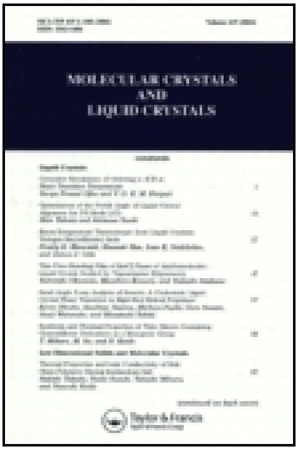

Molecular Crystals and Liquid Crystals

Ketones-Nematogens with Moderate Negative Dielectric Anisotropy and High Clearing Points

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Ketones-Nematogens with Moderate Negative Dielectric Anisotropy and High Clearing Points

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Anisotropic ketones whose rigid cores contain phenyl and cyclohexyl units were synthesized. The carbonyl group was incorporated either in the terminal substituents or in the link between the core units. The mesmorphic behaviour of these ketones is described and correlated with their chemical structure. The 1-(4-alkanoylphenyl)-4-*trans*-alkylcyclohexanes as well as the 1-(4-alkanoylphenyl)-4-*trans*-alkanoylcyclohexanes show nematic phases. In contrast to laterally substituted compounds, these ketones have clearing points which are higher than those of the corresponding hydrocarbons. Another advantage of these nematogens is the ease of synthesis.

INTRODUCTION

The twisted nematic (TN) display has been successful over the years because of its low power consumption and low driving voltage. Today, there is an increasing demand for high information-density displays which use matrix addressing. The capability of the TN-display to use this addressing technique is known to be limited. Therefore, other types of LC-displays are now receiving considerable attention as possible alternatives. One of the promising candidates is that based on electrically controlled birefringence (ECB). Unlike the TN-display, the ECB requires nematic mixtures with negative dielec-

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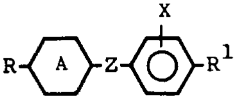
tric anisotropy ($\Delta\epsilon$ -3 to -5). Besides the dielectric properties, the components of these mixtures must fulfil other requirements such as stability (thermal, chemical and photochemical), absence of colour, low viscosity, low melting point, high clearing point, suitable elastic properties, and optical anisotropy (Δn). Nematic mixtures with negative $\Delta\epsilon$ are also required in 'guest-host' displays with positive contrast.

A number of stable nematogens (I) with small to moderate negative $\Delta\epsilon$ (0 to -2) has already been described in the literature.[1-9] They acquire their negative $\Delta\epsilon$, mainly from substituents with large dipole moments laterally attached to the rigid core of the molecule.



I

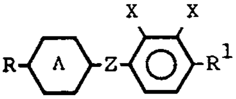
A = phenyl, *trans*-cyclohexyl

X = Halgen ($\mu \cong -1.5$D), CN ($\mu \cong -4.0$D)

Z = —, -COO-, $-CH_2CH_2-$, $-CH_2O-$

R, R^1 = alkyl, 4-alkylphenyl, 4-*trans*-alkylcyclohexyl; alkoxy, 4-alkoxyphenyl

Large negative $\Delta\epsilon$ values (about -13) were obtained in compounds (II) with two lateral substituents located *ortho* to each other.[3,5,6,10-12]



II

(for symbols see I)

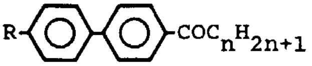
Most of these materials (I and II) however, have relatively low clearing points and high viscosities due to the lateral substituents which decrease the geometrical anisotropy of the molecules. The clearing points of these laterally substituted compounds depend on the volume of the substituent, among other factors, and can be more than 100°C lower than those of the unsubstituted parent compounds.[8] Substituents with large dipole moments also usually lead to high melting points, and this limits the concentration of these materials in a eutectic mixture. Therefore, it was found that the above described compounds can only be used as additives in dielectrically negative mixtures to enhance their $\Delta\epsilon$. The main components of the mixtures however, must be chosen from nematogens with low viscosity, low melting point, high clearing point and at least a moderate negative $\Delta\epsilon$.[12]

In the present work, an attempt is made to synthesize nematic LC's with the above-described properties by incorporating carbonyl groups ($\mu \cong -3D$) in the terminal substituents or in the linkage between the units of the rigid core. The influence of the carbonyl group on the thermodynamic stability of the mesophase of these anisotropic molecules is also discussed.

