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V. Bezborodov^a; R. Dabrowski^b; J. Dziaduszek^b; K. Czuprynski^b; Z. Raszewski^b

^a Institute of Applied Physical Problems, Minsk, Belarus ^b Military University of Technology, Warsaw, Poland

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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. CZUPRYŃSKI and Z. RASZEWSKI

Military University of Technology, Kaliskiego, 01-489 Warsaw, Poland

‡Institute of Applied Physical Problems, Kurchatova, 220064 Minsk, Belarus

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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 ϵ_{\perp} and changes the $\Delta\epsilon/\epsilon_{\perp}$ 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 multistage 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 -dimethylaminoethyl ketones) and 2-alkyl or 2-alkylcyclohexylethyl 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.

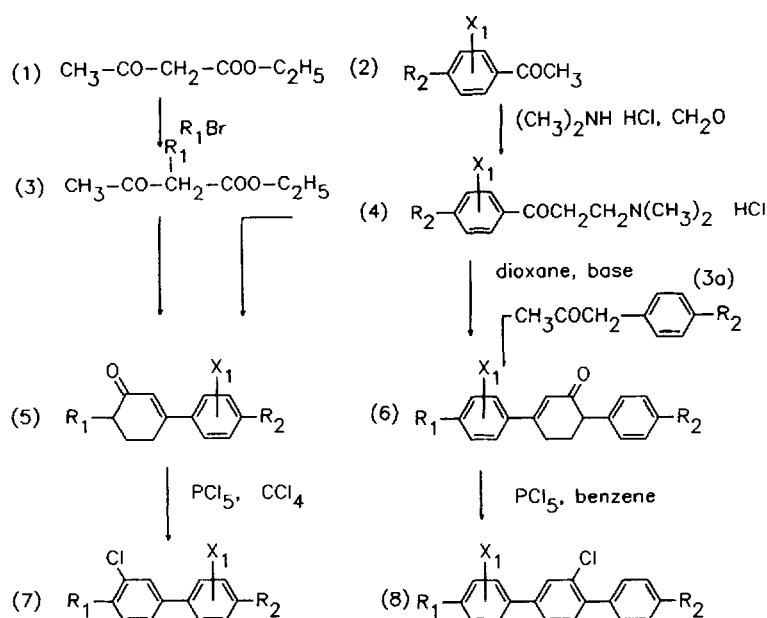
Compounds 5 and 6 were then heated with PCl_5 in CCl_4 or benzene when the carbonyl group undergoes chlorination, followed by aromatization. This is also a multistage reaction which is carried as a one-pot procedure.

3. Mesomorphic properties

The phase transition temperatures for the 3,6-disubstituted cyclohex-2-en-1-ones 5 and 6 are given

*Author for correspondence.

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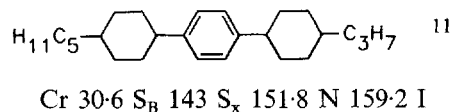
Scheme. The route for the preparation of chloro substituted benzenes; X is a hydrogen or a fluorine atom.

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 **5b** and **10** (table 2)



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-1-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 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

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	*

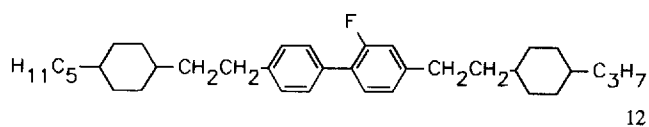
Table 1 (continued)

No.	Structures	Cr	S _B	S _A	N	I
6e		* 127 ^b 1850	—	* 222 1600	—	*
6f		* 137	—	* 238	—	*

^a Cr₁ 46.9 Cr.
740

^b Cr₂ 62.5 Cr₁ 91 Cr.
560 380

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].



