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Synthesis and physical properties of liquid crystals having a chlorine atom in the lateral position of a benzene ring

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Developing syntheses of new liquid crystals

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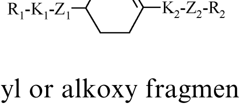
A Commentary on the paper "Synthesis and physical properties of liquid crystals having a chlorine atom in the lateral position of a benzene ring", by V. Bezborodov, R. Dąbrowski, J. Dziaduszek, K. Czupryń Ski and Z. Raszewski. First published in *Liquid Crystals*, **20**, 1–8 (1996).

The results published in the 1996 *Liquid Crystals'* paper 'Synthesis and physical properties of liquid crystals having a chlorine atom in the lateral position of a benzene ring', described a new method of synthesis of simple and sophisticated mesogenic structures in an easy way, which were not possible or difficult to prepare in other ways. Many of such structures have importance for applications of liquid crystals.

In our teams the method is still being successfully developed and we hope that it will be successfully used in the future as a very effective method not only for the synthesis of liquid crystal but also many other chemical compounds. We now give some examples of its usefulness.

We demonstrated that 3,6-disubstituted cyclohex-2-enones are promising intermediates for the preparation of mesogenic compounds. They can be transformed in high yield into laterally substituted chlorobiphenyls, or terphenyls, which are useful components of liquid-crystalline mixtures for display applications. In continuation of these investigations we have synthesized new liquid-crystalline 3,6-disubstituted cyclohex-2-enones by different methods [1] and estimate the possibility of their transformation into various lateral substituted liquid crystals with optimized properties.

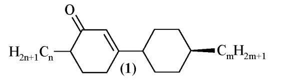
In this Commentary, we summarize and show how new mesogenic laterally substituted derivatives of biphenyl, or terphenyl, or quaterphenyl can be prepared by transformations of the corresponding 3,6-disubstituted cyclohex-2-enones (**I**).



(**I**)

where $R_{1,2}$=alkyl or alkoxy fragments, F, Cl, CN, CF_3, OCF_3 or chiral fragment. $K_{1,2}$=benzene, cyclohexane, or cyclohexene rings; $Z_{1,2}$=single bond or CH=CH, C≡C, CH_2CH_2,bridge fragments

Detailed investigations of the reaction conditions for the preparation of substituted cyclohex-2-enones have shown that the mesogenic 3,6-disubstituted cyclohex-2-enones (**I**) with different combinations of cyclic, bridge, terminal fragments and lateral substituents can be prepared in a 60–80% yield. This is achieved in a short way by the condensation of the corresponding Mannich salts or 2-chloro(bromo)ethylaryl(alkyl)ketones with 2-substituted acetoacetic esters, 4-substituted methylbenzylketones, or analogous ketones and β-dicarbonylic compounds in the presence of potassium carbonate, potassium hydroxide and phase catalysts in boiling diglyme or dioxane [2, 3] or vinyl ketones prepared from esters treated with ethyl magnesium bromide in the presence of isopropyltitanate[1]. For example, with the 3,6-disubstituted cyclohex-2-enones the following



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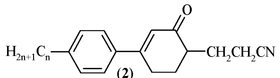

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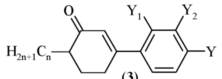

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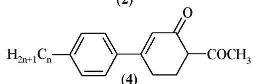

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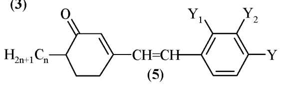

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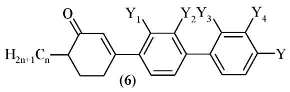

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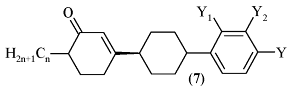

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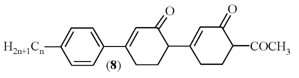

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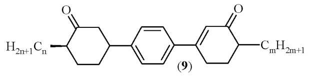

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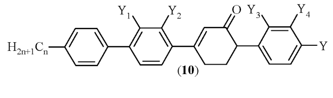

(10)

n, m=1–10; $Y_{1,2,3,4}$=H, F, Cl, CN, CH_3; Y=alkyl or alkoxy fragments, F, Cl, CN, NCS, CF_3, OCF_3, $OCHF_2$ or OCF_2Cl

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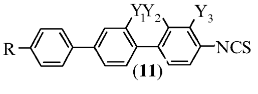
structures (**1**–**10**) can be prepared using these starting materials and the reaction conditions.

