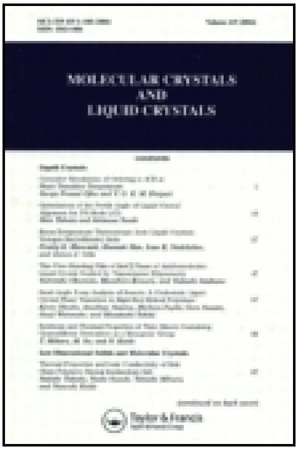

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Liquid Crystalline 6-n-Alkyl-naphthalene-2- and 6-n-Alkyl-trans-Decalin-2-Carboxylates

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Liquid Crystalline 6-*n*-Alkyl-naphthalene-2- and 6-*n*-Alkyl-*trans*-Decalin-2-Carboxylates

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(Received December 21, 1982)

The preparation and liquid crystalline properties of twenty-nine *trans*-decalin-2-carboxylates are described and the esters are found to exhibit wide-range smectic and nematic phases persisting until higher temperatures than those of the corresponding esters containing the *trans*-1,4-disubstituted cyclohexane ring. Compared with analogous naphthalene-2-carboxylates, the clearing points are a little lower, but the melting points are considerably decreased; as a consequence, the decalin esters possess wider mesomorphic temperature ranges.

INTRODUCTION

With the enhanced use of liquid crystals in various electro-optical devices attempts are being made to prepare materials which are nematic at low temperature and which also have high clearing temperatures.

Our previous investigations in this field have dealt with the replacement of aromatic rings by equatorial disubstituted cyclohexane and hetero-alicyclic rings.[1-4] The results indicate that the cyclohexane compounds have lowered melting points and increased clearing points. It is clear therefore that using the non-planar and somewhat flexible cyclohexane ring in such positions has advantageous effects on N-I transition temperatures.

In this paper we examine the effect of changing the naphthalene ring system to a decalin ring system in the following compounds

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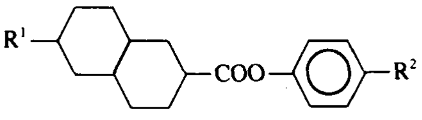
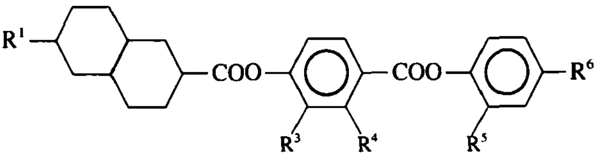
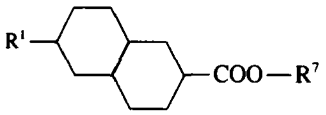


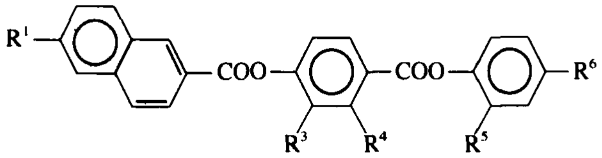
1.1–1.8



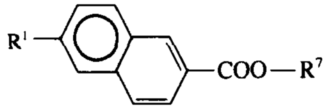
2.1–2.17



3.1–3.4



4.1–4.18



5.1–5.9

R^1 = C_4H_9, C_8H_{17}
R^2 = CN, C_3H_7, $C_6H_{13}O$
R^3 = H, Cl, CH_3, C_2H_5

R^4 = R^5 = H, CH_3
R^6 = CN, C_5H_{11}, $C_nH_{2n+1}O$
R^7 = various ring systems

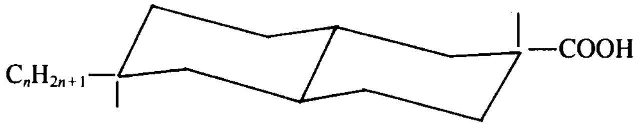
RESULTS AND DISCUSSION:

