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Liquid Crystalline Phenylcyclohexanes with A Lateral Methyl Substituent

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LIQUID CRYSTALLINE PHENYLCYCLOHEXANES WITH A LATERAL METHYL SUBSTITUENT

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Abstract With several methods, a large number of liquid crystalline compounds were obtained, which contained a cyclohexane fragment with a lateral methyl substituent. Novel mesogens were studied for chemical, physicochemical, and mesomorphic properties.

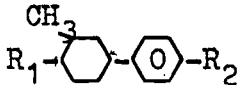
INTRODUCTION

Introduction of a number of substituents across the long axis of a liquid crystalline molecule (a lateral substituent) is a conventional method just as for lowering the melting point of the mesogen studied and reducing its smectogeneity, so also for decreasing its clearing points.[1-4] The effects of the lateral substituent in the cyclohexane fragment on the mesomorphic properties of mesogens are as yet imperfectly understood.[5,6]

EXPERIMENTAL AND DISCUSSION OF RESULTS

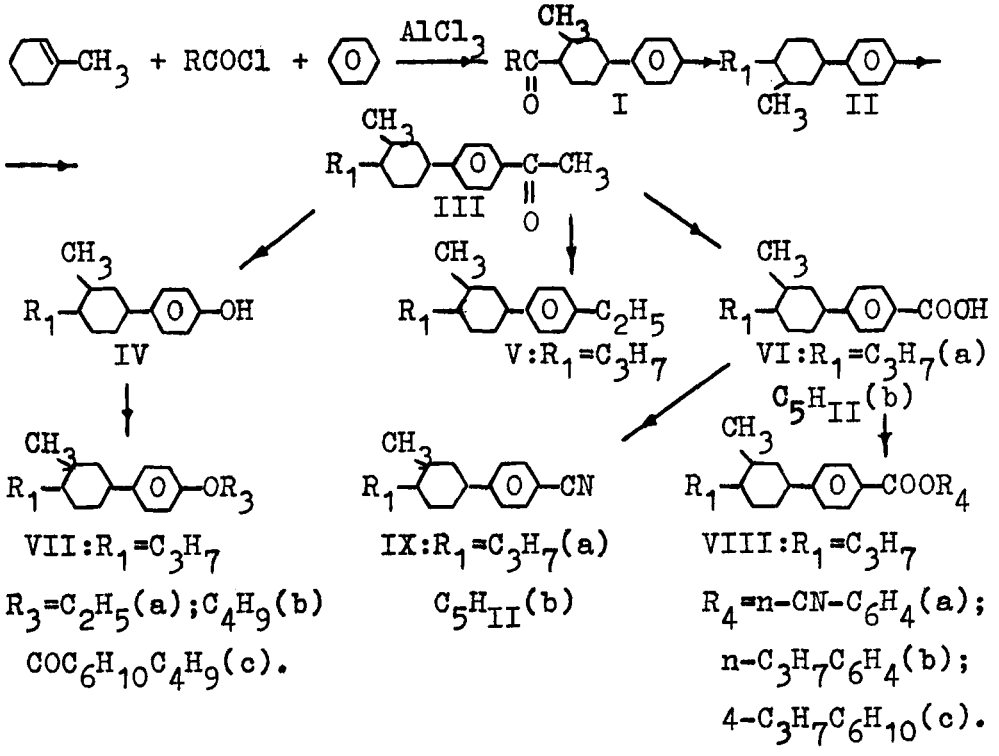
In the present investigation, the Nenitzescu[7] method

was applied to produce a wide range of phenylcyclohexane compounds with a lateral methyl substituent in the saturated cycle.



The mesogens (V-IX) obtained by Scheme 1 via a number of standard conversions simulate all the known types of phenylcyclohexane mesogens that have found wide application (R_1=n-Alk; R_2=n-Alk, $-OR_3$, CN, $COOR_4$).

