	–	94
IXh	156	●	–	171	●	174 ●	179 (decomp.)

chain functional groups on the formation and stabilization of liquid crystalline state. Esters **VIIIe** and **VIIIf** showed no mesomorphic properties, although pentyloxybenzyl and dodecyloxybenzyl ether derived from phenol **IV** gave rise to smectic mesophase in a fairly wide temperature range [1]. Dehydration leading to formation of an enone fragment in the side chain weakens intermolecular polar interaction. Presumably, this is the reason why alkoxybenzoates **VIIIe** and **VIIIf** possessing two benzene rings do not form mesophase. Esterification of α,β-unsaturated ketone **V** with substituted biphenyl- and bicyclohexylcarboxylic acids leads to esters **VIIIg** and **VIIIh** which contain three rings. Compound **VIIIg** gives a smectic liquid crystalline mesophase C in the range 80.5°C, whereas ester **VIIIh**, apart from smectic phase C in the range 85°C, gives rise to less ordered smectic phase A in the range 8°C. Thus, increase in the number of rings (from two to three) in esters **VIII** having an enone fragment in the side chain leads to appearance of a mesophase. Stabilization of the mesophase and extension of the corresponding temperature range are accompanied by increase of the melting point, which is clearly seen with compounds **VIIIe**–**VIIIg** as examples and is consistent with published data [2, 3].

Propoxybenzoate **IXc** with a β-chloro ketone moiety in the side chain produces a monotropic liquid crystalline phase A in the range 3°C. For homologous hexyloxybenzoate **IXd**, we observed stabilization of thermotropic smectic mesophases C (in the range 6.5°C) and A (in the range 1.5°C). Thus β-chloro ketones **IXc** and **IXd**, as welll as analogous esters containing a β-hydroxy ketone fragment in the side chain [1], are smectogenic substances, but smectic phases produced by the former exist in a narrower temperature range and their melting points are lower. This is likely to result from weakening of polar interaction in going from compounds possessing a β-hydroxy ketone fragment in the side chain to their analogs having a β-chloro ketone moiety. Like esters **VII** [1], compounds **IXa** and **IXb**, whose molecules contain polar groups in the terminal part, exhibit no liquid crystalline properties. Esters **IXh** gives rise to both smectic mesophases C and A and nematic phase in the range 5°C; the latter was not observed for bi(cyclohexyl)carboxylic acid ester **VIIIh** having a side-chain enone fragment.

To conclude, it should be noted that compounds **V** and **VI** may be used in further modifications of side chains in liquid crystalline compounds with a view to analyze their mesomorphic properties with regard to the presence of different functional groups in the side chains of their molecules. The results of our further studies in this field will be reported elsewhere.

EXPERIMENTAL

The phase transition temperatures were determined on a heating device coupled with a polarizing microscope. The IR spectra were obtained from solutions in chloroform on a Specord 75 IR spectrometer using KBr cells. The UV spectra were measured from solutions in methanol on a Specord M40 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz) using $CDCl_3$ as solvent and HMDS as internal reference. The phase-transition temperatures of compounds **VIIIe–VIIIh**, **IXa**–**IXd**, and **IXh** are given in table.

