Liquid Crystals

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Phenacyl esters

A new class of liquid-crystalline compound

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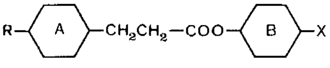
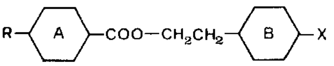
Reaction of aliphatic, alicyclic, and aromatic acids with 4-substituted α-bromoacetophenones yields a series of new liquid-crystalline phenacyl esters. Their mesomorphic properties are discussed according to the structure of the acid and ketone parts of the molecule.

Using a wide range of *n* in the series of liquid-crystalline esters with the central group $(CH_2)_nCOO$ as an example, we have shown that even *n* values are preferable for mesomorphism [1]. This means that the central fragment of the liquid-crystalline ester must contain an even number of atoms forming a chain, in spite of the mode of their connection, which is shown, for example, by the mesogenity of the propionic acid esters [2, 3]



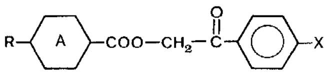
(I)

and their structural isomers [4]



(II)

Here, the central bridging group in the esters **II** was modified by replacing the CH_2 unit by the carbonyl group conjugated with the aromatic ring



(III)

Phenacyl esters (**III**) were synthesized by the conventional method [5] by reacting the corresponding acids and α-bromoacetophenones in acetonitrile in the presence of K_2CO_3 and polyethylene glycol as a catalyst. The nature of the *R* and *X* substituents, the transition temperatures of the phenacyl esters (**III**), as well as the esters taken for comparison are presented in table 1.

Introduction of the carbonyl group into the bridging fragment of compounds **III** produces two effects:

(1) the presence of a polar group increases the intermolecular dipole–dipole interaction, which causes an increase of the melting point (as compared to model compounds) and promotes the appearance of smectic phases;

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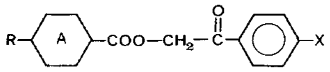
Table 1. Transition temperatures for the phenacyl esters **III**†



Compound no.	*R*	*A*	*X*	T_{CS}/°C	T_{SN}/°C	T_{NI}/°C	ΔT_{CS_A}/°C	ΔT_{SN}/°C
1	C_4H_9	C_6H_{10}	OC_2H_5	—	72(35·5)	97(75·5)	—(—)	25(40)
2	C_4H_9	C_6H_{10}	Br	—	—	111·7	—	—
3	C_4H_9	C_6H_{10}	CN	95·6	101(55·8)	105(67·9)	4·4(—)	4·0(12·1)
4	C_4H_9	C_6H_{10}	–cychex.–C_3H_7	152·1(64; 97)	174·1(116)	190·2(189)	22·0(52)	16·1(73)
5	C_4H_9	C_6H_{10}	–ϕ–Br	113(118$_B$; 137$_A$)	—(189)	219(220)	106(71)	—(31)
6	C_4H_9	C_6H_{10}	–ϕ–CN	90(—)	140(94)	190(258)	50(—)	50(164)
7	C_6H_{13}	C_6H_{10}	OC_2H_5	64	72·5(43)	106(75)	8·5(—)	33·5(32)
8	C_6H_{13}	C_6H_{10}	OC_8H_{17}	50·1; 60·5$_C$; 103·3$_A$(38$_B$; 59$_A$)	—(70)	114(78)	63·9(32)	—(8)
9	C_6H_{13}	C_6H_{10}	–cychex.–C_3H_7	148$_E$; 154$_A$	169·5	184·5	21·5	15·0
10	C_4H_9	C_6H_4	Br	—	—	101	—	—
11	C_4H_9	C_6H_4	CN	—	[94]([41·1])	109·8(66·1)	—	—
12	C_6H_{13}	C_6H_4	OC_8H_{17}	63·8$_C$; 82·5$_A$	87·5	94·5	23·7	7·0
13‡	C_6H_{13}	C_6H_4	OC_8H_{17}(–F)	—	—	80	—	—
14	C_6H_{13}	C_6H_4	$OC_{10}H_{21}$	71·8$_A$(—)	—(45)	94·7(58)	22·9(—)	—(13)
15	C_7H_{15}	C_6H_4	C_6H_{13}	64·8$_A$	65·6([24])	68·9(30)	4·1(—)	—(—)
16	C_7H_{15}	C_6H_4	OC_8H_{17}	70·8$_C$; 86·3$_A$	89·8	95·5	19·0	5·7
17‡	C_7H_{15}	C_6H_4	OC_8H_{17}(–F)	—	—	81·5	—	—
18	C_7H_{15}	C_6H_4	OC_9H_{19}	71·8$_C$	88·8	90·8	17·0	2·0
19	C_7H_{15}	C_6H_4	$OC_{10}H_{21}$	67·8$_A$	—	98·7	30·9	—
20	$C_6H_{13}O$	C_6H_4	OC_6H_{13}	—(—)	[102·9](64·5)	107·5(90)	—(—)	—(25·5)