The naphthalene-2-carboxylic acids were prepared similarly to the procedure described by Coates and Gray.[5] Decalin-2-carboxylic acids were obtained by catalytic high-pressure hydrogenation of naphthalene carboxylic acids. Our knowledge about the general requirements relating to molecular shape of liquid crystals materials makes it obvious that the molecules are markedly elongated and rodlike. This geometry is only given in *trans*-decalins with an equatorial arrangement of substituents in the

2,6-positions. The cyclohexane rings in *trans*-decalin are fused by two equatorial bonds.[6,7] Consequently, any ring conversion would cause these bonds to become axial-axial. This is geometrically impossible, and therefore *trans*-decalin derivatives are conformationally rigid. That means, that every substituent is clearly defined as axial or equatorial, and the latter gives the thermodynamically most stable compounds.

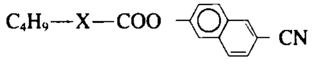
The hydrogenation procedure seemed difficult. Dauben and Hoerger[8] obtained with PtO_2 in acetic acid solution more of the *cis*-product in very low yield, and other authors using Raney-nickel in dioxan and 24 MPa hydrogen pressure obtained only 5,6,7,8-tetrahydronaphthalene-2-carboxylic acid.[9,10]

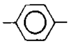
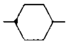
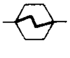
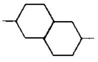
We achieved complete hydrogenation with Raney-nickel, using 15 MPa hydrogen pressure, a temperature of 300°C and a reaction time of about 120 h.[11] The separation of isomers was possible simply by crystallization of the esters and column chromatography.



$n = 4$ bp: 172–173°C/0,04 kPa (mixture of isomers)
$n = 8$ K 117 N 166 I (pure trans isomer)

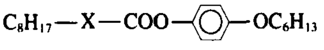
The esters were made by interacting the acid chlorides, obtained from the acids and thionyl chloride, with the substituted phenols and cyclohexanols in dry pyridine. The esters *1.–3.* exhibit stable wide-range mesomorphic phases persisting until much higher temperatures than those of the corresponding cyclohexane carboxylates,[2] but with somewhat lower clearing points than those of the analogous naphthalene carboxylates. For example:

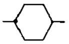
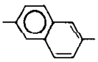
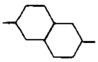


X	K	N	I	$\Delta T_{K\text{-}I}$	Lit.
	• 80,5	• 142,5	•	62	5
	• 85	• 167	•	82	12
	• 108	• 202	•	96	13
	• 102	• 226	•	124	1.7

Comparison of these esters indicates that the thermal stability of the nematic mesophase increases in the order benzene < cyclohexane < bicyclo[2.2.2]octane < decalin. The N-I transition temperatures increase much more than the melting points and therefore the thermal range of the mesophases is much greater.

The situation is similar with the following hexyloxyphenyl esters.



X	K	S	N	I	$\Delta T_{K\text{-}I}$	Lit.
	• 42	• 62,5	• 78	•	36	14
	• 70	• 73	• 109	•	39	*5.4*
	• 47	• 90	• 104	•	57	*1.3*

Compound *2.15* has the best melting behavior, with a melting point of 44°C and a range of persistence of the nematic phase of 119°C. The melting behavior of the laterally substituted esters corresponds with common experiences, i.e., these esters (*2.*) have decreased clearing points, no smectic phases and lowered melting points.

The mesomorphic properties of the decalin-2-carboxylates indicate that geometrical factors are very important and that many saturated ring systems ranging from cyclohexane to cholestane are possible as suitable building units for the molecules of liquid crystal materials.

EXPERIMENTAL

Melting points and transition temperatures were determined using a Boetius polarizing microscope. All the new compounds had satisfactory infrared spectral properties and elemental analyses.