3-(4-Hydroxyphenyl)-5-pentyl-4,5-dihydroisoxazole (III). Gaseous phase over concentrated hydrochloric acid was withdrawn using a syringe and was then passed through a solution of 1.6 g (11.7 mmol) of 4-hydroxybenzaldehyde oxime in 50 ml of dimethylformamide. *N*-Chlorosuccinimide, 1.7 g (12.7 mmol), was then added in portions under stirring over a period of 2.5 h, the mixture was stirred for 1 h at room temperature and cooled to 0°C, 3.3 ml (23.5 mmol) of 1-heptene was added, and a solution of 1.8 ml of triethylamine in 35 ml of dimethylformamide was added dropwise over a period of 2.5 h. The mixture was stirred for 12 h at room temperature, diluted with 50 ml of chloroform, and treated with dilute (1:5) hydrochloric acid. The organic phase was separated, the aqueous layer was extracted with chloroform, and the combined extracts were washed with two portions of a saturated solution of sodium chloride and dried over sodium sulfate. The most part of the solvent was removed under reduced pressure, and the residue was diluted with a 5-fold volume of water. The crystals of dihydroisoxazole **III** were filtered off and washed with water and petroleum ether. Yield 1.9 g (70%), mp 109.5–111°C (from toluene–ethyl acetate) [4]. IR spectrum, ν, cm^{-1}: 3595, 3530–3080 (O–H); 3010 ($C–H_{arom}$); 2955, 2930, 2860 ($C–H_{aliph}$); 1605, 1515 ($C=C_{arom}$); 1270 (C–O). ^1H NMR spectrum, δ, ppm: 0.84 t (3H, CH_3, J = 6.5 Hz), 1.14–1.82 m (8H, CH_2, alkyl), 2.90 d.d (1H, 4-H, J_1 = 8.2, J_2 = 16.5 Hz), 3.32 d.d (1H, 4-H, J_1 = 10.2, J_2 = 16.5 Hz), 4.54–4.74 m (1H, 5-H), 6.92 d and 7.47 d (2H each, H_{arom}, J = 8.5 Hz).

1-(4-Hydroxyphenyl)-2-octen-1-one (V). *a*. To a solution of 0.44 g of β-hydroxy ketone **IV** (prepared from 4,5-dihydroisoxazole **III** according to the procedure described in [1]) in 15 ml of dioxane we added 0.3 ml of a 70% solution of perchloric acid. The mixture was stirred for 18 h at 15–17°C, and 40 ml of ethyl acetate and 40 ml of a saturated aqueous solution of sodium chloride were added. The aqueous phase was separated and extracted with ethyl acetate (2× 15 ml). The extracts were combined with the organic phase, washed in succession with 20 ml of a saturated solution of sodium hydrogen carbonate and 20 ml of a saturated solution of sodium chloride, and dried over sodium sulfate. The solvent was distilled off under reduced pressure, and the residue was recrystallized from toluene–petroleum ether. Yield 0.27 g (65%), mp 67–68°C (from toluene–petroleum ether). IR spectrum, ν, cm^{-1}: 3590, 3100–3500 (O–H); 3035, 3015 ($C–H_{arom}$); 2965, 2935, 2875, 2865 ($C–H_{aliph}$); 1662 (C=O); 1618 (C=C); 1605, 1585, 1513 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, C^8H_3, J = 7.2 Hz), 1.20–1.40 m (4H, C^6H_2, C^7H_2), 1.50 quint (2H, C^5H_2, J = 7 Hz), 2.28 distorted q (2H, C^4H_2, J = 7 Hz), 6.82–6.98 m (2H, 2-H, 4'-OH), 7.05 t.d (1H, 3-H, J_1 = 7, J_2 = 15 Hz), 6.90 d and 7.89 d (2H each, H_{arom}, J = 8.5 Hz).

b. A solution of 0.1 g (0.42 mmol) of hydroxy ketone **IV** and 0.2 ml (1.44 mmol) of triethylamine in 5 ml of 2-propanol was heated for 24 h under reflux. The solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography on silica gel using ethyl acetate–cyclohexane (1:3) as eluent. Yield of ketone **V** 0.014 g (15%). The subsequent elution gave 0.084 g of initial β-hydroxy ketone **IV**. The yield of enone **V**, calculated on the reacted initial ketone **IV**, was 94%.

c. Alkaline aluminum oxide (according to Brockmann), 10 g, was added to a solution of 0.5 g of β-hydroxy ketone **IV** in 50 ml of toluene. The mixture was stirred for 1 h at the boiling point, the heating bath was removed, and the mixture was stirred for an additional 1 h. Aluminum oxide was filtered off and washed on a filter first with 150 ml of toluene and then with 150 ml of ethyl acetate. The ethyl acetate solution was evaporated, and the residue was subjected to column chromatography on silica gel using ethyl acetate–petroleum ether (1:4) as eluent. Removal of the solvent from the eluate gave 0.092 g (20%) of ketone **V**.