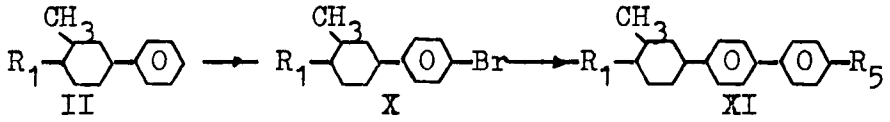
SCHEME 1



Liquid crystalline derivatives of cyclohexyldiphenyl with a lateral methyl substituent (XI) were prepared by Scheme 2 using various modified Grignard's reacti-

ons.

SCHEME 2



II X XI

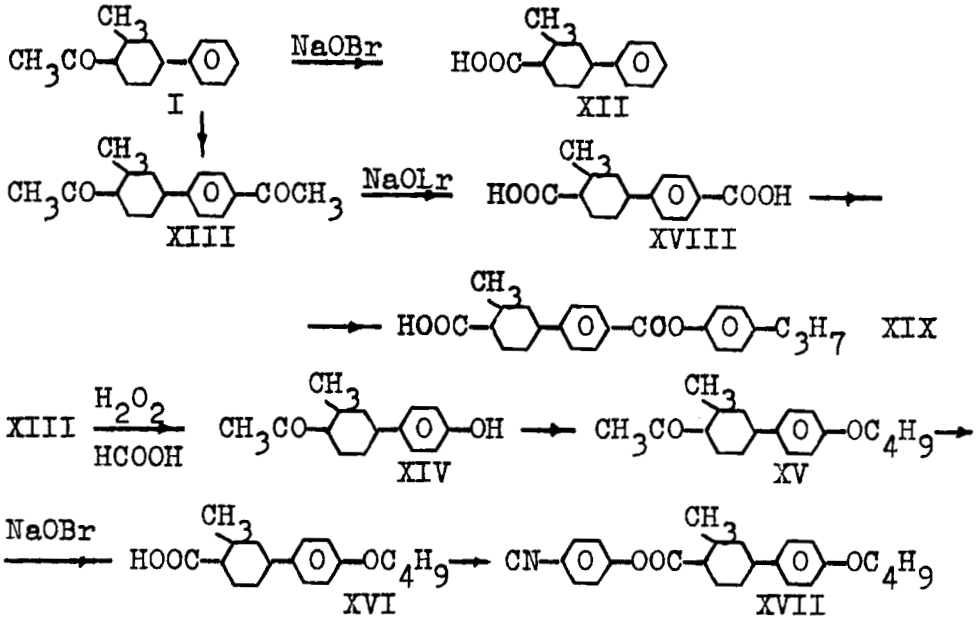
XI: $R_1=C_3H_7$; R_5=CN(a); C_5H_{11}(b); $C_5H_{11}C_6H_{10}$(c);
$R_1=C_5H_{11}$; R_5=CN(d); C_2H_5(e); C_3H_7(f).

The phase transition temperatures for the newly synthesized trisubstituted cyclohexanes and their analogues having no lateral methyl substituents are listed in Table I.

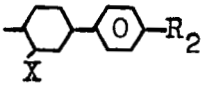
It is of interest to note that introducing a methyl group into the cyclohexane ring, at the position next to the carbon that bears a carbonyl function, causes steric hindrances to a number of reactions. For example, methyl=substituted ketone I, unlike trans-4-phenyl-1-acetylcyclohexane, fails to undergo the Baeyer-Villiger reaction. In contrast, hypobromite oxidation of ketone I readily yields acid (XII) (Scheme 3). Using acid XII as an example, the equatorial arrangement of the methyl substituent in the cyclohexane ring was evidenced by double ^{1}H NMR. The above experimental findings enabled us to perform selective oxidation of the acetyl substituent in the aromatic diketone XIII nucleus and, from the resultant 2-methyl-4(4-hydroxydiphenyl)1-acetylcyclohexane (XIV) to prepare a new liquid crystalline acid XVI, on whose basis mesomorphic ester XVII was obtained. Diketone XIII oxidation gave rise to diacid XVIII. An attempt to produce diester with 4-propylphenol from it also indicated a screening effect of the lateral methyl substi-

tuent against esterification of the adjacent carbonyl site. As a result, mesomorphic acid XIX, an esterification product, was isolated from a more active and sterically unhindered carboxy group (Scheme 3).

