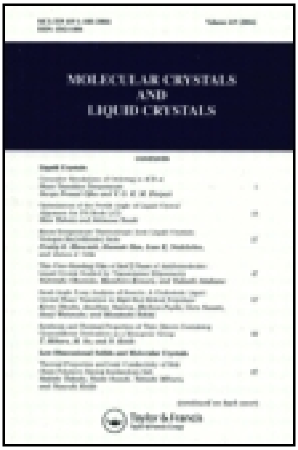

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Liquid Crystalline 1,3-Disubstituted Cyclopentanes

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LIQUID CRYSTALLINE 1,3-DISUBSTITUTED CYCLOPENTANES

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Abstract Novel liquid crystalline 1,3-disubstituted cyclopentanes were studied for physicochemical and temperature characteristics.

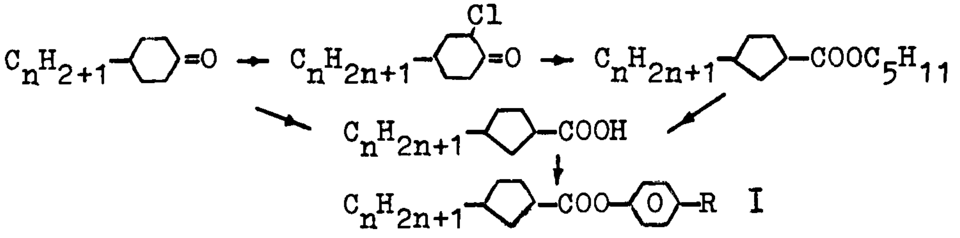
INTRODUCTION

Our further work on the synthesis and study into the properties of mesogens in the alicyclic series yielded over 70 novel liquid crystalline compounds such as 1,3-disubstituted cyclopentane derivatives. The synthesized mesogens in the cyclopentane series simulate all conventional types of liquid crystalline molecules, trans-1,4-disubstituted cyclohexanes, in particular.

1. Esters of Cyclopentanecarboxylic Acids

3-n-Alkylcyclopentanecarboxylic acids and their esters were prepared by the known methods[1-3] according to Scheme 1, the characteristics of the novel mesogens are given in Table I.

SCHEME 1



SCHEME 1 (continued)

I: R=C_6H_4CN, n=I(a),3(b),5(c);
R=$C_6H_{10}C_5H_{11}$, n=I(d); R=OC_2H_5, n=3(e); R=CN, n=3(f)

TABLE 1 Phase transition temperatures for compounds I (°C)

Index	n	R	Cyclopentanes			Cyclohexane analogues[4]		
			T_{C-S}	T_{S-N} C-N	T_{N-I}	T_{C-S}	T_{C-N} S-N	T_{N-I}
Ia	1	C_6H_4CN		(41.3)	53.5			
Ib	3	C_6H_4CN		52.2	66.5			
Ic	5	C_6H_4CN	36.9	71.4	80.8	-	85	241
Id	1	$C_6H_{10}C_5H_{11}$	(47)	-	60.0			
Ie*	3	OC_2H_5	-	-	-	-	47	78.5
If*	3	CN	-	-	-	-	54.5	69.5