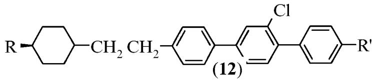
It was found [4, 6] that such compounds are really promising intermediates for the preparation of various mesomorphic chiral and non-chiral derivatives of cyclohexene, cyclohexane, bicyclohexane, phenylcyclohexane or biphenyl, which are, in turn, useful components for liquid-crystalline mixtures. Both nematic and smectic liquid-crystalline compounds can be easily prepared by transformations (see Scheme 1) of the cyclohexenone fragment and functional groups can be located in the lateral position. It should be noted that different reaction possibilities for the functional groups and cyclohexenone fragment allow the transformations to be achieved selectively and provide the opportunity of preparing liquid-crystalline compounds with novel combinations of structural fragments of mesogenic molecules

From many 3,6-disubstituted cyclohex-2-enones (**I**) and their derivatives, which have been synthesized, we are able to describe in detail the following:

a) Low viscosity high birefringence liquid-crystalline compounds and mixtures with high positive dielectric anisotropy [6, 7]



(11)



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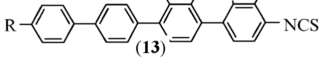
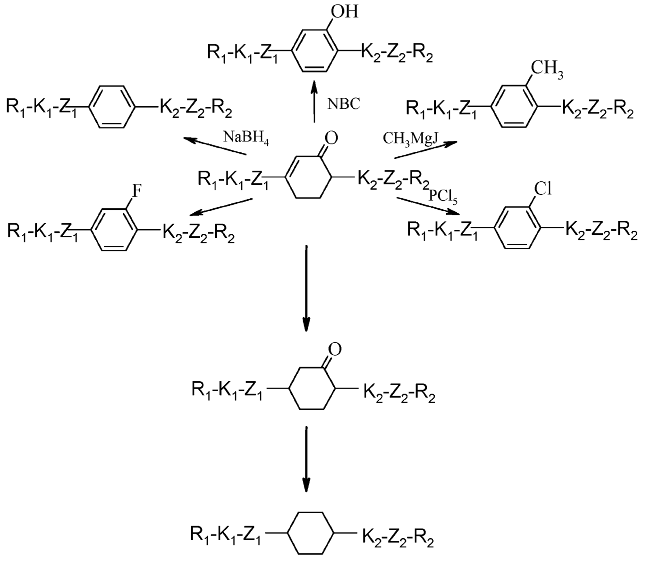


(13)

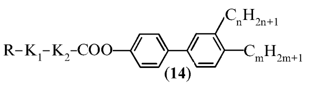
$Y_{1,2,3,4}$=H, F, Cl, CH_3; R, R′=alkyl or alkoxy fragments

These compounds are useful in liquid-crystalline mixtures because they have low melting points and wide smectic or nematic ranges, excellent solubility in mesogenic media and an optical anisotropy which increases from the biphenyl derivatives ($\Delta\tilde{n}\sim 0.25$) to the derivatives of quaterphenyl (**13**) ($\Delta\tilde{n}\sim 0.45$).

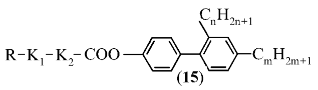


Scheme 1

b) The lateral alkyl substituted biphenyls (**14**–**55**) [8].



(14)

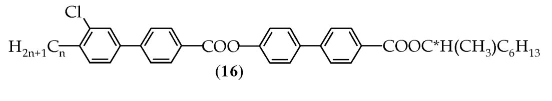


(15)

R=alkyl chain; K_1,K_2=benzene, cyclohexane or 1,3,2-dioxaborinane fragments, n=1 or 2; m=3–6.

It has been found that these compounds can be successfully used for the preparation of high multiplexing mixtures with low threshold and saturation voltages for the twist-effect, step voltage-contrast characteristics and fast response times

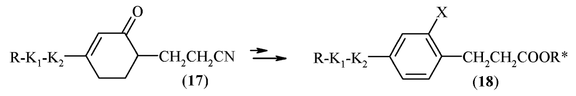
c) Optically active aryl esters of chloro biphenylcarboxylic acids (**16**), forming ferroelectric smectic C phase with a wide temperature range and having a switching angle of 88° [9].



(16)

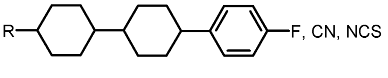
n=8−10

d) 3-(2-cyanoethyl)-6-substituted cyclohex-2-enones (**17**) [10] and other substituted cyclohex-2-enones containing additional functional groups. Different reaction possibilities for the functional groups and the cyclohexenone fragment give the opportunity of preparing nematogenic and smectogenic C compounds (**18**) with novel combinations of structural fragments of the mesogenic molecules.



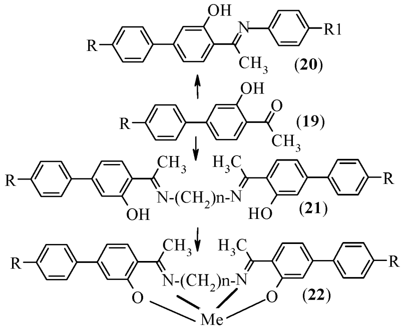
R=alkyl chain, R*=chiral alkyl fragment; K_1,K_2=benzene or cyclohexane fragments; X=H, F, Cl, CH_3.

e) The method eliminates the necessity to use high pressures to synthesize bicyclohexane structures. We have prepared many different commercially important bicyclohexane structures, such as



by this method [1].

f) 4-substituted 2-hydroxyacetophenones (**19**), which can be used for the preparation of liquid-crystalline azomethines and then different liquid-crystalline metal complexes and dyes (**22**) [11].



