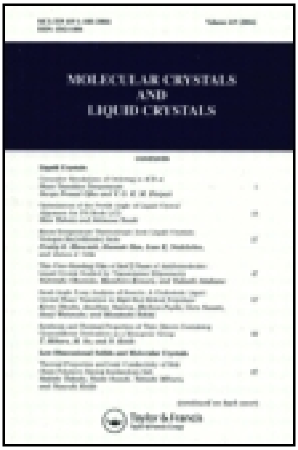

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Cycloalkanoylcontaining Mesogens

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CYCLOALKANOYLCONTAINING MESOGENS

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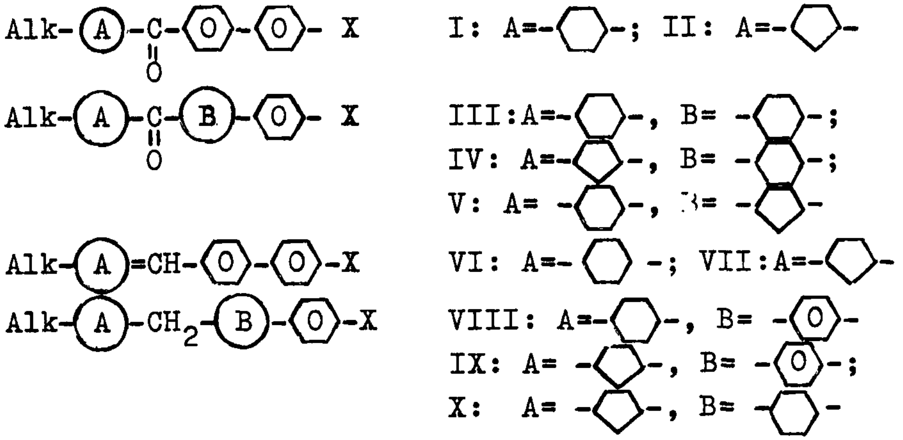
Abstract A number of cyclohexyl- and cyclopentyl-containing mesogens with a bridge group that is a trigonal or tetrahedral carbon atom were synthesized and examined for their properties.

INTRODUCTION

The direction of bonds at carbonyl carbon is 120°, i.e. a molecule containing the keto group shows a failure to satisfy one of the major requirements of thermotropic mesogens , that is a need for linear, geometrically anisotropic structure. However, there is evidence that liquid crystalline properties are shown by a number of ketones with a terminal acyl substituent such as diphenyls acylated with sufficiently long aliphatic acids[1], n-substituted aceto- and propiophenones[2]. We demonstrated that compounds with the central keto group alkylcyclohexanoyldiphenyls (I) also have a narrow smectic phase A at sufficiently long terminal substituents in the saturated and aromatic portions, whereas their aromatic analogues are nonmesomorphic[3,4].

EXPERIMENTAL

In the present investigation, Friedel-Crafts' acylation of diphenyl yielded various cycloalkanoyldiphenyls (I, II), and the Nenitzescu method[5] was employed by using chloric anhydrides of alkylcycloalkanecarboxylic acids, cycloalkenes and benzene were used to synthesize saturated analogues (III-V). Reduction of ketones (I, II) with lithium alumohydride followed by dehydration, depending on a dehydrating agent, leads either to compounds (VI, VII) with a exocyclic double bond (dehydration with $KHSO_4$), or mainly to isomeric cycloalkenylarylmethanes with a double bond in the cycle (dehydration with toluene sulphonic acid). The structure of cyclohexylidene- (VIb) and cyclopentylidenemethane (VIIb) is evidenced by IR (conjugated double bond, 1665 cm^{-1}) and ^1H NMR (=C<u>H</u>, δ: 6.43) spectra. Isomeric cyclohexenylmethane has a proton signal at the double bond shifted to a stronger field (δ: 5.73). Kishner-Wolff's reduction of ketones (I, IV) yields compounds (VIII, IX), respectively). It should be noted that the cyclopentane derivatives (II) are mixtures of stereoisomers with predominant 1,3-diequatorial (> 90% as shown by ^1H NMR data).