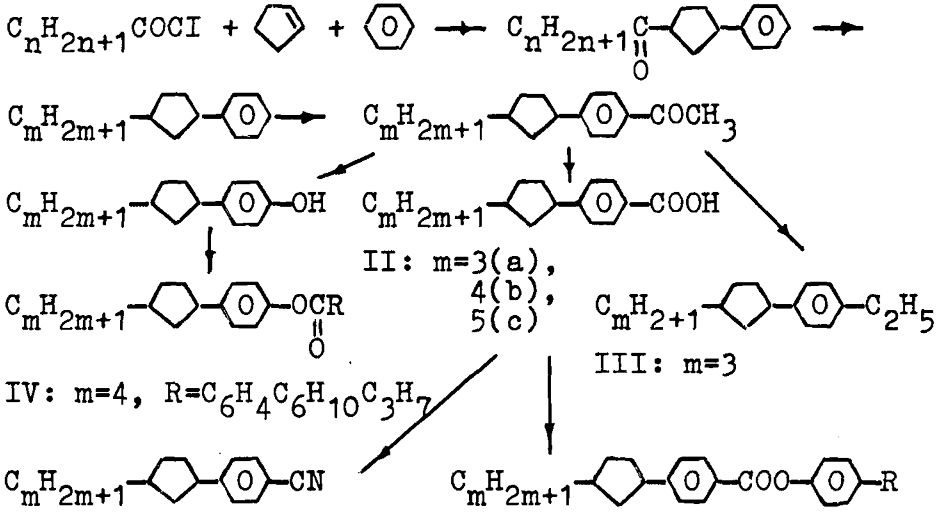
( ) = monotropic transition; * = liquid

As seen from Table I, the mesogens in the cyclopentane series have lower melting points and substantially lower clearing temperatures than the cyclohexane analogues (by 160° C). Only three-ringed esters display liquid crystalline properties, cyanodiphenyl and cyclohexylphenyl esters of methylcyclopentanecarboxylic acid showing only monotropic nematic and smectic phases, respectively. Two-ringed esters Ie, f are nonmesomorphic.

2. Phenylcyclopentanes

To produce cyclopentane analogues of liquid crystalline phenylcyclohexanes, the Nenitzescu method[5] was employed along with a number of standard chemical reactions (Scheme 2). The properties of the resultant mesomorphic phenylcyclopentanes(II-VI) are listed in Table II. As in the case of esters (I), mesogens in the phenylcyclopentane series demonstrate a pronounced depression of clearing temperatures (by 130-160°C) and an appreciable tendency to formation of a smectic phase as compared to cyclohexane analogues. The latter observation makes it possible to compare the effect of introduction into a molecule of the cyclopentane fragment with that of the alkyl radical elongation. As is the case with two-ringed esters (I), cyclopentylbenzonitriles (Y) are nonmesomorphic.

SCHEME 2



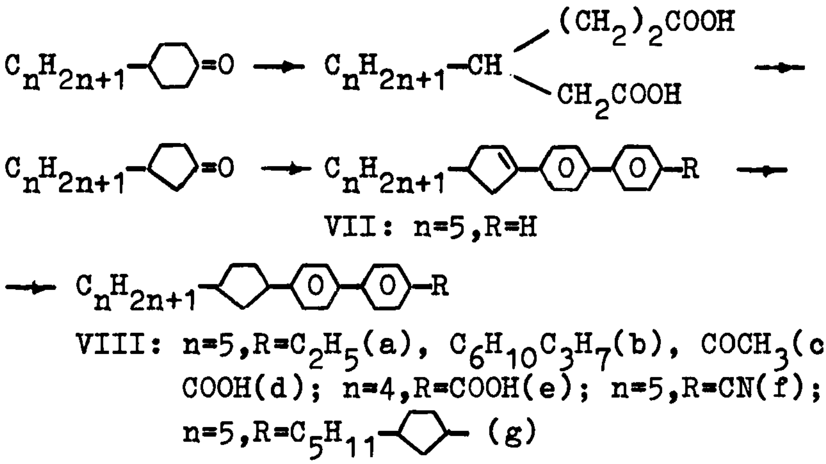
V: m=3(a),5(b)

VI: m=3,$R=C_3H_7$(a); m=4,R=C_3H_7(b); m=4,$R=C_5H_{11}$(c); m=3,R=CN; m=5,R=CN(e); m=5,$R=OC_2H_5$(f); m=3,R=C_6H_4CN(g); m=4,$R=C_6H_4$CN (h); m=4,$R=C_6H_{10}C_3H_7$(i)

3. Cyclopentyldiphenyls

Liquid crystalline cyclopentenyl- (VII) and cyclopentyldiphenyls (VIII) were prepared by organomagnesium synthesis using 3-alkylcyclopentanones that were in turn synthesized by ring narrowing from corresponding 4-alkylcyclohexanone[6] (Scheme 3). A series of standard conversions gave rise to 4'-substituted 3-alkylcyclopentyldiphenyls (VIIIa-g), their constants being given in Table III.