R, R_1=C_nH_{2n+1} or $C_nH_{2n+1}O$; n=2–6; Me=Cu, Ni

g) Since the derivatives of biphenyl and terphenyl have rigid rod-like molecules we have suggested that in the smectic C* phases of such compounds the thickness of the smectic layers and the tilt angle should be weakly temperature dependent. Taking this into account we have designed new FLC materials based upon biphenyl and terphenyl derivatives [12–14] and we have found the main criteria for the preparation of FLCDs with uniform and stable alignment of FLC materials. The FLC materials developed and the cells possess a wide temperature range for the SmC* phase, as well as, bistability, a gray scale capability, a low operational voltage, a high optical contrast ratio (1:700) and very good thermal and mechanical stability. In fact, they are really promising for the preparation of shock-free FLCDs. Our investigations have shown that mechanical shock (in our experiments the thickness of the cells was decreased from 3.5 µm to 1.5 µm under pressure) does not cause irreversible destruction of the alignment in the cells. We did not find any changes in alignment conditions after dozens of very serious tests. All of the cells have the same alignment quality and are defect-free.

The results presented demonstrate that the molecular core and the lateral substitution of the fragments incorporated into the molecular core of nematic and ferroelectric liquid crystals can provide desirable variations in their mesomorphic, dielectric and optical properties, in the values of spontaneous polarization and the tilt angle for improved satisfaction of the requirements for using them as the components of materials for liquid-crystalline display applications.

We plan to synthesize other structurally similar liquid-crystalline compounds to assess their ability to form the nematic or Sm C* phases at low temperatures and over wide temperature ranges. We hope that the new results of our investigations may lead to a better understanding of the nature of ferroelectric liquid crystals and will facilitate their use for display applications and in particular that the methods will be very useful for many other researchers.

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Synthesis and physical properties of liquid crystals having a chlorine atom in the lateral position of a benzene ring[†]

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Novel liquid crystalline 3,6-disubstituted cyclohex-2-en-1-ones and 1,4-disubstituted 2-chlorobenzenes are presented. The method of transformation of cyclohex-2-en-1-ones into chloroarenes in a one-pot procedure, together with the nature of the mesomorphic phases and some physical properties of single compounds and nematic mixtures comprising them are reported.

1. Introduction

The introduction of a polar group in a lateral position is a method for decreasing melting points and depressing smectic phases in mesogens [1 4]. This action also increases the perpendicular component of the dielectric anisotropy $\varepsilon_\perp$ and changes the $\Delta\varepsilon/\varepsilon_\perp$ ratio, which influences the steepness of electro-optical curves in TN and STN displays [1, 5]. It also has an important significance for materials used for two frequency addressed displays and for ferroelectric displays [6, 7]. For these reasons laterally substituted compounds, especially those, which contain a fluorine atom have been extensively studied in recent years; for example see [8 16]. Usually the synthetic routes involved are multi-stage and need low temperatures and inert atmosphere, lithiation procedures, palladium-catalysed coupling of aryl boronic acids [17 20], or Grignard coupling [3].

Recently we have described a new approach for preparing liquid crystal materials with a laterally substituted benzene, cyclohexane or cyclohexene ring using easily prepared 3,6-disubstituted cyclohex-2-en-1-ones [21].

As Brettle *et al.* [22, 23] showed, it is also possible to separate these compounds into individual enantiomers having a strong twisting power, which when added to non-chiral smectic C materials convert them into S_C^* systems.

In this paper we report a simple one-stage method for preparing some 1,4-disubstituted 2-chlorobenzenes with a more sophisticated chemical structure than those previously mentioned in [24], by direct transformation of cyclohex-2-en-1-ones.

2. Synthesis

Mannich salts (compounds **4**) are easily formed and separated as crystalline solids when appropriate acetophenones **2** are treated with paraformaldehyde and dimethylamine hydrochloride. Using the Mannich salts **4** (hydrochlorides of 4-alkylphenyl-β-dimethyl-aminoethyl ketones) and 2-alkyl or 2-alkyl-cyclohexylethyl acetoacetic esters **3** or arylacetones **3a** under the conditions of a condensation reaction similar to that described by Novello *et al.* [25], we obtained 3,6-disubstituted cyclohex-2-en-1-ones **5** and **6** in yields between 60 and 70 per cent.

Compounds **5** or **6** are formed from **3** or **3a** and **4** in a multistage reaction, which proceeds as a one-pot process. First the compounds **4** generate *in situ* vinyl ketones which react with the acetoacetic esters **3** or arylacetones **3a** yielding cyclic products carrying the carboethoxy group [25]. Then this group is lost after acidification and the final compounds **5** or **6** form in the reaction mixtures. Another possibility for the synthesis of similar compounds was lately tested by Brettle *et al.* [23], who used chloropropiophenones to generate vinyl ketones.