3-Chloro-1-(4-hydroxyphenyl)octan-1-one (VI). Concentrated hydrochloric acid, 1 ml, was added to a solution of 0.766 g of β-hydroxy ketone **IV** in 20 ml of dioxane. The mixture was stirred for 22.5 h at 20°C, and 40 ml of toluene and 50 ml of a saturated aqueous solution of sodium chloride were added. The aqueous phase was separated and extracted with toluene (2× 20 ml). The extracts were combined with the organic phase, washed in succession with 30 ml of a saturated solution of sodium hydrogen carbonate and 30 ml of a saturated solution of sodium chloride, and dried over sodium sulfate. The solvent was distilled off under reduced pressure, and the residue was recrystallized from toluene–petroleum ether. Yield 0.577 g (70%), mp 56–57°C (decomp., from toluene–petroleum ether). UV spectrum, λ_{max}, nm: 221.1, 279.8. IR spectrum, ν, cm^{-1}: 3585, 3100–3500 (O–H); 3025, 3010 ($C–H_{arom}$); 2960, 2930, 2875, 2865 ($C–H_{aliph}$); 1675 (C=O); 1605, 1585, 1510 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.88 t (3H, C^8H_3, J = 6.8 Hz), 1.20–1.38 m (4H, C^6H_2, C^7H_2), 1.40–1.62 m (2H, C^5H_2), 1.69–1.89 m (2H, C^4H_2), 3.18 d.d (1H, J_1 = 5.6, J_2 = 16.4 Hz) and

3.50 d.d (1H, J_1 = 8, J_2 = 16.4 Hz) (C^2H_2); 4.48–4.57 m (1H, C^3H), 5.74 br.s (1H, 4'-OH), 6.88 d and 7.89 d (2H each, H_{arom}, J = 8.8 Hz).

4-(2-Octenoyl)phenyl 4-pentyloxybenzoate (VIIIe). A catalytic amount of 4-(dimethylamino)pyridine was added to a solution of 0.1 g (0.46 mmol) of α,β-unsaturated ketone **V**, 0.1 g (0.48 mmol) of 4-pentyloxybenzoic acid, and 0.095 g (0.46 mmol) of *N*,*N'*-dicyclohexylcarbodiimide in 15 ml of methylene chloride. The mixture was stirred for 26 h at 20°C and filtered through a layer of aluminum oxide, the sorbent was washed with 40 ml of methylene chloride, the solvent was removed from the filtrate under reduced pressure, and the residue was recrystallized from 2-propanol. Yield 0.113 g (61%). IR spectrum, ν, cm^{-1}: 3010 ($C–H_{arom}$); 2965, 2925, 2870, 2855 ($C–H_{aliph}$); 1732 (C=O, ester); 1668 (C=O, *s-cis*); 1648 (C=O, *s-trans*); 1599, 1580, 1511, 1506 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, J = 6.8 Hz) and 0.93 t (3H, J = 7.2 Hz) ($C^{5'}H_3$ and $C^{8''}H_3$); 1.26–1.58 m (10H, CH_2 alkyl); 1.82 quint (2H, $C^{2'}H_2$, J = 7 Hz); 2.31 d.q (2H, $C^{4''}H_2$, J_1 = 1.2, J_2 = 7.2 Hz); 4.04 t (2H, $OC^{1'}H_2$, J = 7 Hz); 6.87 distorted d (1H, 2''-H, J = 15.2 Hz); 7.08 t.d (1H, 3''-H, J_1 = 7.2, J_2 = 15.2 Hz); 6.96 d (2H, J = 8.8 Hz), 7.30 d (2H, J = 8.8 Hz), 8.00 d (2H, J = 8.8 Hz), and 8.13 d (2H, J = 8.8 Hz) (H_{arom}).