SCHEME 3



The phase transition temperatures for all the resultant mesogens are listed in Table I. For comparison, the literature data[1] and those from the "Merck" prospects for their unsubstituted analogues are given.

TABLE I Phase transition temperatures for compounds with the general formula 

No	R_1	R_2	X	T_{C-S} / T_{C-N}	T_{S-N}	T_{N-I}
1	2	3	4	5	6	7
V	C_3H_7	C_2H_5	CH_3			-115

TABLE I (continued)

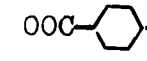
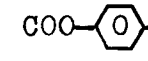
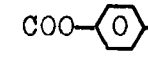
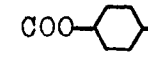
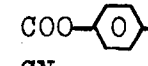
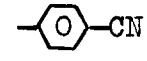
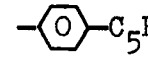
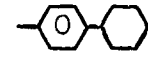
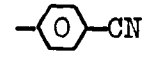
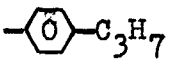
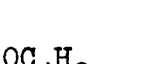
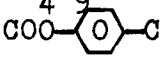
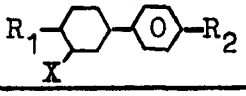
I	2	3	4	5	6	7
			H			- 70
VIa	C_3H_7	COOH	CH_3	165	-	236
			H	217	-	275
VIb	C_5H_{11}	COOH	CH_3	138	-	221
			H	180	-	265
VIIa	C_3H_7	OC_2H_5	CH_3	liquid		
			H	41	-	37
VIIb	C_3H_7	OC_4H_9	CH_3	liquid		
			H	36	-	32
VIIc	C_3H_7		CH_3	54.6	-	122.5
			H	64	116	189
VIIIa	C_3H_7		CH_3	80	-	162
			H	122	-	227
VIIIb	C_3H_7		CH_3	65	-	107
			H	89	-	186
VIIIc	C_3H_7		CH_3	48	-	95.5
			H	95	(93)	160
VIIId	C_3H_7		CH_3	92.2	-	155
IXa	C_3H_7	CN	CH_3	32	-	- 27
			H	43	-	45
IXb	C_5H_{11}	CN	CH_3	34	-	- 37
			H	30	-	55
XIa	C_3H_7		CH_3	102	-	176
			H	130	-	230
XIb	C_3H_7		CH_3	34	55	91
			H	43	150	167
XIc	C_3H_7		CH_3	40	177	245
			H	61	251	311
XId	C_5H_{11}		CH_3	97	-	158
			H	95	-	219

Table I (continued)

1	2	3	4	5	6	7
XIe	C_5H_{11}		CH_3	40	-	90.5
			H	34	146	164
XIf	C_5H_{11}		CH_3	20	43.5	98.5
			H	14	-	158
XVI	HOOC	OC_4H_9	CH_3	99.7	107.1	160.7
XVII	NC  OOC	OC_4H_9	CH_3	89.3	94.7	126.7
XIX	HOOC	COO 	CH_3	215	223.5	253

The data given in Table I show that the introduction of a lateral methyl group in the cyclohexane ring as in the aromatic ring generally results in a reduction of melting and **smectic-nematic transition temperatures** and, to a greater extent, **clearing** points of the new mesogens as compared to their unsubstituted analogues.