Compounds **5** and **6** were then heated with PCl_5, in CCl_4 or benzene when the carbonyl group undergoes chlorination, followed by aromatization. This is also a multistage reaction which is carried as a one-pot procedure.

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*Corresponding author.

[†] Presented at the European Conference on Liquid Crystals, Bovec, Slovenia, March 1995.

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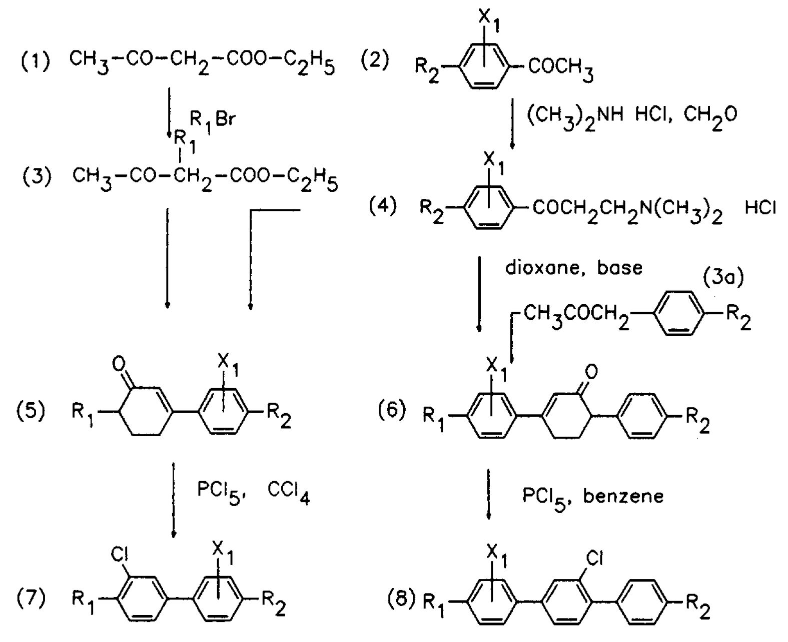


Scheme. The route for the preparation of chloro substituted benzenes; *X* is a hydrogen or a fluorine atom.

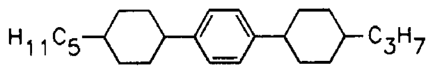
3. Mesomorphic properties

The phase transition temperatures for the 3,6-disubstituted cyclohex-2-en-1-ones **5** and **6** are given in table 1 and for the 1,4-disubstituted 2-chlorobenzenes **7** and **8** in table 2. They were measured using a Linkam heating stage, in conjunction with a PZO polarizing microscope, and confirmed using a Setaram DSC 92. Liquid crystalline phases were identified by the textures observed. The cyclohex-2-en-1-ones, except for compounds **5a** and **5b** show enantiotropic phases. The three ring compounds **5a**, **b** and **c** exhibit only nematic phases this results from the presence of a fluorine atom in the lateral position. Compounds **5d** and **5e** have the nematic and the smectic A phase.

The four ring compounds **6a**, **b** and **c** with distinctly asymmetric molecules (the benzene and cyclohexane rings present in the rigid core of the molecules alternate and the end group is short, such as F or OCH_3) show smectic A and nematic phases. The other four ring compounds show smectic A and B phases.

The compounds having fluorine in the terminal position have higher melting points than the others, see compounds **5a**, **b**, **6a** and **c**, even if they possess a second fluorine in a lateral position (**5a**, **b**, **c**). This results from the presence of two strongly polar bonds, C=O and C F, which are responsible for high intermolecular dipole dipole interactions. This was also observed by others [18], for classes of compounds containing a fluorine atom in the presence of other polar groups.

Comparing the cyclohex-2-en-1-ones with the hydrocarbons of similar structure, for example the compounds **5e** and **11** or **5h** and **10** (table 2)