Compounds **VIIIg** and **VIIIh** were synthesized in a similar way by esterification of phenol **V**.

4-(2-Octenoyl)phenyl 4'-decyloxy-1,1'-biphenyl-4-carboxylate (VIIIg). Yield 80%. IR spectrum, ν, cm^{-1}: 3025, 3015 ($C–H_{arom}$); 2955, 2930, 2855 ($C–H_{aliph}$); 1734 (C=O, ester); 1668 (C=O, *s-cis*); 1647 (C=O, *s-trans*); 1618 (C=C); 1605, 1600, 1520, 1505, 1498 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, J = 6.8 Hz) and 0.90 t (3H, J = 7 Hz) ($C^{10''}H_3$ and $C^{8'''}H_3$); 1.20–1.58 m (20H, CH_2, alkyl); 1.80 quint (2H, $C^{3''}H_2$, J = 7 Hz); 2.31 d.q (2H, $C^{4'''}H_2$, J_1 = 1.2, J_2 = 6.8 Hz); 4.00 t (2H, $OC^{1''}H_2$, J = 7 Hz); 6.88 distorted d (1H, 2'''-H, J = 15.6 Hz); 7.09 t.d (1H, 3'''-H, J_1 = 6.8, J_2 = 15.6 Hz); 6.99 d (2H, J = 9 Hz), 7.33 d (2H, J = 9 Hz), 7.58 d (2H, J = 9 Hz), 7.69 d (2H, J = 9 Hz), 8.02 d (2H, J = 9 Hz), and 8.22 d (2H, J = 9 Hz) (H_{arom}).

4-(2-Octenoyl)phenyl 4'-pentyl-1,1'-bi(cyclohexyl)-4-carboxylate (VIIIh). Yield 91%. IR spectrum, ν, cm^{-1}: 3025, 3015 ($C–H_{arom}$); 2930, 2860 ($C–H_{aliph}$); 1750 (C=O, ester); 1668 (C=O, *s-cis*); 1648 (C=O, *s-trans*); 1618 (C=C); 1600, 1505 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, J = 7 Hz) and 0.90 t (3H, J = 7 Hz) ($C^{5''}H_3$ and $C^{8'''}H_3$); 0.80–1.38 m (22H), 1.45–1.59 m (3H), 1.66–1.79 m (4H), 1.80–1.88 m (2H), and 2.10–2.22 m (2H) (CH_2, alkyl, cyclohexyl); 2.29 d.q (2H, $C^{4'''}H_2$, J_1 = 1.2, J_2 = 6.8 Hz); 2.46 t.t (1H, 4-H, J_1 = 3.6, J_2 = 12.4 Hz); 6.83 distorted d (1H, 2'''-H, J = 15.6 Hz); 7.05 t.d (1H, 3'''-H, J_1 = 6.8, J_2 = 15.6 Hz); 7.15 d and 7.94 d (2H each, H_{arom}, J = 8.8 Hz).