Phase transition temperatures for the novel mesogen are given in Table I, dielectric and optic parameters for some of them are given in Table II (they were calculated via a mixture with ZLI-1132 (10%) at

TABLE I Phase transition temperatures for compounds I-X (°C)

Index	Alk	X	T_{C-S} S_1-S_2	T_{S-N} C-N	T_{S-I} N-I C-I
1	2	3	4	5	6
Ia	C_6H_{13}	OC_7H_{15}	104_A	-	110
Id	C_4H_9	Br	-	-	112-114
Ie	C_4H_9	CN	-	-	111
IIa	C_4H_9	Br	$(64)_A$	-	68
IIb	C_5H_{11}	Br	57	-	66
IIc	C_4H_9	CN	$(60)_A$	66-67	80
IId	C_5H_{11}	CN	68.7	72.1	81.5
IIe	C_4H_9	OC_7H_{15}	96.5	-	129.2
IIf	C_4H_9	$OCOC_8H_{17}$	$45.2_E, 84_A$	-	125.3
IIIa	C_4H_9	COOH	-	-	235
IVa	C_5H_{11}	COOH	130;165; 180_A	-	216
IVb	C_5H_{11}	$COOC_6H_4OC_7H_{15}$	$137_C;143_A$	-	216
V	C_4H_9	COOH	-	161	179
IIIb	C_4H_9	CN	-	-	118
VIa	C_6H_{13}	OC_7H_{15}	-	-	68-70
VIb	C_4H_9	CN	-	-	30-32
VIIa	C_4H_9	Br	$109_C, 116_A$	-	136
VIIb	C_4H_9	CN	-	85	195
VIIc	C_4H_9	OC_7H_{15}	52; 81_A	-	140
VIId	C_5H_{11}	CN	-	93	165
VIIIa	C_4H_9	Br	-	-	83.5-84.5
VIIIb	C_4H_9	CN	-	-	83-84
VIIIc	C_6H_{13}	OC_7H_{15}	-	-	72.6-73.4
IXa	C_3H_7	COOH	-	114	118
IXb	C_3H_7	$COOC_6H_4C_6H_4CN$	93_A	129.5	217.4
Xa	C_3H_7	COOH	20	-	35

TABLE I (continued)

1	2	3	4	5	6
Xb	C_3H_7	$COOC_6H_4C_6H_4CN$	73_A	177	205

( ) = monotropic transition.

20°C **; the sign • - means the direct measurements).**

RESULTS AND DISCUSSION

The data given in Table make us conclude that a combination of two 6-membered cycles (saturated or aromatic) linked with a trigonal (including carbonyl) or tetrahedral carbon atom is not mesogenic. On the contrary, the cyclopentane analogues show liquid crystalline properties that vary with the position of a 5-membered cycle. The acid (IVa) with a terminal 5-membered cycle and an internal cyclohexane ring is characterized by a set of smectic phases in a fairly wide temperature range (86°C), the inverse combination results in a purely nematic compound (V). Finally, the acid (IIIa) with two 6-membered cycles is not mesomorphic. Thus, the terminal 5-membered cycle is similar, in terms of its effects, to elongation of the alkyl substituent. But introducing this non-linear fragment into the liquid crystalline molecule leads to disturbed geometric anisotropy, lower intermolecular interactions and, thus, changing the type of a mesophase and reducing its thermal stability. A combination of the terminal cyclopentane ring with the central methylene group produces mesogens (X) with predominant smectic properties in case of the central saturated 6-membered cycle and with prevalent nematic properties in case of the central aromatic ring (IX).

TABLE II Physicochemical parameters for compounds I-VII

Index	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\Delta\varepsilon$	n_e	n_o	Δn
Id	23.8	7.4	16.4			
IIa	29.8	9.6	20.2	1.7016	1.5380	0.1636
IIb	23.8	7.9	15.9	1.6967	1.5350	0.1635
Ie	29.7	7.2	22.5	1.6716	1.5430	0.1286
IId*	25.1	6.7	18.4			
IId*	7.3	6.2	1.1			
IIIb	27.6	7.1	20.5	1.5666	1.5030	0.0636
VIIc	31.7	7.2	24.5	1.6366	1.5230	0.1136
VIIb*	15.4	4.6	10.8			
VIIb*	16.0	4.5	11.5			
Vb	28.0	8.5	19.5	1.6266	1.5030	0.1236
Vc	28.3	7.9	20.4	1.6376	1.5120	0.1256

As seen from Table II, compounds I and II have comparable dielectric properties, the values for optic anisotropy Δn for cyclopentane derivatives being greater than that for cyclohexane derivatives: $\Delta n_{II} > \Delta n_{I}$. Reduction of ketones II to compounds VII causes a decrease in the optic anisotropy: $\Delta n_{II} > \Delta n_{VII}$. As compared to their saturated analogues III, compounds I have higher values of dielectric anisotropy $\Delta\varepsilon$ and optic anisotropy Δn, as was expected.

Thus, the present study shows that modifying the size and position of alicycle and the nature of the central group, one may obtain novel mesogens with predictable properties.

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