21	$C_6H_{13}O$	C_6H_4	OC_8H_{17}	$102{\cdot}2_{\mathrm{A}}$(—)	107·3 (51)	108·2 (89)	6·1 (—)	0·9 (38)
22	$C_6H_{13}O$	C_6H_4	Br	—	—	108·9	—	—
23	$C_6H_{13}O$	C_6H_4	CN	[126] (—)	—(70·5)	131 (81·0)	—(—)	—(60·5)
24	$C_8H_{17}O$	C_6H_4	C_6H_{13}	—(56_{A})§	82 (57)	90·2 (66)	—(1)	8·2 (9)
25¶	$C_8H_{17}O(-F)$	C_6H_4	C_6H_{13}	$53{\cdot}9_{\mathrm{C}}$; $75{\cdot}6_{\mathrm{A}}$	79	81·8	25·1	2·8
26	$C_8H_{17}O$	C_6H_4	OC_6H_{13}	—(55_{C}; 66_{A})	107 (—)	109 (89·5)	—(34·5)	2 (—)
27	$C_8H_{17}O$	C_6H_4	OC_8H_{17}	93·5 ($62{\cdot}5_{\mathrm{C}}$; 73_{A})	101 (—)	109·3 (90·5)	7·6 (28)	8·3 (—)
28¶	$C_8H_{17}O(-F)$	C_6H_4	$OC_{10}H_{21}$	67·8	71·5	75·7	7·9	4·0
29¶	$C_8H_{17}O(-F)$	C_6H_4	-cychex.-C_3H_7	$61{\cdot}8_{\mathrm{C}}$; $121{\cdot}3_{\mathrm{A}}$	150·4	175·5	88·6	25·1
30	$C_{18}H_{37}O$	C_6H_4	OC_8H_{17}	74·9	—	105·5	30·6	
31	Br	C_6H_4	OC_6H_{13}	103	—	109	6·0	—
32	CN	C_6H_4	OC_6H_{13}	97 (—)	102 (85·5)	129 (89·5)	5·0 (—)	18·0 (4·0)
33	C_3H_7-cychex.-	C_6H_{10}	Br	139	143	200	4	57
34	C_3H_7-cychex.-	C_6H_{10}	-cychex.-C_5H_{11}	191_{A}	191·9	212	0·9	20·1
35‡	C_3H_7-cychex.-	C_6H_4	$OC_8H_{17}(-F)$	99·1	—	148·9	49·8	—
36	C_3H_7-cychex.-	C_6H_4	Br	—	166·9	195	—	28·1
37	C_5H_{11}-cychex.-	C_6H_4	OC_8H_{17}	96	121	170	25	49

† The transition temperatures for analogues with the bridging fragment –COO–[6] are given in parentheses.

‡ A 4-*n*-octyloxy-3-fluoroacetophenone derivative.

ϕ and cychex. denote phenyl and cyclohexane rings, respectively.

§ For $X = C_5H_{11}$.

¶ A 4-*n*-octyloxy-3-fluorobenzoic acid derivative.