4-(2-Octenoyl)phenyl 4-dodecyloxybenzoate (VIIIf). A solution of 0.056 g (0.11 mmol) of ester **VIIf** (prepared from compound **IV** according to the procedure described in [1]) in 10 ml of pyridine was cooled to 0°C, and 0.03 ml of methanesulfonyl chloride was added with stirring. The mixture was stirred for 30 min, the cooling bath was removed, and the mixture was stirred for 24 h at 20°C and for 1 h at 70°C. Ethyl acetate, 40 ml, and dilute (1 : 5) hydrochloric acid, 50 ml, were added, the aqueous phase was separated, and the organic phase was treated in succession with 25 ml of water, 25 ml of a saturated aqueous solution of sodium hydrogen carbonate, and 25 ml of water again and dried over sodium sulfate. The solvent was distilled off under reduced pressure, and the residue was recrystallized from 2-propanol. Yield of **VIIIf** 0.032 g (59%). UV spectrum: λ_{max} 273.1 nm. IR spectrum, ν, cm^{-1}: 3025, 3010 ($C–H_{arom}$); 2925, 2855 ($C–H_{aliph}$); 1732 (C=O, ester); 1668 (C=O, *s-cis*); 1648 (C=O, *s-trans*); 1618 (C=C); 1606, 1600, 1581, 1511, 1506 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, J = 7.2 Hz) and 0.90 t (3H, J = 7.2 Hz) ($C^{12'}H_3$ and $C^{8''}H_3$); 1.16–1.40 m (20H) and 1.41–1.58 m (4H) (CH_2, alkyl); 1.81 quint (2H, $C^{2'}H_2$, J = 7 Hz); 2.31 d.q (2H, $C^{4''}H_2$, J_1 = 1.2, J_2 = 6.8 Hz); 4.03 t (2H, $OC^{1'}H_2$, J = 7 Hz); 6.87 distorted d (1H, 2''-H, J = 15.6 Hz); 7.08 t.d (1H, 3''-H, J_1 = 6.8, J_2 = 15.6 Hz); 6.96 d (2H, J = 8.8 Hz), 7.30 d (2H, J = 8.4 Hz), 8.00 d (2H, J = 8.4 Hz), and 8.13 d (2H, J = 8.8 Hz) (H_{arom}).

Compounds **IXa**–**IXd** and **IXh** were synthesized in a similar way by esterification of phenol **VI**.

4-(3-Chlorooctanoyl)phenyl 4-fluorobenzoate (IXa). Yield 70%. UV spectrum: λ_{max} 250.4 nm. IR spectrum, ν, cm^{-1}: 3025, 3020 ($C–H_{arom}$); 2955, 2925, 2875, 2855 ($C–H_{aliph}$); 1740 (C=O, ester); 1690 (C=O); 1600, 1510 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, $C^{8'}H_3$, J = 7 Hz); 1.20–1.40 m (4H, $C^{6'}H_2$, $C^{7'}H_2$); 1.42–1.64 m (2H, $C^{5'}H_2$); 1.71–1.91 m (2H, $C^{4'}H_2$); 3.25 d.d (1H, J_1 = 5.6, J_2 = 17.2 Hz) and 3.56 d.d (1H, J_1 = 7.6, J_2 = 17.2 Hz) ($C^{2'}H_2$); 4.50–4.60 m (1H, 3'-H); 7.19 distorted t (2H, J = 8.8 Hz), 7.32 d (2H, J = 8.8 Hz), 8.04 d (2H, J = 8.8 Hz), and 8.22 distorted d.d (2H, J_1 = 5.6, J_2 = 8.8 Hz) (H_{arom}).

4-(3-Chlorooctanoyl)phenyl 4-cyanobenzoate (IXb). Yield 76%. IR spectrum, ν, cm^{-1}: 3025 ($C–H_{arom}$); 2960, 2930, 2860 ($C–H_{aliph}$); 2235 (C≡N); 1745 (C=O, ester); 1685 (C=O); 1600, 1500 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.90 t (3H, $C^{8'}H_3$, J = 6.8 Hz); 1.18–1.40 m (4H, $C^{6'}H_2$, $C^{7'}H_2$); 1.42–1.64 m (2H, $C^{5'}H_2$); 1.71–1.92 m (2H, $C^{4'}H_2$); 3.24 d.d (1H, J_1 = 5.2, J_2 = 17.2 Hz) and 3.57 d.d (1H, J_1 = 7.6, J_2 = 17.2 Hz) ($C^{2'}H_2$); 4.45–4.59 m (1H, 3'-H); 7.34 d (2H, J = 8.4 Hz), 7.83 d (2H, J = 8.4 Hz), 8.06 d (2H, J = 8.4 Hz), and 8.30 d (2H, J = 8.4 Hz) (H_{arom}).