RESULTS AND DISCUSSION

A number of anisotropic ketones whose rigid cores contain phenyl and/or cyclohexyl moieties were synthesized. The carbonyl group was incorporated either in the terminal substituents or in the linkage between the cyclic units of the rigid core. The mesomorphic properties of these ketones are given in Tables I, III, IV and VI. They are also compared to those of the corresponding hydrocarbons in Tables II and V.

Aromatic ketones with a rigid biphenyl core (III) were early found to show only smectic phases,[13–15] and their dielectric properties were not investigated.



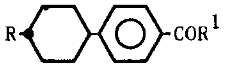
III

R = alkyl, alkoxy, alkanoyl

Recently, it has been shown that the stereochemistry of the rigid core of an anisotropic molecule plays an important role in determining the type of mesophase formed.[16] Geometrically uniform rigid cores, i.e.,

TABLE I

Mesomorphic properties of the 1-(4-alkanoylphenyl)-4-*trans*-alkylcyclohexanes



	R	*R*¹	*C*		*S*		*N*		*I*	
1)	C_3H_7	CH_3	·	53.9	—		—		·	No mesophase down to 30°C
2)		C_2H_5	·	49.2	—		·	56.5	·	No smectic phase down to 25°C
3)		C_3H_7	·	60.9	—		—		·	No mesophase down to 40°C
4)		C_4H_9	·	57.5	—		—		·	
5)	C_5H_{11}	CH_3	·	66.7	—		—		·	No mesophase down to 40°C
6)		C_2H_5	·	56.6	—		·	68.8	·	No smectic phase down to 40°C
7)		C_3H_7	·	54.2	—		(·	42.9)	·	
8)		C_4H_9	·	40	·	52.3	·	57.9	·	
9)	C_7H_{15}	CH_3	·	64.7	—		·	42.2	·	
10)		C_2H_5	·	52.2	—		·	73.0	·	No smectic phase down to 25°C
11)		C_3H_7	·	50.8	—		(·	50.6)	·	No smectic phase down to 35°C
12)		C_4H_9	·	56.3	(·	50.9)	·	63.5	·	

C = crystalline, *S* = smectic, *N* = nematic, *I* = isotropic. Values given in brackets represent a monotropic phase and a dot shows the existence of a phase transition while a dash indicates that the corresponding phase is missing. All values are given in °C.

those composed of similar units (either flat or staggered in nature), tend to stack in a layered structure, thus leading to smectic phases. Molecules whose rigid cores consist of geometrically different units, i.e., flat *and* staggered units, find it more difficult to pack in a layered structure and therefore tend more to give nematic phases. Therefore, we replaced one of the flat phenyl groups of the 4-alkanoyl-4′-alkylbiphenyls by a staggered cyclohexyl moiety. As expected, the resulting 1-(4-alkanoylphenyl)-4-*trans*-alkylcyclohexanes are nematic, unlike the biphenyl derivatives (Table I).

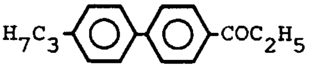
The clearing points of the alkanoylphenylcyclohexanes 1–12 are generally lower than those of the corresponding biphenyl derivatives (compare 2/13 and 8/14). However, the smectic phase is replaced by a nematic phase in most of the alkanoylphenylcyclohexanes. No smectic phase could be detected even on supercooling the melts of the lower members of the series. In the higher homologues (ten or more carbon atoms in the alkyl chains), the smectic phase is strongly suppressed and a nematic phase is observed above the smectic phase. In contrast to the laterally substituted compounds I and II, the 1-(4-alkanoylphenyl)-4-*trans*-alkylcyclohexanes have much higher clearing points than the unsubstituted dialkylphenylcyclohexanes as can be seen from Table II. Their melting points are also higher than

TABLE II

Comparison of the mesomorphic properties of the alkyl and alkanoyl derivatives of phenylcyclohexane

	R	R¹	C		S		N		I
15)	C_5H_{11}	C_3H_7	·	−12.7	—		·	−11.2	·[16]
6)		COC_2H_5	·	56.6	—		·	68.8	·
16)		C_5H_{11}	·	−0.8	(·	−8)	(·	−5.0)	·[16]
8)		COC_4H_9	·	40	·	52.3	·	57.9	·
17)	C_7H_{15}	C_3H_7	·	−0.5	·	6.4	·	8.0	·[16]
10)		COC_2H_5	·	52.2	—		·	73.0	·

those of the corresponding hydrocarbons, but the absolute values are still relatively low.