11

Cr 30·6 S_B 143 S_x 151·8 N 159·2 I

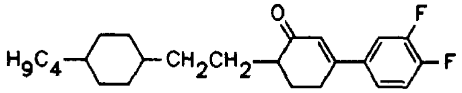
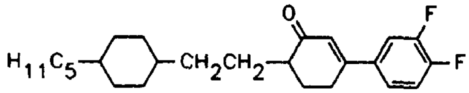
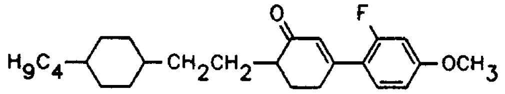
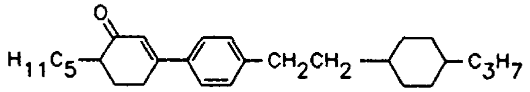
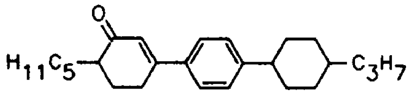
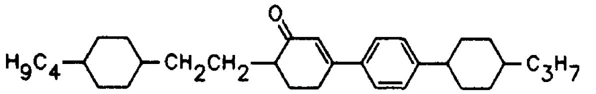
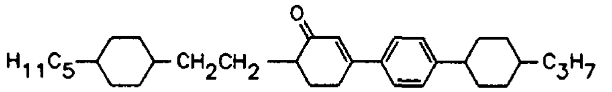
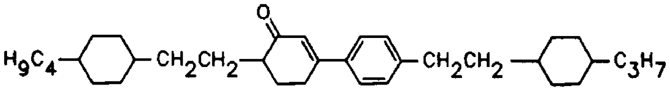
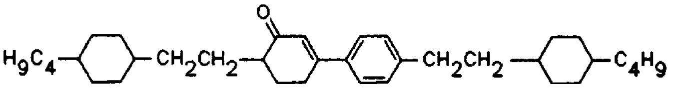
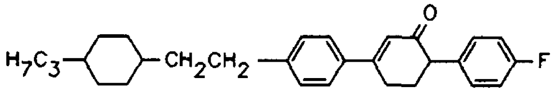
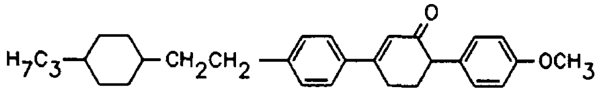
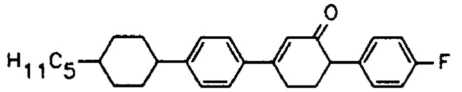
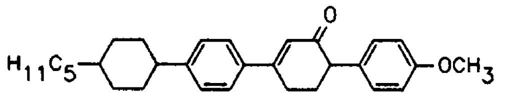
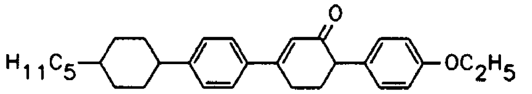
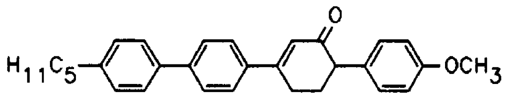
we can conclude that clearing points for the cyclohex-2-en-1-ones are a little lower those of the hydrocarbons. The thermodynamic stability of the smectic phases in both groups of compounds are similar, but in the case of the cyclohex-2-en-l-ones, they are less ordered at lower temperatures; only the smectic A and smectic B phase are observed above room temperature.

The exchange of the carbonyl group for a chlorine atom, coupled with aromatization of the cyclohexenone ring, influences the mesomorphic properties distinctly, but in a rather different way in the case of the three ring compounds, compared with the four ring compounds.

For all compounds the phase transitions are changed meaningfully, but the smectic phases to the biggest degree; they are eliminated for **7g**, **h**, **8b**, **c**, **d** and **e**.

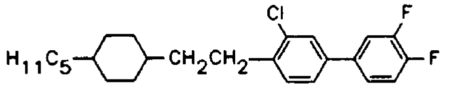
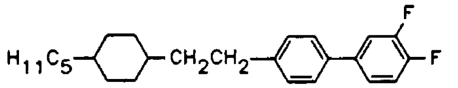
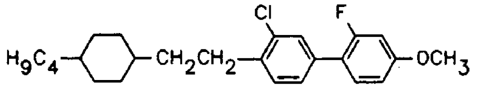
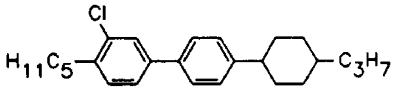
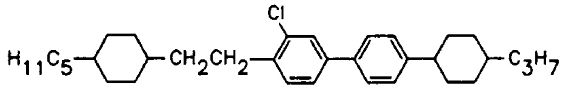
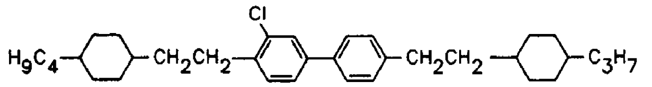
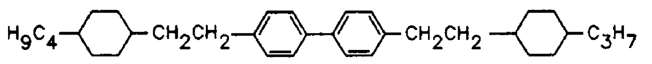
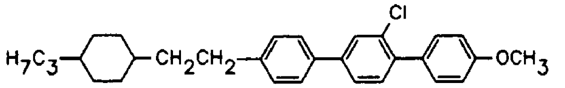
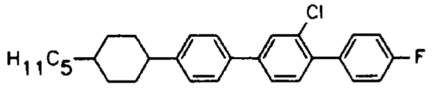
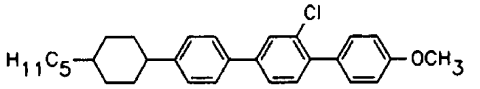
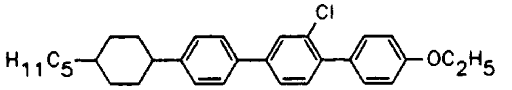
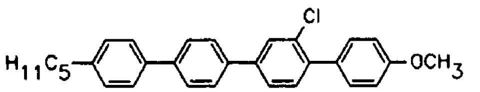
The clearing points decrease by 30 to 60 degrees for the three ring compounds and also for the four ring compounds when their rigid cores have no more than three rings. For all the rest of the four ring compounds, the clearing points are higher by 10 to 60 degrees. The cyclohex-2-en-1-one ring in the rigid core of four ring molecules is therefore less convenient than the

