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Liquid-crystalline 1,4-disubstituted cycloheptanes

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A new series of liquid-crystalline alicyclic compounds, the 1,4-disubstituted cycloheptane derivatives, have been synthesized. The physicochemical and electrooptical characteristics of the new mesogens have been compared with those of analogues in the cyclopentane and cyclohexane series, including cyclohexanes having a side methyl group.

The fact that the mesomorphic derivatives in the alicyclic series are of promise is evidenced by the wide use of *trans*-1,4-disubstituted cyclohexanes in liquid-crystalline materials designed for various applications. This is associated with the unique set of valuable properties in these mesogens, such as low viscosity, low optical anisotropy, good solubility and their mesophase range. The representatives of the alicyclic series with a saturated ring of another size may be expected to behave in the same way. These considerations have recently given impetus to some synthetic studies with cyclopentane mesogens [1, 2], 1,4-disubstituted cyclohexanes having a side methyl group at positions 2 and 3 [3–7]. and to the present investigation which deals with the synthesis of 1,4-disubstituted cycloheptanes.

Table 1 compares the transition temperatures for four series of alicyclic mesogens such as the 1,3-disubstituted cyclopentanes (**I**), 1,4-disubstituted cyclohexanes (**II**), 3-methyl-substituted 4-alkylcyclohexanes (**III**), and the newly synthesized 1,4-disubstituted cycloheptanes (**IV**). It should be noted that all of these compounds may exist as geometric *cis–trans* isomers, and, unlike the respective cyclohexanes (**II, III**), the mesogens having five and seven membered cycles are less subject to separate into pure *cis–trans* isomers. Depending on the structure, the end product may contain as much as 10 per cent *cis* isomer as evidenced by double ^{1}H NMR [1] and by gas liquid chromatography (see table 1). It is likely that we have observed transition temperatures which are too low in mesomorphic cycloheptanes that are, in the general case, in a position midway between cyclopentanes (**I**) and 3-methylcyclohexanes (**III**).

Molecular models indicate that the molecular distortion from linearity in equatorial 1,4-disubstituted cycloheptanes is less than that in the analogous 1,3-*e*,*e*-disubstituted cyclopentanes and, in contrast, more than that in 3*r*-methyl-4*t*-alkyl-1*c*-arylcyclohexanes (though the latter have a wide aliphatic fragment due to the side methyl substituent). These geometrical factors have been consistently reflected in the transition temperatures observed experimentally.

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Table 1. Transition temperatures for cyclopentanes (**I**), cyclohexanes (**II**), 2-methyl-cyclohexanes (**III**) and cycloheptanes (**IV**).

R_1-ⓝ-R_2.

