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This paper describes the synthesis and mesomorphic properties of some new liquid crystalline cyclohexene derivatives.

1. Introduction

During the past 20 years, a new class of liquid crystal—the cyclohexene derivatives—has emerged, which has remarkable physico-chemical and electrooptic properties [1–6]. Some of these liquid crystals are particularly promising components of liquid crystalline materials for display applications. In continuation of our work [4–6], we synthesized some novel liquid crystalline cyclohexene derivatives and investigated their mesomorphic properties with a particular interest in their structure–property relationships.

2. Results and discussion

It has been shown that cyclohexenes, without lateral substituents or containing halogen atoms, cyano groups or other functional groups at the double bond, may be prepared by the reduction of cyclohex-2-enones or by the modification of the corresponding cyclohexanones using simple reagents [5, 7, 8]. Taking into account that the mesomorphic 3,6-disubstituted cyclohex-2-enones (II) and 2,5-disubstituted cyclohexanones (III) can be easily synthesized [9–13], we used them for obtaining the liquid crystalline cyclohexenes with or without lateral substituents at the double bond.

The cyclohexenes (I) containing a double bond at the aryl or styryl fragment (Z is benzene or biphenyl or CH=CH fragment) were prepared by the reduction of the corresponding 3,6-disubstituted cyclohex-2-enones (II) using the Hyan–Minlon's method.

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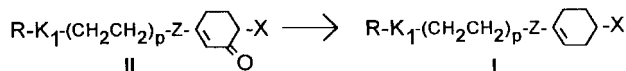
The terminal group X is a hydrogen or a alkyl, alkoxy radical, or halogen atom, and p is 0 or 1; K_1 is a single bond, or benzene, or cyclohexene, or cyclohexane rings; R is an alkyl radical; Z is a CH=CH fragment, or benzene ring, or biphenyl fragment.

We found that the highest yield of final products (70–80 per cent) was observed during the reduction of 3-aryl-6-alkylcyclohex-2-enones (II, Z=benzene or biphenyl). The cyclohexenes containing two double bonds in the chemical structure (I, Z is CH=CH, K_1 is benzene) or (I, Z is benzene or biphenyl, p=0, K_1 is cyclohexene) were formed with yields of 20–25 per cent and 10–15 per cent, respectively. It was not possible to synthesize the corresponding compounds containing the acetyl fragment (I, X=COCH$_3$) due to the formation of by-products.

It was found that the cyclohexenes (VIII) (see scheme 1) could be obtained with a high yield (60–80 per cent) by the dehydration of the corresponding isomeric alcohols (IV, V) which were synthesized by the reduction of the ketones (III) by sodium borohydride. p-Toluenesulphonic acid in boiling toluene or phosphorus oxychloride in pyridine were used as catalysts for the dehydration of the alcohols. We would like to point out that during the reaction of the alcohols (IV, V) in a boiling mixture of pyridine and phosphorus oxychloride besides the cyclohexenes (VIII), the corresponding cyclohexylchlorides (IX) were formed with a

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
IX Cl

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
VIII ↑ - H₂O

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
V HO

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
IV HO

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
X CH₃ ↑ - H₂O

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
VII HO CH₃

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
VI HO CH₃

NaBH₄   CH₃MgJ

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
O **III**

PCl₅   (CH₃)₂C(CN)OH

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XI Cl Cl

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XII O Cl

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XIII Cl   ↓ - HCl

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XIV Cl

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XV HO CN

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XVI HO CN   ↓ - H₂O

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XVII CN

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XVIII CN   ↓ H₂

R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
XIX CN

III --DAST--> R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X **XX** --KOH-->
F F

--> R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X **XXI** --H₂--> R-K₁-(CH₂CH₂)ᵣ-⟨⟩-K₂-(CH₂CH₂)ₘ-⟨⟩-K₃-X
F   F **XXII**

Scheme 1.

yield which depended on the term of the reaction and was 5–30 per cent. In this case, it was necessary to boil the mixtures in the presence of potassium hydroxide or other strong bases for the full transformation of the alcohols (**IV**, **V**) to the cyclohexenes (**VIII**). The weak heating of the mixture of alcohols with phosphorous oxychloride in pyridine for a short time with this reaction usually led to the corresponding esters of phosphoric acid which were not easily modified to the cyclohexenes (**VIII**).