13

C 42 S 130 I

14

C 90 S 106.2 S 110.5 I

The high clearing points are probably due to conjugation between the carbonyl and phenyl groups which increases the polarizability of the molecule and to hydrogen bonding between the carbonyl group and the hydrogen atom in the *ortho*-position. The hydrogen bond keeps the carbonyl group in plane and increases the rigidity of the molecule. A comparison of the thermal data for compound 18, where the alkanoyl group is attached to the cyclohexyl unit, with those for compound 6, where the alkanoyl group is attached to the phenyl moiety, clearly illustrates this effect.

18

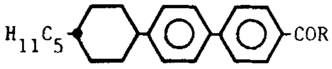
C 29.1 I

6

C 56.6 N 68.8 I

TABLE III

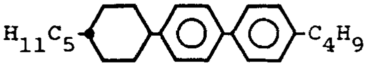
Mesomorphic properties of
4-(4-*trans*-pentyl)-1-(4′-alkanoylbiphenyl)cyclohexanes



	R	C		S		S		N		I
19)	C_2H_5	·	96	·	159	·	207	·	235	·
20)	C_3H_7	·	124	·	170	·	192	·	202	·
21)	C_4H_9	·	132	·	175	·	208	·	209	·

As will be seen later for the 4-alkyl-4′-alkanoylbicyclohexanes, the alkanoylcyclohexanes generally have almost the same clearing points as the corresponding alkyl derivatives. Therefore, compound 18 is expected to have a clearing point of about −11°C (as for 4-*trans*-pentyl-4′-propylphenyl-cyclohexane[16]) which is below its freezing temperature.

Similar results to those obtained for the alkanoylphenylcyclohexanes were observed for the cyclohexylbiphenyl series. As can be seen from Table III, the clearing point of compound 20 is much higher than that of the corresponding dialkyl derivative 22.



22

C 18 S 159 N 171 I[17]

Replacing both phenyl units of the 4-alkanoyl-4′-alkylbiphenyls by cyclohexyl moieties leads to the 4-*trans*-alkanoyl-4′-*trans*-alkylbicyclohexanes, whose mesomorphic properties are given in Table IV. The geometrically uniform bicyclohexyl core favours smectic properties. Remarkably enough, only the propionyl derivatives show nematic phases above the smectic phases.

The clearing points of the alkanoylbicyclohexanes 23–34 are much higher than those of the corresponding phenylcyclohexanes (Table I), due to the uniformity of the rigid core and the possible denser packing.[13] However, they are more or less the same as those of the

TABLE IV

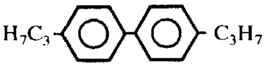
Mesomorphic properties of the 4-*trans*-alkanoyl-4′-*trans*-alkylbicyclohexanes

	R	*R*¹	*C*		*S*		*N*		*I*
23)	C_3H_7	CH_3	·	37	·	54.5	—		·
24)		C_2H_5	·	63.2	(·	46.5)	·	82.9	·
25)		C_3H_7	·	36	·	88.1	—		·
26)		C_4H_9	·	55	·	96.2	—		·
27)	C_5H_{11}	CH_3	·	40	·	67.3	—		·
28)		C_2H_5	·	55	·	70.8	·	93.7	·
29)		C_3H_7	·	52	·	97.3	—		·
30)		C_4H_9	·	51	·	106.6	—		·
31)	C_7H_{15}	CH_3	·	62	·	66.9	—		·
32)		C_2H_5	·	65	·	78.8	·	94.2	·
33)		C_3H_7	·	54	·	97.5	—		·
34)		C_4H_9	·	59	·	106.6	—		·

dialkylbicyclohexanes (Table V). This indicates that a carbonyl group adjacent to a cyclohexyl moiety either does not contribute much to the stability of the mesophase, or its contribution is compensated by steric effects. This is in contrast to the effect of carbonyl groups conjugated to aromatic moieties, as can be seen from a comparison of compounds 13/35 and 14/36 (Table V). The same effect was ob-

TABLE V

Comparison of the mesomorphic properties of the alkyl and alkanoyl derivatives of biphenyl and bicyclohexane

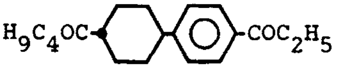
			C		*S*		*S*		*N*		*I*
35)			·	61.2	—		—		—		·
13)		$-COC_2H_5$	·	42	—		·	130	—		·
36)	$H_{11}C_5-$	$-C_5H_{11}$	·	26	·	47.6	·	52.2	—		·[16]
14)		$-COC_4H_9$	·	90	·	106.2	·	110.5	—		·
37)			·	64.2	—		·	81.8	—		·[16]
24)		$-COC_2H_5$	·	63.2	—		(·	46.5)	·	82.9	·
38	$H_{11}C_5-$	$-C_5H_{11}$	·	40	—		·	110.4	—		·
30)		$-COC_4H_9$	·	51	—		·	106.6	—		·

served in the alkanoylphenylcyclohexanes (Table II) as has already been discussed.