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 compound **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

Compound 7b

		Temperatures/°C		
		20	30	40
1. Viscosity (mm ² s ⁻¹):	η	142.5		48.0
2. Optical indices ($\lambda = 589$):	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:	ϵ_{\parallel}	5.39	5.15	4.72
	ϵ_{\perp}	3.77	3.74	3.70
	$\Delta\epsilon$	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

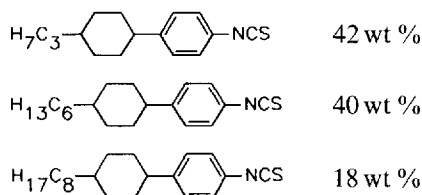
		Temperatures/°C		
		20	30	40
1. Optical indices ($\lambda = 589$):	n_e	1.657	1.649	1.642
	n_o	1.517	1.515	1.512
	Δn	0.140	0.134	0.130
2. Dielectric constants:	ϵ_{\parallel}	4.32	4.14	3.93
	ϵ_{\perp}	4.57	4.30	4.08
	$\Delta\epsilon$	-0.24	-0.16	-0.15

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 <i>5310</i>	—	* 47 <i>170</i>	*
9		* 74.8	—	* 95.9 ^a	*
7c		* 45.2 <i>7930</i>	—	* 97 <i>250</i>	*
7e		* 29 <i>6650</i>	* 72.2 <i>200</i>	* 92 <i>140</i>	*
7g		* 78.5 <i>6120</i>	—	* 220 <i>490</i>	*
7h		* 63.3 ^b <i>2750</i>	—	* 191	*
10		184.4 ^c <i>1400</i>	* 208.2 <i>260</i>	* 229 <i>1170</i>	*
8b		* 92.6 <i>6290</i>	—	* 232	*
8c		* 105 <i>3380</i>	—	* 210	*
8d		* 90.3 <i>7610</i>	—	* 273	*
8e		* 102 <i>6600</i>	—	* 275	*
8f		* 115.0 <i>5130</i>	* 141	* 298	*

^a Ref. [11].^b Cr₁ 53.1 Cr.^c Cr < 20 S_{X2} 102.5 S_{X1} 151.8 S_B.
930 770

good enough, were tested as 10 wt % solutions in eutectic mixture A consisting of three 4-(*trans*-4-alkylcyclohexyl)-benzeneisothiocyanates.



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

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 $\Delta\epsilon/\epsilon_{\perp}$. 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-propylcyclohexyl)-1-pentylbenzene up to 50 wt % forming a mixture with the following properties

$T_{N-I}/^{\circ}\text{C}$	Δn	n_o	n_e	$\eta_{20}/\text{mm s}^{-1}$
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 ^1H 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**)

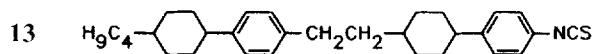
Sodium (4 g, 0.17 mol) was dissolved in dry ethanol (150 cm^3) and ethyl acetoacetate was added (22.1 g, 0.17 mol). The mixture was stirred and heated until boiling, and 2-(*trans*-4-pentylcyclohexyl)ethyl bromide, [27], was added dropwise (39 g, 0.15 mol) while maintaining gentle boiling. The mixture was heated under reflux for 10 h, when part of the ethanol was distilled 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

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

Mixture	$T_{N-I}/^{\circ}\text{C}$	$\eta/\text{mm}^2 \text{ s}^{-1}$	$\eta^a/\text{mm}^2 \text{ s}^{-1}$	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.



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.

5.2. 4-(trans-4-Propylcyclohexyl)phenyl

2-(dimethylamino)ethyl ketone hydrochloride (4)

A mixture of 4-(trans-4-propylcyclohexyl)acetophenone (2) (244 g, 1 mol), paraformaldehyde (30 g, 1 mol), dimethylamine hydrochloride (85.6 g, 1 mol), isopropyl alcohol (1000 cm³) and concentrated hydrochloric acid (2 cm³) 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-1-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))acetate, potassium t-butoxide (35.8 g, 0.294 mol), and dioxan (200 cm³) 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 cm³ of water and 400 cm³ of concentrated hydrochloric acid with vigorous stirring. The product was filtered off and crystallized from a mixture of isopropyl alcohol and tetrahydrofuran (1:1, 1000 cm³). 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 (CH₂-C₆H₆O-Ph-C₆H₁₀-C₃H₇)⁺, 296 (C₆H₆O-Ph-C₆H₁₀-C₃H₇)⁺, 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), PCl₅ (1.3 g, 0.006 mol) and benzene (50 cm³) 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 (MgSO₄). 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 (C₃H₇-C₆H₁₀-Ph-PhCl-CH₂)⁺, 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 PCl₅. 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 birefringence and a low ratio of Δε/ε_⊥. 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.

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