Table 1. Mesomorphic properties of compounds 5 and 6. Phase transition temperatures (°C) and phase transition enthalpies (cal mol^{-1}) in italics.

No.	Structures	Cr	S_B	S_A	N	I
5a		* 91.5			* (89)	*
5b		* 96.5			* (84)	*
5c		* 76			* 126	*
5d		* 71 *5480*		* 131 *850*	* 139 *700*	*
5e		* 77 *6490*		* 149 *710*	* 157 *360*	*
5f		*	* 174	* 243	* 252	*
5g		* <20	* 175 *870*	* 248 *1900*		*
5h		* <20	* 161 *2850*	* 222 *275*		*
5i		* 71 *3930*	* 187 *1410*	* 226 *2870*		*
6a		* 125.5^{a} *4810*		* 140	* 175 *650*	*
6b		* 122 *4200*		* 135	* 193	*
6c		* 148		* 157.5	* 200	*
6d		* 116 *2260*	* 134 *76*	* 173 *210*	* 224	*
6e		* 127^{b} *1850*		* 222 *1600*		*
6f		* 137		* 238		*

[a] Cr_1 46.9 Cr.
740
[b] Cr_2 62.5 Cr_1 91 Cr.
560 *380*

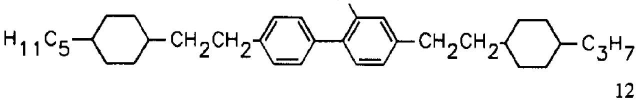
Table 2. Mesomorphic properties of compounds **7** and **8**. Phase transition temperatures (°C) and phase transition enthalpies (cal mol^{-1}) in italics.

No.	Structures	Cr	S_A	N	I
7b		* 14.7 *5310*		* 47 *170*	*
9		* 74.8		* 95.9^a	*
7c		* 45.2 *7930*		* 97 *250*	*
7e		* 29 *6650*	* 72.2 *200*	* 92 *140*	*
7g		* 78.5 *6120*		* 220 *490*	*
7h		* 63.3^b *2750*		* 191	*
10		184.4^c *1400*	* 208.2 *260*	* 229 *1170*	*
8b		* 92.6 *6290*		* 232	*
8c		* 105 *3380*		* 210	*
8d		* 90.3 *7610*		* 273	*
8e		* 102 *6600*		* 275	*
8f		* 115.0 *5130*	* 141	* 298	*

^{a}Ref. [11]. ^{b}Cr$_1$ 53.1 Cr. ^{c}Cr<20 S_{X2} 102.5 S_{X1} 151 8 S_B.
930 *770*

2-chlorobenzene ring for building a liquid crystal structure with minimal repulsive forces.

These results show that it is possible to obtain four ring mesogens containing a chlorine atom in a lateral position of the molecule with low melting points and very large ranges of the nematic phase, see compounds **7g**, **h**, **8b**, **d** and **e**. Being in the lateral position, the chlorine also depresses the smectic phases more effectively than a fluorine, compare compound **7h** with compound **12**. A similar conclusion has resulted from other work [1].



12

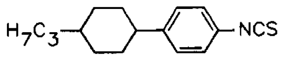
Cr 76·4 S_B 103·5 S_A 123·3 N 207·1 I [26]

In the three ring systems, the chlorine atom depresses clearing points very strongly. In the four ring compounds the smectic phases are depressed more efficiently and the clearing points are decreased in a moderate way. The large volume of the chlorine atom increases the breadth of molecules, but its influence on the length/breadth ratio (*l*/*d*), which is critical for the mesomorphic properties, is less pronounced in the case of four ring molecules than three ring molecules.

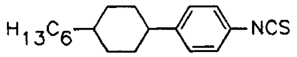
4. Physical properties of compounds and mixtures

Compound **7b** is a liquid at room temperature and **7c**, after melting, crystallizes only with difficulty; therefore it was possible to measure the optical indices and dispersion relations, dielectric constants and viscosities for single compounds; see below.

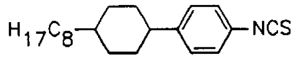
Other 2-chlorobenzenes **7** and **8**, whose solubility was good enough, were tested as 10 wt% solutions in eutectic mixture A consisting of three 4-(*trans*-4-alkylcyclohexyl)-benzeneisothiocyanates.