Compound	*n*	R_1	R_2	Phase *X* T_{XY}/°C Phase *Y*
IIa	6	C_3H_7	-OOC-ϕ-cychex.-C_5H_{11}	C [55] S 67 N 154 I
IVa†	7	C_3H_7	-OOC-ϕ-cychex.-C_5H_{11}	C <20 N 32·7 I
IVb†	7	C_3H_7	-OOC-ϕ-ϕ-C_5H_{11}	C 41·7 S 44·3 N 52·0 I
Ic	5	C_3H_7	-ϕ-COOH	C 94–96 N 144 I
IIc	6	C_3H_7	-ϕ-COOH	C 217 N 275 I
IIIc	6(CH_3)	C_3H_7	-ϕ-COOH	C 165 N 236 I
IVc	7	C_3H_7	-ϕ-COOH	C 104·7 S 146·7 N 211·9 I
Id	5	C_3H_7	-ϕ-COO-ϕ-C_3H_7	C <20 N 40 I
IId	6	C_3H_7	-ϕ-COO-ϕ-C_3H_7	C 78 S 87 N 186 I
IIId	6(CH_3)	C_3H_7	-ϕ-COO-ϕ-C_3H_7	C 65 N 107 I
IVd	7	C_3H_7	-ϕ-COO-ϕ-C_3H_7	C 51·5–52 S 54 N 77·4 I
IVe‡	7	C_3H_7	-ϕ-COO-ϕ-F	C [70] N 80–82 I
If	5	C_3H_7	-ϕ-COO-ϕ-ϕ-CN	C 100 S 100·4 N 264 I
IIf	6	C_3H_7	-ϕ-COO-ϕ-ϕ-CN	C 165 N 280 I
IVf	7	C_3H_7	-ϕ-COO-ϕ-ϕ-CN	C 132–134 S_A 190 N 232–233 I
Ig	5	C_5H_{11}	-ϕ-ϕ-$COCH_3$	C 88 S_A 96 I
IIg	6	C_5H_{11}	-ϕ-ϕ-$COCH_3$	C 122·5 S 136 I
IVg†	7	C_5H_{11}	-ϕ-ϕ-$COCH_3$	C 88 S_A 94 N 112 I
IVh†	7	C_3H_7	-ϕ-ϕ-$COCH_3$	C 84 N 98 I
Ii	5	C_5H_{11}	-ϕ-ϕ-C_2H_5	C <20 S_A 37·5 I
IIi	6	C_5H_{11}	-ϕ-ϕ-C_2H_5	C 34 S 146 N 164 I
IIIi	6(CH_3)	C_5H_{11}	-ϕ-ϕ-C_2H_5	C 34 S 55 N 91 I
IVi†	7	C_5H_{11}	-ϕ-ϕ-C_2H_5	C 65 N 100·3 I
IIk	6	C_3H_7	-ϕ-ϕ-CN	C 133 N 230 I
IIIk	6(CH_3)	C_3H_7	-ϕ-ϕ-CN	C 102 N 176 I
IVk§	7	C_3H_7	-ϕ-ϕ-CN	C 65–67 N 104·5–106 I
Il¶	5	C_5H_{11}	-ϕ-ϕ-CN	C 49·5 N 60·2 I
IIl	6	C_5H_{11}	-ϕ-ϕ-CN	C 96 N 222 I
IIIl	6(CH_3)	C_5H_{11}	-ϕ-ϕ-CN	C 70 S 97 N 158 I
IVl§	7	C_5H_{11}	-ϕ-ϕ-CN	C 63 S 75·4 N 106·7 I
IVm	7	C_5H_{11}	-ϕ-ϕ-COOH	C 232 S 247 N 294 I
IVn†	7	C_5H_{11}	-ϕ-ϕ-COO C_2H_5	C 44 S 98·7 N 102·5 I
IVo§	7	C_3H_7	-ϕ-ϕ-OOC-cychex.-C_4H_9	C 55·7 S_I 122·9 S_{II} 134·6 N 230 I
IVp	7	C_5H_{11}	-ϕ-ϕ-CO NH_2	C 223 S 236 N 247 I

ϕ and cychex. denote phenyl and cyclohexane rings, respectively.

† 10 per cent of *cis* isomer (by GLC)

‡ 1 per cent of *cis* isomer (by GLC).

§ 4–5 per cent of *cis* isomer by (GLC).

¶ 10 per cent of *cis* isomer (by ^{1}H NMR [1]).

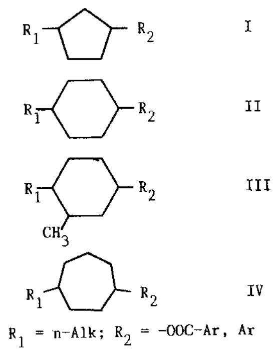
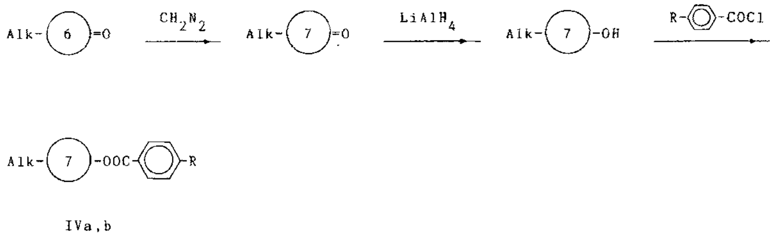


Table 2. Dielectric and optical properties of compounds I–IV

Compound	$\Delta\varepsilon$	Δn	T/T_{NI}
IVa	−0·6	0·056	0·96
IIa	−1·2†	0·080†	
IVb	−0·5		0·95
IVd	+0·23		0·97
IVf	+13·1‡	0·108‡	0·95
IVk	+8·4	0·116‡	0·95
IVl	+6·5	0·110‡	0·95
Il	+10·1‡	0·075‡	0·95
IIl	+9·1	0·114‡	0·95
IIIl	+3·5	0·050‡	0·95

† Merck Liquid Crystals.