(2) conjugation with the carbonyl group enhances the anisotropy of the molecular polarizability, to a greater extent, when there is a polarizable substituent such as an alkoxy chain, a cyano group or a phenyl ring in the *n*-position of the aromatic ring. This increases the clearing point of the phenacyl esters, as compared to common esters.

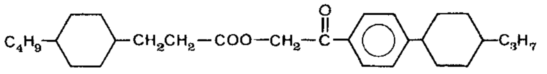
These two factors compete, depend on the structure of the molecule as well as the R and X substituents. In fact, comparing the transition temperatures for phenacyl esters of alkylcyclohexane carboxylic acids (**1–9**) (see table 1) and the corresponding Demus esters leads to the conclusion that the phenyl esters have higher melting and clearing points, showing a distinct tendency to form smectic phases and an increase of their interval, which is caused by R and X elongation. Even classic nematogens such as cyano derivatives (**3**, **6**) exhibit smectic properties.

This tendency is much more apparent for the derivatives in the aromatic series (**10–30**). It should be noted that the best mesomorphic characteristics are demonstrated by asymmetrically substituted phenacyl esters or those having various substituents in the ketone and acid fragments. In contrast, symmetrically or equally substituted (dialkyl—**15**, dialkoxy—**20**, **21**, **26**, **27**) compounds have high melting points and a narrow range or even a monotropic mesophase. As the substituents (R or X) become larger, the melting points generally decrease (compounds **26** and **27**). It is also noteworthy to follow the change in the mesophase pattern in the homologous series (**16**, **18**, **19**, **26** and **27**) and in the pairs of structural isomers showing a contribution to the molecular mesogenity of its ketone and acid fragments. For example, an obvious advantage is shown by donor substituents in the ketone fragment (**12** and **24**, **15** and **16**, **18** and **19**) and acceptor ones in the acid fragment (**22** and **31**, **23** and **32**, **13** and **25**, **29** and **35**). Introducing the fluorine atom at the ortho position to the alkoxy substituent into the ketone fragment results in the disappearance of a mesophase (**12** and **13**, **16** and **17**). In contrast, introducing the same atom into the acid fragment increases the mesomorphic range (**24**, **25** and **29**).

Table 1 shows that phenacyl esters with sufficient sizes of R and X form smectic C phases with good temperature characteristics, differing from the similar alkoxyphenylbenzoates in their higher thermal stability of the smectic C phase. The DSC technique was used to measure the crystal–smectic transition enthalpies for compounds **12**, **14**, **16**, **18**, and **19**; these are $\Delta H = 20{\cdot}84\,\mathrm{kJ\,mol^{-1}}$; $\Delta H = 23{\cdot}14\,\mathrm{kJ\,mol^{-1}}$; $\Delta H = 22{\cdot}85\,\mathrm{kJ\,mol^{-1}}$; $\Delta H = 23{\cdot}89\,\mathrm{kJ\,mol^{-1}}$; $\Delta H = 24{\cdot}44\,\mathrm{kJ\,mol^{-1}}$ for **12**, **14**, **16**, **18**, and **19**, respectively. Comparing the ΔH values of the neighbouring homologues, we can see that for a CH_2 unit, values of 0·54–1·05 and $1{\cdot}30$–$1{\cdot}67\,\mathrm{kJ\,mol^{-1}}$ correspond to alkoxy and alkyl substituents, respectively. The total mean value ΔH per CH_2 unit is $1{\cdot}46 \pm 0{\cdot}04\,\mathrm{kJ\,mol^{-1}}$ for both substituents. Hence it may be supposed that the transition from a crystalline to a smectic phase in these compounds is largely associated with the melting of the end aliphatic substituents. It should be noted that the ΔH values of melting in these compounds are comparatively small, which makes it possible to use them as components of mixtures. However, the presence of the reactive CH_2 group in the bridging fragment, the tendency to keto–enol tautomerism diminish their chemical stability, which limits the practical application of the new esters in liquid-crystalline materials.