42 wt %



40 wt %



18 wt %

The results of the measurements are given in table 3.

Compound **7b** as an individual substance has a large viscosity (142 mm s^{-1}) at room temperature. The viscosity of its mixtures changes with concentration in a strongly non-linear way. The value of its viscosity estimated from the 10 wt% solution (mol ratio ~0.075) is only 45 mm s^{-1}, that is three times smaller than directly measured for the single component. The values of the viscosities for other compounds **7** and **8** estimated from the properties of the dilute solutions, together with the estimated values of Δn are listed in table 3. The introduction of four ring compounds **7** and **8** into

*Compound **7b***

		Temperatures/°C		
		20	30	40
1. Viscosity (mm^2 s^{-1}):	η	142.5		48.0
2. Optical indices (λ=589):	n_e	1.620	1.609	1.591
	n_o	1.513	1.512	1.513
	Δn	0.107	0.097	0.078
3. Dielectric constants:	$\varepsilon_{\parallel}$	5.39	5.15	4.72
	$\varepsilon_{\perp}$	3.77	3.74	3.70
	$\Delta\varepsilon$	1.62	1.41	1.02
4. Dispersion of optical indices at 17°C				
	λ	$n_{\parallel}$	$n_{\perp}$	Δn
	470	1.6440	1.5250	0.1190
	500	1.6358	1.5205	0.1153
	560	1.6246	1.5136	0.1110
	589	1.6214	1.5120	0.1094
	620	1.6182	1.5112	0.1070
	650	1.6155	1.5102	0.1053
	670	1.6140	1.5095	0.1045

*Compound **7c***

		Temperatures/°C		
		20	30	40
1. Optical indices (λ=589):	n_e	1.657	1.649	1.642
	n_o	1.517	1.515	1.512
	Δn	0.140	0.134	0.130
2. Dielectric constants:	$\varepsilon_{\parallel}$	4.32	4.14	3.93
	$\varepsilon_{\perp}$	4.57	4.30	4.08
	$\Delta\varepsilon$	−0.24	−0.16	−0.15

Table 3. Viscosity and optical properties of mixtures containg 90 wt% of A and 10 wt% of chlorobenzenes **7** or **8** at 20°C.

Mixture	$T_{\mathrm{N}\ \mathrm{I}}$/°C	η/mm^2 s^{-1}	η^a/mm^2 s^{-1}	n_e	n_o	Δn	Δn^a
A	42	12.9		1.6902	1.5222	0.1680	
and **7b**	41.5	15.3	45	1.6731	1.5164	0.1567	0.014
and **7c**	45.3	15.1	44	1.6866	1.5225	0.1641	0.115
and **7e**	45	16.5	60	1.6880	1.5214	0.1666	0.15
and **7g**	61.5	15.5	56	1.6950	1.5181	0.1769	0.32
and **8c**	54	16.8	70	1.6874	1.5226	0.1648	0.12
and **8d**	61	16.5	68	1.7016	1.5231	0.1785	0.32
and **8f**	60.5	15.6	54	1.7042	1.5222	0.1820	0.38
and **7e** and **7g**[b]	64	19.4	58	1.6922	1.5198	0.1724	0.20
and **7e** and**7g** and **13**[b]	87.5	23.0		1.7002	1.5184	0.1818	

[a]Viscosity and birefringence estimated for the single compound from the properties of its 10 wt% solution. [b]10 wt% of each.

mixture A in 10 20 wt% concentration, effectively raises the clearing point, but increases the viscosity only by $\leqslant 20\,\mathrm{mm\,s^{-1}}$.

The birefringence of compounds containing a fluorine atom in the terminal and/or lateral position (compounds **7b**, **c** and **8c**), measured directly or estimated, is small or moderate despite the fact that the molecules contain a biphenyl or terphenyl unit. Compounds containing the methoxy group and a terphenyl or quaterphenyl unit show very large birefringences (measured for mixtures), probably higher than 0.4 for the pure compounds. The estimated value of Δn for compound **8f** is 0.38. This is only a rough value, because, as an example, compound **7b** shows that the estimates from dilute solutions may give lower values of Δn than expected. Compound **7b** has a small positive dielectric anisotropy and compound **7c** a small negative dielectric anisotropy and both compounds have a small value of the ratio $\Delta\varepsilon/\varepsilon_\perp$. Some compounds **7** and **8** have excellent solubility in mesogenic media; for example **7e** dissolves at room temperature in the non-polar solvent 4-(*trans*-4-propyl-cyclohexyl)-1-pentylbenzene up to 50 wt% forming a mixture with the following properties $T_{\mathrm{N}\rightarrow\mathrm{I}}$/°C Δn n_o n_e η_{20}/mm s^{-1} 26 0.0706 1.5118 1.5824 31.2

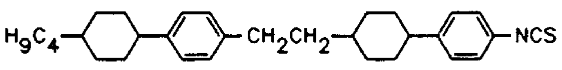
5. Experimental

Confirmation of the structures of intermediates and products was obtained using a GC/MS mass spectrometer (HP 5972 MSD) and ^{1}H NMR spectroscopy. The purity of the compounds was checked using a HP 5890 capillary gas chromatograph fitted with an HP1 column.