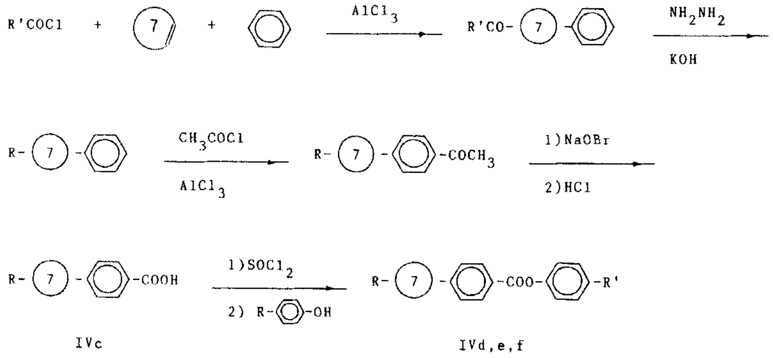
‡ Obtained by extrapolation from the mixture with ZLI-1132 (10 per cent).



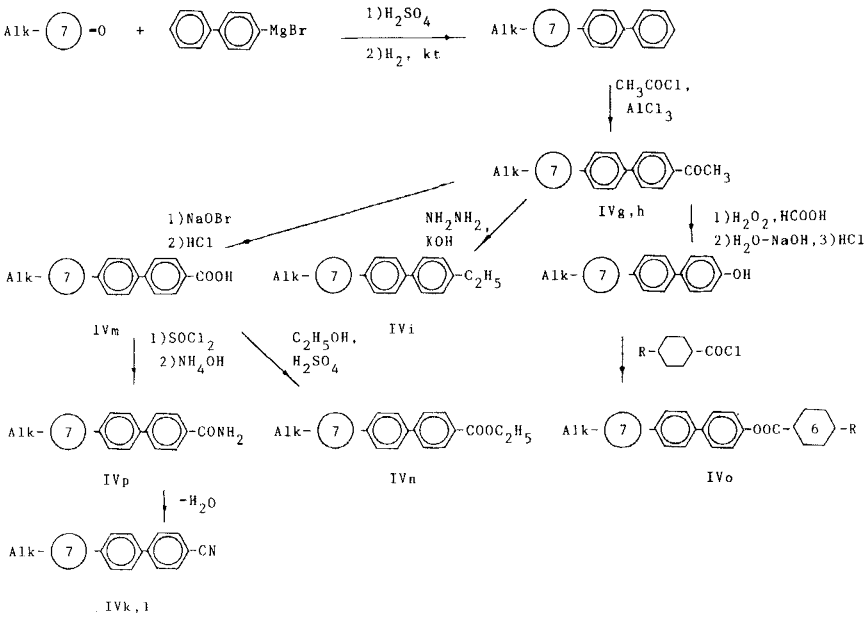
Scheme 1.

It is of interest to follow a change in the type of mesophase for pairs of analogues in the biphenyl and phenylcyclohexane series (**IVa** and **IVb**, respectively, see table 1), as well as in the homologous pairs of ketones (**IVg** and **h**) and nitriles (**IVk** and **l**). In most cases the introduction of a cycloheptane fragment promotes smectic phase formation. The presence of high temperature smectic and nematic phases was found, unexpectedly, in the cycloheptane amide (**IVp**). The homologous amide with a shorter propyl chain has no mesophase (mp = 249°C).

Table 2 gives the dielectric and optical properties of the cycloheptanes synthesized, as well as those of cyclohexanes, cyclopentanes, and 3-methyl-substituted cyclohexanes



Scheme 2.