All-*trans* 6-*n*-alkyldecalin-2-carboxylic acids

The 6-*n*-alkylnaphthalene-2-carboxylic acid[5] (0.15 mol) in 10% aqueous KOH (250 ml) was stirred for 120–150 h in an autoclave with Raney nickel

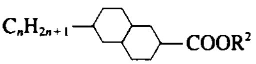
(20 g), at 14 MPa hydrogen pressure and 300°C. The catalyst was separated off and the hot solution acidified with concentrated HCl. The oily product was distilled and recrystallized from methanol.

ESTERIFICATION

A solution of the phenolic or alcoholic components in anhydrous pyridine was added to an equimolar amount of the crude acid chloride. The mixture was stirred at room temperature for 24 h and then for 3 h at 80°C. The reaction mixture was poured onto crushed ice mixed with sulfuric acid. The precipitate was extracted into ether and the etherel solution was washed with 10% aqueous sodium bicarbonate and water. Removal of the solvent afforded a white product which was crystallized several times from methanol until the transition temperatures were constant.

TABLE I

Transition temperatures (°C) of some *trans*-6-*n*-alkyldecalin-2-carboxylates *1*



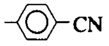
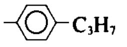
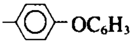
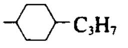
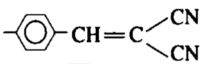
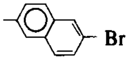
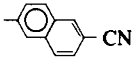
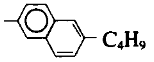
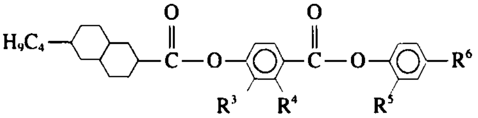
No.	*n*	R^2	K	S	N	I
1.1.	8		• 64,5	- -	• 121,5	•
1.2.	8		• 52	• 67	• 86	•
1.3.	8		• 47	• 90	• 104	•
1.4.	8		• 69	- -	• 80	•
1.5.	4		• 71	• 96	• 134	•
1.6.	4		• 135	- -	• 189,5	•
1.7.	4		• 102	- -	• 226	•
1.8.	4		• 77	- -	• 152	•

TABLE II

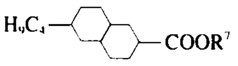
Transition temperatures (°C) of some *trans*-6-*n*-butyldecalin-2-carboxylates *2*.



No.	R^6	R^3	R^4	R^5	K	S	N	I
2.1.	C_5H_{11}	H	H	H	• 69	• 151	• 224	•
2.2.	OC_4H_9	H	H	H	• 71	• 140	• 249	•
2.3.	OC_5H_{11}	H	H	H	• 70	• 149	• 230	•
2.4.	OC_6H_{13}	H	H	H	• 73	• 163	• 234	•
2.5.	OC_7H_{15}	H	H	H	• 62	• 160	• 216	•
2.6.	OC_8H_{17}	H	H	H	• 64	• 177	• 219	•
2.7.	C_5H_{11}	Cl	H	H	• 91	– –	• 174	•
2.8.	OC_7H_{15}	Cl	H	H	• 78–80	– –	• 200,5	•
2.9.	OC_4H_9	CH_3	H	H	• 71	– –	• 221	•
2.10.	OC_7H_{15}	CH_3	H	H	• 62	– –	• 193	•
2.11.	C_5H_{11}	C_2H_5	H	H	• 54–56	– –	• 113	•
2.12.	OC_4H_9	C_2H_5	H	H	• 53	– –	• 178	•
2.13.	OC_4H_9	H	CH_3	H	• 61	– –	• 191	•
2.14.	OC_7H_{15}	H	CH_3	H	• 48,5	– –	• 155	•
2.15.	OC_8H_{17}	H	CH_3	H	• 44	– –	• 163	•
2.16.	C_5H_{11}	H	H	CH_3	• 88,5	– –	• 185	•
2.17.	CN	H	H	H	• 101	– –	• 296	•

TABLE III

Transition temperatures (°C) of some *trans*-6-*n*-butyl-decalin-2-carboxylates *3*.