SCHEME 3



VII: n=5,R=H

VIII: n=5,R=C_2H_5(a), $C_6H_{10}C_3H_7$(b), $COCH_3$(c); COOH(d); n=4,R=COOH(e); n=5,R=CN(f); n=5,R=C_5H_{11}–⟨cyclohexyl⟩– (g)

TABLE II Phase transition temperatures for compounds (II-VI) (°C)

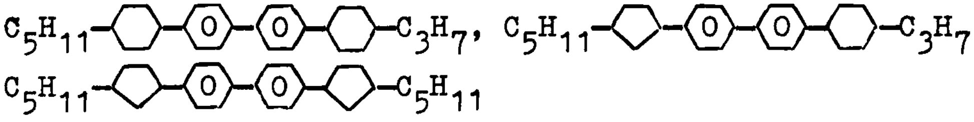
Index	m	R	Cyclopentanes			Cyclohexanes		
			T_{C-S}	T_{C-N} S-N	T_{N-I}	T_{C-S}	T_{C-N} S-N	T_{N-I}
1	2	3	4	5	6	7	8	9
IIa	3	COOH	-	94-6	144	-	217	275
IIb	4	COOH	86	92	165.5	-	201	265
IIc	5	COOH	70.5	80.5	139.5	-	180	265
III*	3	C_2H_5	-	-	-	-	-70	0

TABLE II (continued)

1	2	3	4	5	6	7	8	9
IV	4	$C_6H_4C_6H_{10}C_3H_7$	80_B 84_A	98	168.5			
Va*	3	CN	-	-	-	-	43	45
Vb*	5	CN	-	-95**	-	-	31	55
VIa	3	$COOC_6H_4C_3H_7$	-	18.4	34.5	-	89	186
VIb	4	$COOC_6H_4C_3H_7$		40.8	52	86	90	176
VIc	4	$COOC_6H_4C_5H_{11}$	41	51	86.5	83	109	165
VId	3	$COOC_6H_4CN$	55	60	90	-	122	227
VIe	5	$COOC_6H_4CN$	-	55	81	-	108	217
VIf	5	$COOC_6H_4OC_2H_5$	-	50.7	78.3			
VIg	3	$COOC_6H_4C_6H_4CN$	100	104.5	264	-	165	280
VIh	4	$COOC_6H_4C_6H_4CN$	105	148	245			
VIi	4	$COOC_6H_4C_6H_{10}C_3H_7$	106	114	214			

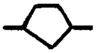
* = liquid; ** = apparent clearing temperature estimated in the mixtures with liquid crystalline azoxy compounds.

As with the considered cyclopentane derivatives, mesomorphic cyclopentyldiphenyls have depressed clearing temperatures of ~ 125-160°C and a tendency to a narrower nematic phase range and a wider smectic phase range. These properties are particularly marked in the series:



when the cyclohexane fragment is sequentially replaced by a cyclopentane one.