We used the same conditions for the preparation of the cyanocyclohexenes (**XVII**, **XVIII**) from the corresponding cyanoalcohols (**XV**, **XVI**). However, in this case the boiling of the reaction mixture resulted, as a rule, to the formation of the cyanocyclohexenes (**XVII**) with a yield of 50–60 per cent. These compounds are characterized by the position of the double bond at the second carbon atom of the cyclohexene ring. The isomers (**XVIII**) were obtained by the careful separation and dehydration of alcohols (**XV**, **XVI**) with a yield of 5–10 per cent.

It is known that the gem-dichlorides and vinylchlorides may be obtained by the interaction of ketones with phosphorous pentachloride [5]. However, as our investigations have shown, the reaction of 3,6-disubstituted cyclohexanones (**III**) with phosphorous pentachloride leads to the mixture of the gem-dichlorides (**XI**) and α-chloroketones (**XII**) which are not stable and are converted into the chlorocyclohexenes (**XIII, XIV**) and by-products. Hence, for the isolation of the chlorocyclohexenes (**XIII**) from reaction mixtures, we needed to use some additional crystallizations. It was impossible to isolate the isomers (**XIV**) from the mixtures.

The catalytic hydrogenation cyanocyclohexenes (**XVIII**) in the presence of 10 per cent palladium on carbon gives the corresponding saturated compounds (**XIX**). As our investigation has shown, this method cannot be used for the preparation of chlorocyclohexanes (**IX**) from the corresponding cyclohexenes (**XIII, XIV**) due to the simultaneous formation of the chlorocyclohexanes (**IX**) and their unsubstituted analogues.

The liquid crystalline compounds (**XXI**) containing a lateral fluorine atom in the cyclohexene ring were synthesized with a small yield by treating the 3,6-disubstituted cyclohexanones (**III**) with a fluorinating agent DAST (diethylaminosulphur trifluoride) [14] and then boiling the difluorocyclohexanes (**XX**) in alcoholic potassium hydroxyde (see scheme 1).

It is believed that compounds (**XXII**) may be synthesized with a high yield (70–80 per cent) by interaction of the alcohols (**III,IV**) with DAST at −70°C in dichlo-
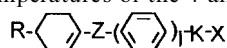
romethylene. The higher temperature of the reaction usually leads to the simultaneous formation of the fluorocyclohexanes (**XXII**) and corresponding cyclohexenes (**VIII**). The yield of latter compounds can reach 5–20 per cent. The terminal group X is hydrogen or alkyl, alkoxy radical, or halogen atom, and l and m are 0 or 1; K_1, K_2, K_3 are single bonds, or benzene or cyclohexane rings; R is an alkyl radical.

The proton NMR spectra (δ,ppm) of the 4-(4-alkoxyphenyl)-1-alkyl-1-cyclohexenes the (**VIII**) revealed that the multiplet at 5·57 belongs to the protons located at the double bond of the cyclohexene ring. The results of the proton NMR spectrum of the *cis*-3-[4-(*trans*-4-propylcyclohexyl)phenyl]-*cis*-6-pentylcyclohexan-1-r-ol (**V**) showed that multiplet signals at 4·05, with a low spin–spin interaction constant of the proton located at the first carbon atom of the cyclohexane ring, confirms the axial position of the hydroxyl group in the ring. Triplet–triplet signals with a larger spin–spin interaction constant at 3·37 of the analogous proton of the isomer (**IV**) indicated the equatorial position of the hydroxy group in the cyclohexane ring. The singlet signal of the hydrogen atoms of the methyl radical located at the double bond was observed at 2·5 in the proton NMR spectrum of the methylcyclohexenes (**X**).

The IR spectra of the cyanocyclohexenes (**XVII**) revealed that the intense band at 2220 cm^{-1} corresponds to the stretching vibrations of the cyano group.