Table II presents dielectric parameters for some of the resultant mesogenes. For comparison, constants for **their unsubstituted analogues are given.**

TABLE II Dielectric properties of compounds with the general formula 

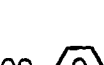
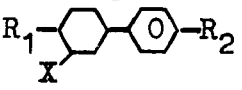
R_1	R_2	X	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	τ	T,°C
1	2	3	4	5	6	7	8
C_5H_{11}		CH_3	11.0	4.6	6.4	0.9	
		CH_3			13.4*		20
		H			12.0		20
C_3H_7	COO 	CH_3	19.8	6.1	13.7	0.85	
		CH_3	18.5	6.4	12.1	0.9	
		CH_3			33.5*		20

TABLE II (continued)

1	2	3	4	5	6	7	8
C_3H_7	COO-⟨O⟩-OC_2H_5	CH_3	4.11	4.21	-0.10	0.85	
		CH_3	3.95	4.02	-0.07	0.9	
C_3H_7	COO-⟨⟩-C_3H_7	CH_3	3.53	4.40	-0.87	0.85	
		CH_3	3.46	4.20	-0.74	0.9	
		H	3.37	3.69	-0.32	0.9	
		CH_3	3.41	4.00	-0.59	0.95	
C_3H_7	COO-⟨O⟩-C_3H_7	CH_3	4.16	3.85	0.31	0.85	
		CH_3	4.00	3.71	0.29	0.9	
		CH_3	3.81	3.60	0.21	0.95	
		CH_3			0.36**		20
		H			0.40***		20
C_3H_7	OOC-⟨⟩-C_4H_9	CH_3	2.73	3.07	-0.34	0.85	
		CH_3	2.69	2.97	-0.28	0.9	
		CH_3	2.65	2.85	-0.20	0.95	
C_3H_7	CN	CH_3			29.8*		20
		H			27.6		20
C_5H_{11}	CN	CH_3			20.6*		20
		H			26.5		20

$\tau = T_{meas.}$, K/T_{N-I}, K; * Calculated in terms of mixture with ZLI-1132 (10%); ** Calculated in terms of mixture with ZLI-3086 (10%); *** "Merck" data

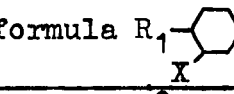
Analysis of the data from Table II indicates a similar behaviour of the dielectric properties displayed by the compared compounds. The optic parameters for our synthesized methyl-substituted cyclohexanes are listed in Table III. For comparison, constants for their unsubstituted analogues are given.

TABLE III Optic properties of compounds with the general formula 

R_1	R_2	X	n_e	n_o	Δn	τ	T°C
C_3H_7	COO-⟨O⟩-CN	CH_3			0.154*		20
C_3H_7	CN	CH_3			0.05*		20
		H			0.13***		20
C_5H_{11}	CH_3	CH_3			0.05*		20
		H			0.13***		20
C_5H_{11}	-⟨O⟩-CN	CH_3			0.135*		20
		H			0.19***		20
C_3H_7	COO-⟨O⟩-C_3H_7	CH_3	1.6090	1.4970	0.1120	0.9	
		CH_3			0.092**		20
		H			0.14***		20
C_3H_7	COO-⟨⟩-C_3H_7	CH_3	1.5682	1.4850	0.0832	0.88	

(Notes are the same as for Table II).

It is seen from Table III that the new mesogens have lower optic anisotropic values than their unsubstituted analogues. In addition, the new mesogens have higher kinematic viscosity than their unsubstituted analogues (Table IV).

TABLE IV Kinematic viscosity values for compounds with the general formula 

R_1	R_2	X	ν, mm^2/s, 20°C
C_3H_7	C_2H_5	CH_3	6.6
		H***	4.0
C_3H_7	COO-⟨O⟩-C_3H_7	CH_3**	115.0
		H***	60.0

(Notes are the same as for Table II).

CONCLUSION

The results presented provide evidence that our synthesized mesogens containing a methyl-substituted fragment are suitable components for the development of liquid crystalline materials applicable to electro-optic devices.

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