4-(3-Chlorooctanoyl)phenyl 4-propoxybenzoate (IXc). Yield 81%. IR spectrum, ν, cm^{-1}: 3030, 3010 ($C–H_{arom}$); 2960, 2930, 2875, 2860 ($C–H_{aliph}$); 1730 (C=O, ester); 1690 (C=O); 1600, 1580, 1510 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.89 t (3H, $C^{8''}H_3$, J = 7 Hz); 1.06 t (3H, $C^{3'}H_3$, J = 7 Hz); 1.18–1.38 m (4H, $C^{6''}H_2$, $C^{7''}H_2$); 1.40–1.64 m (2H, $C^{5''}H_2$); 1.70–1.92 m (2H, $C^{4''}H_2$); 1.84 sext (2H, $C^{2'}H_2$, J = 7 Hz); 3.25 d.d (1H, J_1 = 5.6, J_2 = 17 Hz) and 3.56 d.d (1H, J_1 = 7.6, J_2 = 17 Hz) ($C^{2''}H_2$); 4.00 t (2H, $OC^{1'}H_2$, J = 7 Hz); 4.50–4.60 m (1H, 3"-H); 6.97 d (2H, J = 8.8 Hz), 7.32 d (2H, J = 8.8 Hz), 8.03 d (2H, J = 8.8 Hz), and 8.12 d (2H, J = 8.8 Hz) (H_{arom}).

4-(3-Chlorooctanoyl)phenyl 4-hexyloxybenzoate (IXd). Yield 71%. UV spectrum, λ_{max}, nm: 267.2, 305.1, 317.1, 332.1. IR spectrum, ν, cm^{-1}: 3025, 3010 ($C–H_{arom}$); 2955, 2930, 2875, 2860 ($C–H_{aliph}$); 1730 (C=O, ester); 1680 (C=O); 1600, 1575, 1505 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.82–0.96 m (6H, $C^{6'}H_3$, $C^{8''}H_3$); 1.20–1.64 m (12H, CH_2, alkyl); 1.81 quint (2H, $C^{2'}H_2$, J = 6.4 Hz); 1.71–1.91 m (2H, $C^{4''}H_2$); 3.24 d.d (1H, J_1 = 5.6, J_2 = 17.2 Hz) and 3.56 d.d (1H, J_1 = 7.6, J_2 = 17.2 Hz) ($C^{2''}H_2$); 4.04 t (2H, OCH_2, J = 6.4 Hz); 4.50–4.60 m (1H, CHCl); 6.96 d (2H, J = 8.4 Hz), 7.32 d (2H, J = 8.4 Hz), 8.02 d (2H, J = 8.4 Hz), and 8.12 d (2H, J = 8.4 Hz) (H_{arom}).

4-(3-Chlorooctanoyl)phenyl 4'-pentyl-1,1'-bi(cyclohexyl)-4-carboxylate (IXh). Yield 75%. UV spectrum: λ_{max} 254.2 nm. IR spectrum, ν, cm^{-1}: 3030, 3015 ($C–H_{arom}$); 2930, 2855 ($C–H_{aliph}$); 1755 (C=O, ester); 1690 (C=O); 1625, 1600, 1505 ($C=C_{arom}$). ^1H NMR spectrum, δ, ppm: 0.87 t (3H, J = 7 Hz) and 0.89 t (3H, J = 7 Hz) ($C^{5''}H_3$ and $C^{8'''}H_3$); 0.94–1.18 m, 1.18–1.38 m, 1.40–1.63 m, and 1.66–1.90 m (33H, CH_2, alkyl, and CH_2, CH, cyclohexyl); 2.11–2.19 m (2H, C^3H_2, C^5H_2); 2.46 t.t (1H, 4-H, J_1 = 3.6, J_2 = 12.4 Hz); 3.22 d.d (1H, J_1 = 5.6, J_2 = 17 Hz) and 3.53 d.d (1H, J_1 = 7.6, J_2 = 17 Hz) ($C^{2'''}H_2$); 4.48–4.58 m (1H, CHCl); 7.16 d and 7.97 d (2H each, H_{arom}, J = 8.6 Hz).

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