The phase transition temperatures of the liquid crystals synthesized in this work are listed in tables 1–3. As can be seen from table 1, the 1-(4-alkoxyphenyl)-

Table 1. Transition temperatures of the 4-alkyl-1-arylcyclohex-1-enes.

$$R\text{-}\langle\bigcirc\rangle\text{-}Z\text{-}(\langle\hexagon\rangle)_l\text{-}K\text{-}X$$

Compound	R	Z	I	K	X	Cr		Sm		N		I	Ref.
								Transition temperatures/°C				
1a	H$_3$C	—	1	—	OC$_4$H$_9$	●	74					●	
1b	H$_7$C$_3$	—	1	—	OC$_4$H$_9$	●	57			●	74	●	
1c	H$_7$C$_3$	—	1	—	OC$_5$H$_{11}$	●	71			(●	69)	●	
1d	H$_{11}$C$_5$	—	1	—	OC$_2$H$_5$	●	79			(●	76)	●	[5]
1e	HOOCH$_2$C	—	1	—	Cl	●	126					●	
1f	HOOCH$_2$C	—	1	—	OC$_2$H$_5$	●	130					●	
1g	HOOC(H$_2$C)$_2$	—	1	—	OC$_2$H$_5$	●	175					●	
1h	H$_9$C$_4$	CH=CH	1	—	OC$_2$H$_5$	●	77	●	88	●	113	●	
1i	H$_{11}$C$_5$	CH=CH	1	—	OC$_2$H$_5$	●	81	●	102	●	125	●	
1j	H$_{13}$C$_6$	CH=CH	1	—	OC$_2$H$_5$	●	75	●	98	●	116	●	
1k	H$_{11}$C$_5$	—	2	—	Br	●	165			●	235	●	
1l	H$_{11}$C$_5$	—	1	CE[a]	C$_5$H$_{11}$	●	91	●	144	●	167	●	
1m	H$_{11}$C$_5$	—	2	CE[a]	C$_5$H$_{11}$	●	75	●	216			●	
1n	H$_5$C$_6$(H$_2$C)$_2$	—	2	—	CH$_3$	●	156	●	177	●	198	●	

[a] CE denotes 1,4-cyclohexen-1-enylene.
Parentheses denote a monotropic transition.

4-alkylcyclohexenes with short alkyl(alkoxy) terminal substituents are not mesomorphic (compound **1 a**). Increasing their lengths results in the appearance of the nematic phase or monotropic nematic to isotropic phase transitions (compounds **1 b**–**1 d**). The efficiency of the cyclohexene fragment incorporated into the molecular core of the two-ring alkyl–alkoxy derivatives can be expressed by the following order of increasing clearing temperature for the system **1** (see tables 1 and 3 [5, 15, 16]):

$$H_{11}C_5\text{- A-}\langle\rangle\text{-OC}_2H_5 \quad (1) \qquad T_{cl} \rightarrow A: \langle\rangle < \langle\rangle < \langle\rangle < \langle\rangle$$

The attachment of the CH_2COOH or $(CH_2)_2 COOH$ to the 1,4-cyclohexenylene fragment incorporated into the molecular core of the 1-(4-substituted phenyl)-4-substituted cyclohexenes does not produce a mesophase due to high melting temperatures (compounds **1 e**–**1 g**). The insertion of the $CH=CH$ linking group into the molecular core of compound **1 d** to produce the compound **1 i** increases the melting and clearing points and introduces the smectic phase (see also compounds **1 h**, **1 j**). This can be explained in terms of increasing molecular polarizability. The same effects have been observed for many other liquid crystalline derivatives [17].
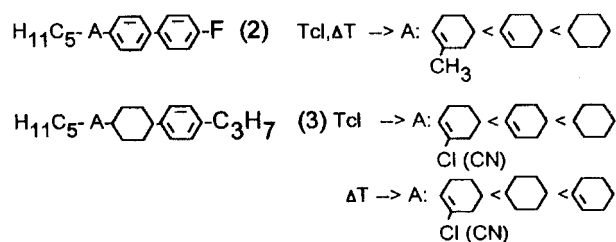
The introduction of the 1,4-cyclohexenylene or 1,4 phenylene fragments into molecular core of 1-(4-substituted phenyl)-4-substituted cyclohexenes to produce three and four-ring compounds gives rise to increased clearing temperatures (compounds **1 k**–**1 m**). This is usually observed for many other three and four-ring liquid crystalline derivatives [3–6, 15].