Another possibility for incorporation of a carbonyl group in an anisotropic molecule in order to acquire a negative $\Delta\epsilon$ is to use it as a link between the units of the rigid core. This is the case in many esters which have been extensively reported in the literature. However, the dipole moment of the carbonyl group is partially compensated in the esters by the involvement of the other oxygen atom ($\mu_{CO} = -3.0D$, $\mu_{COO} = -1.8D$). To avoid this, we synthesized some ketones in which the units of the rigid core are linked by a $-COCH_2-$ group. Their mesomorphic behaviour is compared to that of the corresponding esters in Table VI.

From the data in Table VI, it is clear that such ketones have lower clearing points than the corresponding esters irrespective of whether the carbonyl group is adjacent to a phenyl or a cyclohexyl moiety. The few representatives of these ketones which we synthesized show only smectic phases. A correlation between their properties and structures is not possible at the moment, and a more detailed investigation is necessary.

Since the dipole moment of the carbonyl group in monoketones lies at an angle smaller than 90° to the long molecular axis, it contributes to $\epsilon_{\parallel}$ as well as to $\epsilon_{\perp}$. In order to overcome this problem, two carbonyl groups were incorporated in the molecule at both ends of the rigid core. The parallel components of the dipole moments are opposite to each other and therefore, cancel. The net dipole moment across the long molecular axis in these diketones is not expected to be doubled, due to possible rotation of the carbonyl groups. However, following the Williams equation, their dipole moment should be larger than that of the simple ketones.[21] The mesomorphic behaviour of two representative members of this class is given below.



50

C 100.1 N (62.0) I

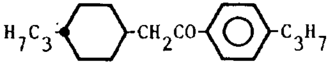
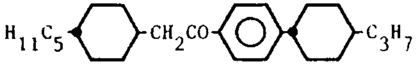
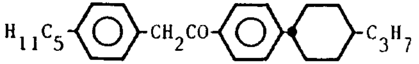
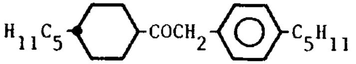
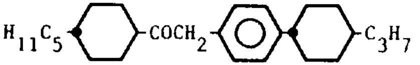
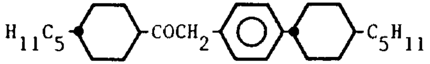
51

C 66.5 N (64.0) I

The clearing points of the diketones are slightly lower than those of the simple ketones (50/6 and 51/10), but they are still higher than those of the corresponding hydrocarbons. $\Delta\epsilon$ of compound 50 was

TABLE VI

Comparison of the mesomorphic behaviour of ketones and esters

		C	*S*	*S*	*N*	*I*	
39)		· 52.2	—	—	—	·	No mesophase down to 25°C
40)	-OOC-	· 10.2	—	—	(· 9.3)	·	
41)		· 95	—	· 127.0	—	·	
42)	-OOC-	· 68	—	· 74	· 153	·[1]	
43)		· 116.7	—	(· 99.3)	—	·	
44)	-OOC-	· 83	—	(· 79)	· 175	·[1]	
45)		· 55.7	—	—	—	·	No mesophase down to 40°C
46)	-COO-	· · 36	—	(· 29)	· 48	·[18]	
47)		· 60	—	· 104.8	—	·	
48)	-COO-	· 41	· 75	· 127.0	· 191.8	·[19]	
49)		· 55	—	· 113.6	—	·	

found to be −3.1 at 20°C.[20] The dialkanoyl phenylcyclohexanes therefore, represent a new class of stable nematogens with moderate negative $\Delta\epsilon$ and relatively high clearing points.

Another advantage of the nematic 1-(4-alkanoylphenyl)-4-*trans*-alkylcyclohexanes and 1-(4-alkanoylphenyl)-4-*trans*-alkanoylcyclohexanes is the ease of synthesis. The first can be prepared either by action of an alkyl Grignard reagent on the commercially available benzonitriles (PCH's), or by acylation of the 4-phenyl-1-*trans*-alkylcyclohexanes[22-24] which are intermediates in the synthesis of the PCH's. The latter were prepared by acylation of the 4-phenyl-1-*trans*-alkanoylcyclohexanes[22-24] which are also precursors of the PCH's.