5.1. *Ethyl 2-(4-*trans*-4-pentylcyclohexylethyl)acetoacetate (3)*

Sodium (4 g, 0.17 mol) was dissolved in dry ethanol (150 cm^3) and ethyl acetoacetate was added (22.1 g, 0.17 mol). The mixture was stirred and heated until boiling, and 2-(*trans*-4-pentylcyclohexyl)ethyl bromide, [27], was added dropwise (39 g, 0.15 mol) while maintaining gentle boiling. The mixture was heated under reflux for 10 h, when part of the ethanol was distillated off and the residue cooled, water was added. The product was extracted into hexane and the extract washed with water and dried (MgSO$_4$). The solvent was evaporated and the residue was distilled *in vacuo* (0.15 mm); a fraction (140 144°C, 35 g) was collected; yield 75 per cent, 95 per cent purity.

13



5.2. *4-(*trans*-4-Propylcyclohexyl)phenyl 2-(dimethylamino)ethyl ketone hydrochloride (4)*

A mixture of 4-(*trans*-4-propylcyclohexyl)aceto-phenone (**2**) (244 g, 1 mol), paraformaldehyde (30 g, 1 mol), dimethylamine hydrochloride (85.6 g, 1 mol), isopropyl alcohol (1000 cm^3) and concentrated hydrochloride acid (2 cm^3) was stirred and heated under reflux for 5 h. The product was filtered off and washed with acetone. The yield of Mannich salt was 78 per cent (240 g).

5.3. *3-(4-(*trans*-4-Propylcyclohexyl)phenyl)-6-(2-(*trans*-4-pentylcyclohexyl)ethyl)cyclohex-2-en-l-one (5g)*

A mixture of 4-(*trans*-4-propylcyclohexyl)phenyl 2-(dimethylamino)ethyl ketone hydrochloride (30 g, 0.089 mol), ethyl 2-(4-(*trans*-4-pentylcyclohexyl))acetoacetate, potassium t-butoxide (35.8 g, 0.294 mol), and dioxan (200 cm^3) was stirred and heated at a temperature between 95 and 100°C for 5 h.

The mixture was cooled and poured into a solution of 600 cm^3 of water and 400 cm^3 of concentrated hydrochloride acid with vigorous stirring. The product was filtered off and crystallized from a mixture of isopropyl alcohol and tetrahydrofurane (1:1, 1000 cm^3). A colourless crystalline product was obtained; yield 26 g (61.4 per cent).

Transition temperatures (°C): Cr<20 S_B 175 S_A 240 I; *m*/*z*: 476(M^+), 309 $(CH_2\ C_6H_6O\ Ph\ C_6H_{10}\ C_3H_7)^+$, 296 $(C_6H_6O\ Ph\ C_6H_{10}\ C_3H_7)^+$, 171.

5.4. *1-(2-(*trans*-4-Pentylcyclohexyl)ethyl)-2-chloro-4-(4-(*trans*-4-propylcyclohexyl)phenyl) benzene (7g)*

A mixture of **5g** (2.9 g, 0.005 mol), PCl_5, (1.3 g, 0.006 mol) and benzene (50 cm^3) was heated under reflux for 6 h. The mixture was cooled and poured into water with ice. The organic layer was separated and washed with a solution of sodium hydroxide, water and dried ($MgSO_4$). Benzene was distilled off and the crude product was purified by column chromatography (silica gel, hexane) and then recrystallized from hexane: ethanol (2:1). The colourless crystalline solid was obtained in a yield of 60.9% (1.5 g).

Transition temperatures (°C): Cr 78.5 N 220 I; *m*/*z*: 494 and 492(M^+), 394 and 392, 327 and 325 $(C_3H_7\ C_6H_{10}\ Ph\ PhCl\ CH_2)^+$, 291, 227 and 225, 205, 165.

6. Conclusion

3,6-Disubstituted cyclohex-2-en-1-ones are easily converted into 1,4-disubstituted 2-chlorobenzenes by treatment with PCl_5. The introduction of a chlorine atom in a lateral position of the terphenyl or quaterphenyl moiety effectively depresses smectic phases and it is possible to obtain compounds with low melting points and large ranges of the nematic phase. The simple synthetic procedure enabled us to prepare a varied range of new liquid compounds with low, moderate and high birefrigence and a low ratio of $\Delta\varepsilon/\varepsilon_\perp$. The compounds may be used to adjust the electro-optical properties of mixtures especially for PDLC displays and non-linear optical applications. Their most promising concentrations in mixtures are below 30 wt%, because of their high viscosities.

Acknowledgement

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