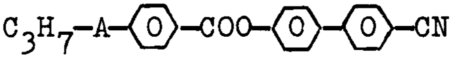
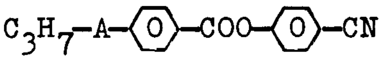
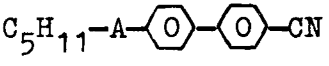
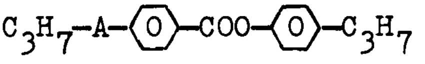
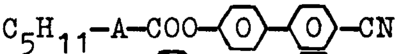
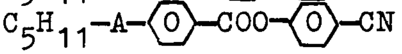
TABLE III Phase transition temperatures for compounds VII, VIII (°C)

Index	n	R	Cyclopentanes			Cyclohexanes		
			T_{C-S} S_1-S_2	T_{C-N} S-N	T_{S-I} N-I	T_{C-N} S_1-S_2	T_{C-N} S-N	T_{N-I}
VII	5	H	65	-	93			
VIIIa	5	C_2H_5	20	-	37.5	34	146	164
VIIIb	5	$C_6H_{10}C_3H_7$	20	165.5	172	55	251	311
			163_A			228_A		
VIIIc	5	$COCH_3$	88_A	--	98			
VIIId	5	COOH	155	242	265			
			178_A					
VIIIe	4	COOH	141	235	258			
VIIIf	5	CN	-	50.5	61	-	94	219
VIIIg	5	C_5H_{11}- 	20	-	73			
			30_A					

Decreased thermal stability of the liquid crystalline phase in cyclopentane derivatives is attributable not only to disturbed linearity in its 1,3-disubstituted compounds but also to their conformational heterogeneity. As shown by double ^1H NMR, hydrogen atoms have mainly an axial configuration, i.e. cyclopentane substituents are diequatorially directed. In addition, compounds Ia and VIIIf were found to have 10-15% of axial-equatorial conformer.

Table IV presents the dielectric properties of mesomorphic cyclopentanes versus cyclohexane analogues.

TABLE IV Dielectric properties of cyclohexane and cyclopentane derivatives

No.	Structural formula	A	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	T_m°C
1		C_5H_8	37.2*	9.7*	27.5*	25
2		C_6H_{10}	36.3*	9.8*	26.5*	25
3		C_5H_8	36.8*	12.9*	23.9*	25
4		C_6H_{10}	37.1*	8.3*	28.8*	25
5		C_5H_8	22.7*	9.5*	13.2*	25
6		C_6H_{10}			12.0**	20
7		C_5H_8	4.8	4.4	0.4	20
8		C_6H_{10}			0.4**	20
9		C_5H_8	13.0	6.8	6.2	τ=0.96
10		C_5H_8	20.6	9.5	11.1	τ=0.96

* as calculated in terms of a mixture (10%) with cyanodiphenyls

** "Merck" data

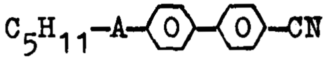
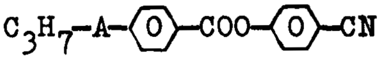
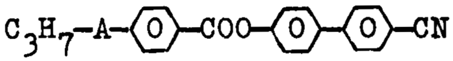
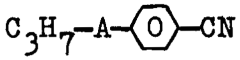
$\tau = T_{measurement}$, K/T_{N-I}, K

Table IV shows that these parameters are comparable. Moreover, the replacement of the cyclohexane ring by a cyclopentane one results in a decrease in viscosity (Table V).

4. Cyclopentylarylmethanes and Cyclopentylarylethanes

An attempt was made to level the geometric distortion of 1,3-disubstituted cyclopentanes by inserting a methylene and ethylene bridge between the 5-membered and aromatic rings (Schemes 4 and 5).