The data presented in table 2 reveal that the intermediate products—two-ring 2-alkyl-5-(4-alkoxyphenyl)-1,1-difluorocyclohexanes—show only the monotropic nematic–isotropic phase transition (compounds **2 a**, **2 b**), while increasing the number of molecular fragments and removal of the ethylene linking group in their cores leads to the appearance of enantiotropic smectic and nematic phases (compound **2 d**). Table 3 presents the phase transition temperatures of the 1-alkyl-2-substituted 4-arylcyclohex-1-enes. Two-ring compounds from these series are not mesomorphic in general (compounds **3 a**–**3 c**). The insertion of an ethylene linking group into the molecular core of compound **3 b** to produce compound **3 e** sufficiently decreases the melting point (see also compound **3 d**). Three-ring and four-ring compounds presented in table 3 exhibit the smectic and nematic phases with moderate clearing temperatures (compounds **3 f**, **3 g**, **3 l**, **3 s**, **3 t**) which are lower than those of the corresponding *trans*-1,4-cyclohexylene derivatives [15, 18, 19].
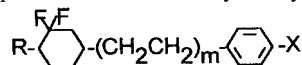
Lateral substitution of the 1,4-cyclohexenylene fragment incorporated into the molecular core of the 1-alkyl-2-substituted 4-arylcyclohex-1-enes by CH_3, CI, CN groups results in the disappearance of the mesophase (compounds **3 g** and **3 j**; **3 m**, **3 n** and **3 o**; see also compound **3 q**). This is due to the lateral substituents broadening the molecule and reducing the intermolecular forces. The same effects have been observed for other liquid crystalline derivatives [13, 15, 20–22].

The efficiency of the cyclohexene fragment incorporated into the molecular core of three-ring liquid crystals can be expressed by the following orders of increasing clearing temperatures T_{cl} and nematic ranges ΔT for systems **2** and **3** (see table 3, [18, 19]):

$$H_{11}C_5\text{- A-}\langle\rangle\langle\rangle\text{-F} \quad (2) \quad T_{cl},\Delta T \rightarrow A: \underset{CH_3}{\langle\rangle} < \langle\rangle < \langle\rangle$$

$$H_{11}C_5\text{- A-}\langle\rangle\langle\rangle\text{-C}_3H_7 \quad (3) \quad T_{cl} \rightarrow A: \underset{CI\,(CN)}{\langle\rangle} < \langle\rangle < \langle\rangle$$

$$\Delta T \rightarrow A: \underset{CI\,(CN)}{\langle\rangle} < \langle\rangle < \langle\rangle$$

The comparison of the liquid crystalline properties of the intermediate products—cyclohexanols (**IV**, **V**)—shows that the compounds containing a hydroxy group
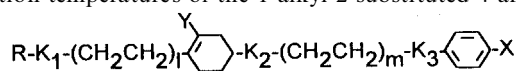
Table 2. Transition temperatures of the 2-alkyl-5-aryl-1,1-difluorocyclohexanes.

$$R\text{-}\langle\overset{F\,F}{\rangle}\text{-(CH}_2CH_2)_m\langle\rangle\text{-X}$$

Compound	*R*	*m*	*X*	Cr		Sm		N		I	Ref.
								Transition temperatures/°C			
2a	H_9C_4	1	OC_2H_5	●	37·4			(●	10)	●	
2b	$H_{11}C_5$	1	OC_2H_5	●	34			(●	13)	●	[5]
2c	H_7C_3	0	H	●	86			(●	78)	●	
2d	$H_{11}C_5$	0	C_3H_7	●	78	●	90	●	99	●	[5]

Parentheses denote a monotropic transition.