Scheme 3.

(I–III) for comparison. The table indicates that the dielectric anisotropy $\Delta\varepsilon$ increases with reduction in the volume of the aliphatic fragment in these derivatives according to: **IV** < **III** < **II** < **I**. The optical anisotropy Δn of the compounds having formula **I**–**IV** increases in the order: **III** < **I** < **II** $\simeq$ **IV**. The nature of the changes is determined by the respective alterations in the polarizability of the compounds.

The cycloheptane derivatives were obtained via a complex multistage synthesis, by extending the ring in the corresponding alkylcyclohexanones with diazomethane [8], followed by purification of the seven membered ketones through semicarbazones. With the Nenitzescu method [9], phenylcycloheptane compounds were synthesized from cycloheptenes, benzene, and alkanoyl chlorides, followed by soft sodium boron hydride reduction of the resultant ketone via tosyl hydrazones [10]. In high alkaline media (Wolff–Kishner reduction), cycloheptylketones were unstable and underwent isomerization. Biphenylcycloheptanes were prepared by organomagnesium synthesis from the corresponding cycloheptanones. The liquid-crystalline derivatives were produced from these compounds by the standard procedures (see schemes 1–3) and purified by multiple recrystallization until the transition temperatures were constant and the elemental analyses were satisfactory.

The transition temperatures for the cycloheptane mesogens were measured by a Mettler-FP-5 apparatus with a polarizing microscope. The structure of the resultant compounds was evidenced by infrared spectroscopy. The infrared spectra were recorded by a Shimadzu IR-435 spectrophotometer with film and KBr discs. The purity of the intermediates and end products was monitored by gas liquid chromatography. The analysis was made by using a Colour-100 apparatus with a plasma ionization detector, a 1–2 m column, the stationary phase 5 per cent XE-60 and SP-2100 on Inerton-Super, the temperature of analysis being 100–280°C. The dielectric and optical parameters of the liquid crystals were determined by the methods described in detail in [11].

References

[1] Karamysheva, L. A., Geyvandova, T. A., Agafonova, I. F., Roitman, K. V., Torgova, S. I., Geyvandov, R. Ch., Petrov, V. F., Rabinovich, A. Z., and Grebyonkin, M. F., 1990, *Molec. Crystals liq. Crystals,* **191,** 237.

[2] Frach, R., Yahn, K., and Deutscher, H.-J., 1989, *8th Liquid Crystal Conference of Socialist Countries*, Krakow, Abstracts, Vol. 1, A28.

[3] Karamysheva, L. A., Roitman, K. V., Agafonova, I. F., Torgova, S. I., Geyvandov, R. Ch., Petrov, V. F., Grebyonkin, M. F., Bezborodov, V. S., Andryukova, N. P., and Bumagin, N. A., 1990, *Molec. Crystals, liq. Crystals,* **191,** 259.

[4] Pohl, L., Scheuble, B., Hittich, R., Eidenschink, R., Kurmeier, H. A., and Waechtler, A., 1986, *Ger. Offen. D. E.* 3 510 432; *Chem. Abs.*, 106; 59036b.

[5] Bezborodov, V. S., 1987, *Zh. Org. Khim.*, **23,** 1268.

[6] Bezborodov, V. S., 1989, *Zh. Org. Khim.*, **25,** 2399.

[7] Ferrato, J. P., 1987, U.S. Patent 4 659 499; *Chems. Abs.*, 107; 68365f.

[8] Cook, J. W., Raphael, R. A., and Scott, A. I., 1951, *J. chem. Soc.*, p. 695.

[9] Nenitzescu, C. D., and Gavăt, J. G., 1935, *Justus Liebigs Annln Chem.*, **519,** 266.

[10] Caglioti, L., and Grasselli, P., 1964, *Chem Ind.*, 153.

[11] Grebyonkin, M. F., Petrov, V. F., Belyaev, V. V., Pavluchenko, A. I., Smirnova, N. I., Kovshev, E. I., Titov, V. V., and Ivashchenko, A. V., 1985, *Molec. Crystals liq. Crystals,* **129,** 245.