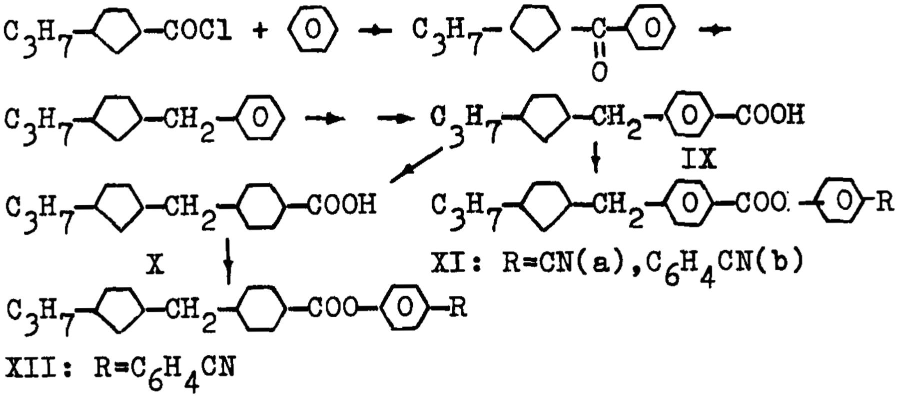
TABLE V Viscosity of cyclohexane and cyclopentane derivatives

No.	Structural formula	A	ν, mm^2/s	T_m, °C
1		C_5H_8	62*	20
2		C_6H_{10}	90**	20
3		C_5H_8	80*	40
4		C_6H_{10}	100**	40
5		C_5H_8	165*	40
6		C_6H_{10}	200**	40
7		C_5H_8	11	20
8		C_6H_{10}	20**	20

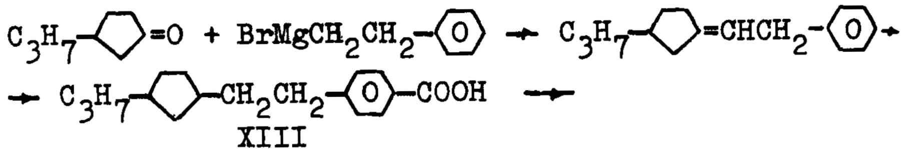
* as calculated in terms of a mixture (10%) with cyanodiphenyls

** "Merck" data

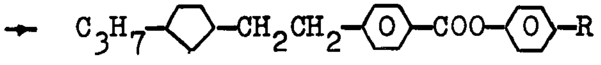
SCHEME 4



SCHEME 5

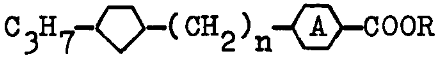


SCHEME 5 (continued)



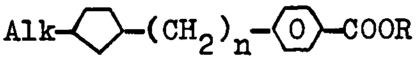
XIV: R=CN(a), C_6H_4CN(b)

TABLE VI Effects of polymethylene bridge on temperature properties of cyclopentanes (IX-XIV)



Index	R	n	A	Phase transition temperatures, °C			Mesophase range, °C
				T_{C-S}	T_{C-N} S-N	T_{S-I} N-I	
IX	H	1	C_6H_4	-	114	118	4
X	H	1	C_6H_{10}	20	-	35	15
XIa	C_6H_4CN	1	C_6H_4	(38)	-	48	
XIb	$C_6H_4H_4CN$	1	C_6H_4	93	129	217	124
XII	$C_6H_4C_6H_4CN$	1	C_6H_{10}		177	203	130
XIII	H	2	C_6H_4	-	210	214	4
XIVa	C_6H_4CN	2	C_6H_4	87	91	167	80
XIVb	$C_6H_4C_6H_4CN$	2	C_6H_4	78	150	238	160

Thus, comparing with appropriate cyclopentylbenzoic acid and its derivatives, the thermal stability of the compounds:



may be arranged as follows: n=2 > n=0 > n=1. In fact, the cyclopentylaryl molecule insertion between two cycles of the methylene link causes the most serious disturbance of its geometry while the introduction of an even ethylene chain generally yields a positive result.

CONCLUSION

Our work provided a wide range of cyclopentane mesogens Their properties were compared with those of cyclohexane analogues. Liquid crystalline cyclopentanes were found to be a mixture of conformational isomers, which may lead to a considerable depression of their clearing temperatures. However, lower melting points and decreased kinematic viscosity of the novel mesogens versus cyclohexane analogues do not rule out the possibility of their usage in special purpose liquid crystalline materials.

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