EXPERIMENTAL

The mesomorphic properties were investigated by differential thermal analysis and polarizing microscopy using a PE-DSC 2 and a Leitz Orthoplan equipped with a Mettler FP 5/52 heating stage. The heating-stage was cooled by means of a cold nitrogen gas stream. The transition temperatures were measured under the microscope at 0.2°C/min heating rate, while the differential thermal analysis runs were carried out at a rate of 5°C/min. Crystal-smectic and smectic-smectic transitions which were optically difficult to observe were detected by DSC. Only the melting points of the stable crystalline phases are given. The purity of all investigated products was 99.7% or better as determined by g.l.c.

Compounds 1–14, 19–21, 23–34

A solution of the desired alkyl bromide (0.4M) in dry ether was added dropwise to a stirred suspension of Mg (0.4M) in dry ether, and the reaction mixture was stirred for 30 min at room temperature. To the Grignard reagent, a solution of the corresponding nitrile (0.1M) in dry ether or THF was added. The nitriles are commercially available from E. Merck and were used without further purification. The reaction mixture was heated under reflux for 5*h*, then worked up to give a quantitative yield of the desired ketone which was crystallized from ethanol.

4-trans-propylcyclohexylmethyl-4-propylphenyl ketone 39

This ketone was prepared by the above-described method using 4-bromopropylbenzene and 4-*trans*-propylcyclohexylacetonitrile as starting materials. The nitrile was obtained from the corresponding bromide[22] by reaction with an excess of solid KCN in DMSO at 100°C for 2h. The ketone was purified by chromatography over silica gel using toluene as eluent, followed by crystallization from ethanol.

Compounds 41 and 43

These were products of the reaction between the Grignard reagents obtained from 4-*trans*-pentylcyclohexylmethyl bromide[25] or 4-pentylbenzyl chloride and 1-(4-cyanophenyl)-4-propylcyclohexane (E. Merck). The crude products were crystallized from ethanol.

Compounds 45, 47 and 49

These ketones were prepared from 4-*trans*-pentylcyclohexylnitrile and the corresponding benzyl chloride. The crude products were purified by chromatography on silica gel using a mixture of hexane ethyl acetate (9 : 1) as eluent, followed by crystallization from ethanol.

4-*trans*-pentylcyclohexylacetonitrile. A solution of 0.1M 4-*trans*-pentylcyclohexane-1-carboxylic acid chloride[18,25] in dioxan was added dropwise to a cooled solution of NH_4OH. The precipitated amide was filtered off, washed with water and dried. A mixture of the amide and an excess of $SOCl_2$ was heated under reflux for 1*h*, then cooled and poured onto ice. The nitrile was extracted into ether, washed until neutral and dried. The crude product was distilled under reduced pressure (130°C/20 bar) to give a colourless liquid (yield = 80%).

Benzyl chlorides. The corresponding carboxylic acids were reduced with $LiAlH_4$ to give the benzyl alcohols, which were interacted with $SOCl_2$ in pyridine at room temperature. The reaction mixture was poured onto ice and the product extracted into ether.

Compounds 50 and 51

A solution of 0.1M 4-phenyl-1-*trans*-alkanoylcyclohexane[22-24] in 100 ml CH_2Cl_2 was added to a cooled suspension of 0.4M $AlCl_3$ in 200 ml CH_2Cl_2 with stirring. To the so-formed complex, a solution of 0.11M of the desired acid chloride was added dropwise at 5–10°C. The reaction mixture was stirred for further 30 min at this temperature, then for 1 h at room temperature. After completion of the reaction which was indicated by the cessation of HCl evolution, the mixture was worked up and the crude product isolated. The product was contaminated with ~4% of the *ortho*-isomer and was purified by filtration through a short silica gel column using ethyl acetate-hexane (1 : 3) as solvent, followed by crystallization from ethanol.

Compounds 18 and 35

The products were prepared by catalytic hydrogenation of the corresponding propionyl derivative in ethanol, using Pd/C as catalyst.

4, 4′-trans, trans-dipentylbicyclohexane 38

This hydrocarbon was obtained by the reduction (Wolf–Kishner) of compound 30 with hydrazine in ethylene glycol.

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