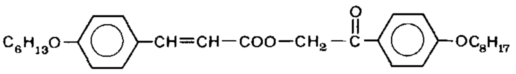
Noteworthy is the impact of the introduction of rigid $-CH{=}CH-$ and mobile $-CH_2-CH_2-$ fragments into the acid part of phenacyl esters on the mesogenity of a molecule.

For the propionic ester



(38)

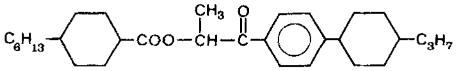
$T_{CS} = 126{\cdot}4°C$, $T_{SN} = 146{\cdot}2°C$ and $T_{NI} = 152°C$ are comparable with those of analogue **4**, whereas for the ester of cinnamic acid



(39)

$T_{CN}[132{\cdot}9]°C$ and $T_{NI} = 133{\cdot}9°C$, such that increasing the melting point results only in a monotropic nematic phase (cf. ester **21**).

Introducing the methyl cross substituent into the central moiety leads to the disappearance of mesomorphic properties:



(40)

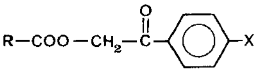
$T_{CI} = 78{\cdot}9°C$.

The examples given in table 2 show that the phenacyl esters of aliphatic acids (**41**–**48**) also possess liquid-crystalline properties. In addition we may obtain mesogens with the terminal acyloxyaceto group, which have low melting points and a wide mesophase range (esters **46**, **48**).

Our work has provided a wide range of mesogenic phenacyl esters. The best mesomorphic characteristics are shown by asymmetrically substituted phenacyl esters. The obvious advantage is shown by donor substituents in the ketone fragment and acceptors in the acid fragment. Furthermore compounds **12**, **16**, **18**, **25** and **29** (see table 1) form smectic C phases with good temperature characteristics. However, the presence of the reactive CH_2 group in the bridging fragment diminishes their chemical stability, which limits the practical application of the new phenacyl esters.

Adequate elementary analysis evidence is available for all of the resultant compounds. The transition temperatures were measured on a Mettler-FP-51 apparatus. NMR spectra were recorded on a Bruker WM-250 spectrometer. The infrared spectra of the compounds were measured with a Shimadzu IR-435 spectrophotometer with

Table 2. Transition temperatures for the phenacyl esters of aliphatic acids



Compound no.	*R*	*X*	T_{CS}/°C	T_{SN}/°C	T_{NI}/°C	ΔT_{CS}/°C	ΔT_{SN}/°C
41	C_3H_7	$-\phi-C_5H_{11}$	85	—	147	62	—
42	C_3H_7	$-\phi-C_8H_{17}$	70	—	144	74	—
43	C_3H_7	$-\phi-Br$	94·4	—	112	17·6	—
44	$CH\equiv C-$	–cychex.–C_3H_7	—	123·8	139·4	—	15·6
45	CF_3	–cychex.–C_5H_{11}	—	—	114·5	—	—
46	C_3H_7	–OOC–cychex.–C_4H_9	41_B; $110{\cdot}8_A$	—	129·5	87·5	—
47	C_3H_7	$-OOC-\phi-C_4H_9$	80·2	90·4	95·6	10·2	5·2
48	C_3H_7	$-OOC-\phi-OC_7H_{15}$	53	68·2	120	14·8	51·8

ϕ and cychex. denote phenyl and cyclohexane rings, respectively.

KBr discs. ^{1}H NMR of compound (**20**) in ($CDCl_3$), δ: 8·1 (d, 2 H, aromatic, $J = 8$ Hz), 7·95 (d, 2 H, aromatic, $J = 8$ Hz), 6·91 (d, 2 H, aromatic, $J = 8$ Hz), 6·98 (d, 2 H, aromatic, $J = 8$ Hz), 5·5 (s, 2 H, $O\text{–}CH_2\text{–}\underset{|}{C}=O$), 1·9–0·9 (m, 26 H). IR: 1725 cm^{-1} ($\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}O\text{–}$), 1695 cm^{-1} ($\text{–}\underset{\underset{\displaystyle O}{\|}}{C}\text{–}$).

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