Table 3. Transition temperatures of the 1-alkyl-2-substituted 4-arylcyclohex-1-enes.

$$R\text{-}K_1\text{-}(CH_2CH_2)_l\text{-}\underset{Y}{\bigcirc}\text{-}K_2\text{-}(CH_2CH_2)_m\text{-}K_3\text{-}\bigcirc\text{-}X$$

| Compound | R | K_1 | I | Y | K_2 | m | K_3 | X | Transition temperatures/°C | | | | |
									Cr	Sm	N	I	Ref.
3a	H_9C_4	—	0	H	—	0	—	OC_4H_9	• 24			•	
3b	$H_{11}C_5$	—	0	H	—	0	—	OC_2H_5	• 24		(• 0)	•	
3c	$H_{11}C_5$	—	0	H	—	0	—	OC_5H_{11}	• 18			•	
3d	H_9C_4	—	0	H	—	1	—	OC_2H_5	• 10			•	
3e	$H_{11}C_5$	—	0	H	—	1	—	OC_2H_5	• 0			•	
3f	$H_{11}C_5$	—	0	H	Bª	0	—	CH_3	• 53	• 114	• 132	•	
3g	$H_{11}C_5$	—	0	H	Bª	0	—	F	• 68		• 107	•	
3h	H_7C_3	—	0	CH_3	Bª	0	—	H	• 28			•	
3i	$H_{11}C_5$	—	0	CH_3	Bª	0	—	H	• 37			•	
3j	$H_{11}C_5$	—	0	CH_3	Bª	0	—	F	• 58			•	[5]
3k	H_7C_3	—	0	F	Bª	0	—	H	• 81		• 87	•	
3l	H_7C_3	—	0	F	Bª	0	—	C_5H_{11}	• 40	• 140	• 148	•	
3m	$H_{11}C_5$	—	0	H	—	0	Cᵇ	C_3H_7	• 82		• 113·6	•	
3n	$H_{11}C_5$	—	0	Cl	—	0	Cᵇ	C_3H_7	• 40·6			•	
3o	$H_{11}C_5$	—	0	CN	—	0	Cᵇ	C_3H_7	• 50·5			•	
3p	H_9C_4	Cᵇ	1	Cl	—	0	Cᵇ	C_3H_7	• 47·5		• 158·5	•	
3q	$H_{13}C_6$	—	0	CH_3	—	0	Cᵇ	C_2H_5	• 47			•	
3r	$H_{13}C_6$	—	0	CH_3	—	0	Cᵇ	C_5H_{11}	• 35	• 52·5		•	
3s	H_7C_3	Bª	1	H	—	0	Cᵇ	C_5H_{11}	• 68	• 188		•	
3t	H_5C_2O	Bª	1	H	—	0	Cᵇ	C_3H_7	• 160	• 175	• 199	•	

ª B-1,4-phenylene; ᵇ C-*trans*-1,4-cyclohexenylene.
Parentheses denote a monotropic transition.

in the axial position (**IV**) are non-mesomorphic and their isomers (**V**) form smectic and nematic phases.

H₇C₃ — ... — C₅H₁₁ (IV)

m.p. 170·4°C

H₇C₃ — ... — C₅H₁₁ (V)

Cr 142·5 Sm 144 N 150·2 I
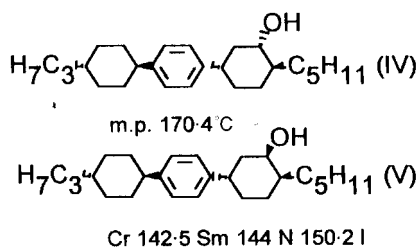
3. Experimental

Phase transition temperatures were measured using a Linkam heating stage in conjunction with a polarizing PZO microscope, and a Setaram DSC 92 differential scanning calorimeter. The 4-alkyl-1-aryl(styryl)-cycloxenes (**I**) were obtained using the Hyan–Minlon method [5].

3.1.1. *The reduction of trans-3,6-disubstituted cyclohexanone by NaBH₄*

A mixture containing 0·1 mol of the *trans*-3,6-disubstituted cyclohexanone (**II**) and 0·1 mol of NaBH₄ in 150 ml of isopropyl alcohol was stirred at 50–60°C for 6 h and then carefully poured into a hydrochloric acid solution. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. The alcohols (**IV, V**) obtained after the solvent had been removed were recrystallized from ethyl alcohol or separated via chromatography.

3.1.2. *1-Alkyl-4-aryl-1-cyclohexenes (VIII)*

Method 1: 0·2 mol of the mixture of 2-alkyl-5-arylcyclohexanols (**IV, V**), a catalytic quantity of *p*-toluenesulphonic acid in 100 ml of toluene were boiled until the water did not distil anymore. The reaction mixture was washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was recrystallized from mixture of methyl and isopropyl alcohols. The yields were 40–60 per cent. The transition temperatures of the 1-alkyl-4-aryl-1-cyclohexenes are given in table 1.