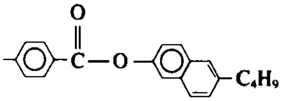
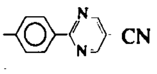
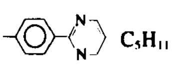
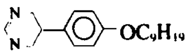
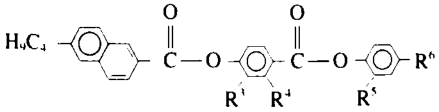
No.	R^7	K	S	N	I
3.1.		• 109	• 132	• 281	•
3.2.		• 114	• 213,5	• 287,5	•
3.3.		• 94	– –	• 219	•
3.4.		• 66	• 190	– –	•

TABLE IV

Transition temperatures (°C) of some 6-*n*-butylnaphthalene-2-carboxylates *4*.



No.	R^6	R^3	R^4	R^5	K	N	I
4.1.	C_5H_{11}	H	H	H	• 106	• 246	•
4.2.	OC_4H_9	H	H	H	• 152,5	• 267,5	•
4.3.	OC_5H_{11}	H	H	H	• 134	• 255	•
4.4.	OC_6H_{13}	H	H	H	• 118	• 251	•
4.5.	OC_7H_{15}	H	H	H	• 116,5	• 243,5	•
4.6.	OC_8H_{17}	H	H	H	• 111	• 238	•
4.7.	C_5H_{11}	Cl	H	H	• 94	• 206	•
4.8.	OC_7H_{15}	Cl	H	H	• 92	• 204	•
4.9.	OC_4H_9	CH_3	H	H	• 109	• 232,5	•
4.10.	OC_7H_{15}	CH_3	H	H	• 97	• 206	•
4.11.	C_5H_{11}	C_2H_5	H	H	• 50,5	• 152	•
4.12.	OC_4H_9	C_2H_5	H	H	• 100	• 182	•
4.13.	OC_5H_{11}	C_2H_5	H	H	• 90,5	• 166	•
4.14.	OC_7H_{15}	C_2H_5	H	H	• 63	• 139	•
4.15.	OC_4H_9	H	CH_3	H	• 107,5	• 215	•
4.16.	OC_7H_{15}	H	CH_3	H	• 95	• 187	•
4.17.	OC_8H_{17}	H	CH_3	H	• 94	• 183	•
4.18.	C_5H_{11}	H	H	CH_3	• 97,5	• 214,5	•

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4. H.-J. Deutscher, H. M. Vorbrodt, and H. Zaschke, *Z. Chem.*, **21**, 9 (1981).
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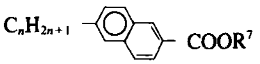
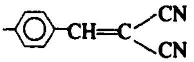
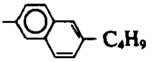
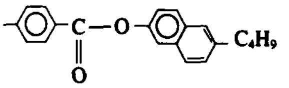
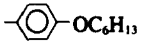
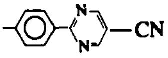
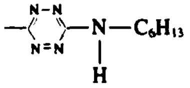
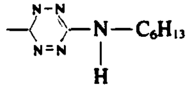
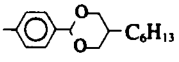
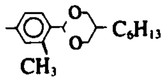
TABLE V

Transition temperatures (°C) of some 6-*n*-alkylnaphthalene-2-carboxylates *5*.



No.	*n*	R⁷	K	S	N	I
5.1.	4		• 124,5	– –	• 141,5	•
5.2.	4		• 94	– –	• 160,5	•
5.3.	4		• 155	– –	• 322	•
5.4.	8		• 70	• 73	• 109	•
5.5.	4		• 155	– –	• 327	•
5.6.	4		• 98	– –	• (92,5)	•
5.7.	8		• 111,5	– –	— —	•
5.8.	4		• 117	– –	• 216	•
5.9.	4		• 103,5	– –	• 165,5	•