Method 2: 0·2 mol of the mixture of 2-alkyl-5-arylcyclohexanols (**IV, V**) and 0·3 mol of phosphorous oxychloride in 20 ml of pyridine was boiled for 6–7 h, and 100 ml of water added. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. 0·3 mol of potassium hydroxide and 100 ml isopropyl alcohol were added to

the residue obtained after the solvent had been removed. The mixture was boiled for 6 h and diluted with 150 ml of water. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was recrystallized from isopropyl alcohol. The yields were 55–70 per cent. The transition temperatures of the compounds (**VIII**) are presented in table 1.

3.1.3. *1-Alkyl-2-chloro-4-aryl-1-cyclohexenes (XIII)*

0·2 mol of 2-alkyl-5-arylcyclohexanone (**III**) and 0·3 mol of phosphorous pentachloride in 50 ml of benzene were boiled for 4–5 h, and 100 ml of water added. The organic layer was washed with dilute potassium hydroxide, water, dried with anhydrous magnesium sulphate and passed through a layer of aluminium oxide. The residue obtained after the solvent had been removed was recrystallized from mixture of methanol and isopropyl alcohol. The yields were 30–50 per cent. The transition temperatures of the 1-alkyl-2-chloro-4-aryl-1-cyclohexenes are given in table 3.

3.1.4. *6-Alkyl-1-cyano-3-aryl-1-cyclohexenes (XVII)*

0·2 mol of 2-alkyl-5-arylcyclohexanone (**III**), 0·5 mol of acetonecyanohydrine and 0·3 mol triethylamine in 50 ml of tetrahydrofuran were left at room temperature overnight, then diluted with 100 ml of water. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was crystallized from methyl alcohol. 0·10 mol of 2-alkyl-1-cyano-5-arylcyclohexanol (**XVI**) and 0·3 mol of phosphorous oxychloride in 20 ml of pyridine were boiled for 6–7 h, and 100 ml of water added. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was recrystallized from methanol alcohol. The yields were 30–40 per cent. The isomers (**XVIII**) were obtained in the same way from the residue after crystallization from alcohol (**XVI**).

3.1.5. *2-Alkyl-5-aryl-1,1-difluorocyclohexanes (XX)*

0·1 mol of 2-alkyl-5-arylcyclohexanone (**III**) and 0·2 mol of DAST in 50 ml of benzene were boiled for 6–10 h. The reaction mixture was washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was purified via chromatography and recrystallized from a mixture of methyl and isopropyl alcohol. The yields were 40–60 per cent. The transition temperatures of these compounds are given in table 2.

3.1.6. *1-Alkyl-2-fluoro-4-aryl-1-cyclohexenes (XXI)*

The mixture of 0·05 mol of 2-alkyl-5-aryl-1,1-difluorocyclohexenes (**XX**), 0·15 mol of potassium hydroxide in 50 ml of propyl alcohol was boiled for 10 h then diluted with 150 ml of water. The organic layer was dissolved by benzene, washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was recrystallized from isopropyl alcohol. The yields were 5–20 per cent. The transition temperatures of the compounds (**XXI**) are presented in table 3.

3.1.7. *1-Alkyl-2-methyl-4-aryl-1-cyclohexenes (X)*

0·2 mol of the mixture of 2-alkyl-5-aryl-1-methylcyclohexanols (**VI**, **VII**) prepared via a Grignard reaction, a catalytic quantity of *p*-toluenesulphonic acid in 100 ml of toluene was boiled until the water did not distil anymore. The reaction mixture was washed with water and dried with anhydrous magnesium sulphate. The residue obtained after the solvent had been removed was recrystallized from the mixture of methyl and isopropyl alcohol. The yields were 40–60 per cent. The transition temperatures of the compounds (**X**) are given in table 3.

4. Conclusions

Systematic studies on the effects of structure–property relations of the liquid crystalline cyclohexene derivatives have been performed. The 1,4-cyclohexenylene fragment and its laterally substituted analogues have been shown to be valuable elements in the design of liquid crystals for display applications.

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