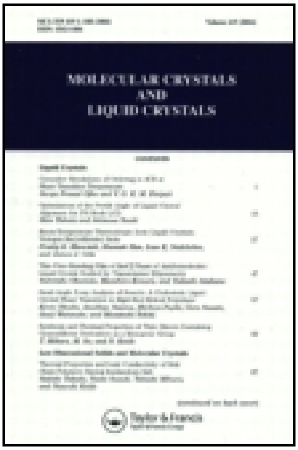

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Liquid Crystalline 7-n-Alkylperhydrophenanthrene-2-carboxylates

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Liquid Crystalline 7-*n*-Alkylperhydrophenanthrene-2-carboxylates†

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The preparation and liquid crystalline properties of 7-*n*-alkylperhydrophenanthrene-2-carboxylates are discribed.[1] The esters are characterized by a wide-range smectic and nematic phases.

Analogous esters, containing the *trans*-1,4-disubstituted cyclohexane ring and the trans-decalin system, exhibit narrower range mesophases. Compared with the 7-*n*-alkyl-9, 10-dihydrophenanthrene-2-carboxylates, the clearing points are lower, but the melting points are also decreased.

INTRODUCTION

The increased use of liquid crystals in various electro-optical devices still requires the synthesis of materials with low melting points, wide nematic range phases and special physical properties. It has been shown that replacement of aromatic rings by equatorial disubstituted cyclohexane or other alicyclic systems generally leads to compounds

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with lowered melting points and increased clearing points.[2–4] In this paper we examine the effect of changing the 9, 10-dihydrophenanthrene ring system[5] to a perhydrophenanthrene ring system, so achieving the following compounds:

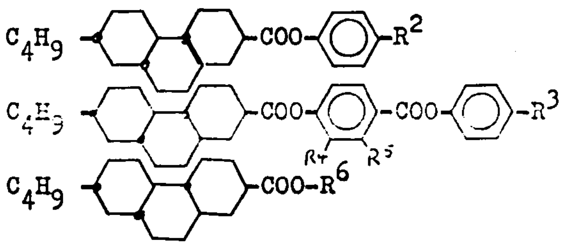


Table I
1.1.–1.5.

Table II
2.1.–2.3.

Table III
3.1.–3.2.

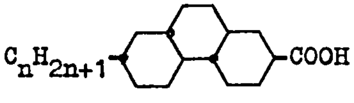
RESULTS AND DISCUSSION

Perhydrophenanthrene-2-carboxylic acids were obtained by catalytic, high pressure hydrogenation of 9, 10-dihydrophenanthrene-2-carboxylic acids.

It was necessary to find out the best hydrogenation conditions to obtain the all-*trans*-perhydrophenanthrenes. Only this isomer with an equatorial arrangement of the substituents in the 2, 7-positions meets the general requirements relating to liquid crystal properties, i.e., a rodlike and elongated molecule. Recently Minas *et al.*[6] obtained the 7-*n*-alkylperhydrophenanthrene-2-ols by a ring closure reaction. After esterfication the compounds exhibited nematic phases of narrow range.

We achieved complete hydrogenation with Raney Nickel, using 15 MPa hydrogen pressure, a temperature of 260–270 °C and a reaction time of about 120 h.

The separation of isomers was readily achieved by recrystallization.



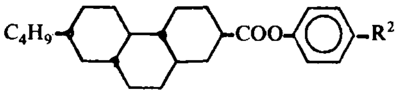
$n = 4$ K 160 N 219 I

$n = 6$ K 125 N 220 I

The esters were prepared by interaction of the acid chlorides, obtained from the acids and thionyl chloride, with the corresponding

TABLE I

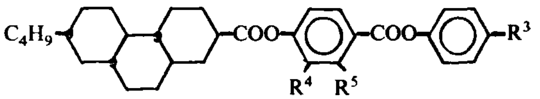
Transition temperatures (°C) of some 7-*n*-butylperhydrophenanthrene-2-carboxylates



No.	R^2	K	S	N	I
1.1.	OC_6H_{13}	● 76	● 136	● 143–144	●
1.2.	C_5H_{11}	● 75	● 114	● 135	●
1.3.	CN	● 79	— —	● 184–185	●
1.4.	$(CH_2)_2CN$	● 105	— —	● 124	●
1.5.	$CH = C(CN)_2$	● 89	— —	● 187	●

TABLE II

Transition temperatures (°C) of some 7-*n*-butylperhydrophenanthrene-2-carboxylates



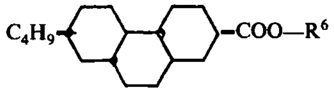
No.	R^3	R^4	R^5	K	S	N	I
2.1.	OC_5H_{11}	H	H	● 70	●	224 ● 288	●
2.2.	OC_4H_9	CH_3	H	● 84	●	114 ● 256	●
2.3.	OC_8H_{17}	H	CH_3	● 64	●	148 ● 198	●

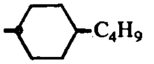
phenols and cyclohexanols in dry pyridine. All substances exhibt stable wide-range mesomorphic phases. Comparison of these esters with others containing different alicyclic rings indicates an increased thermal stability of the nematic mesophase in the order cyclohexane < decaline < perhydrophenanthrene. The N-I-transition temperatures increase much more than the melting points and therefore the temperature ranges of the mesophases become much greater.

Our investigations and results emphasize the great influence of geometrical factors on liquid crystalline behavior. The novel perhydrophenanthrene compounds also represent a step on the way from cyclohexane through the decalin and the bicyclohexane ring systems to the cholesteryl frame work.

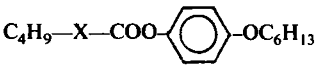
TABLE III

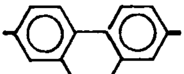
Transition temperatures (°C) of some 7-*n*-butylperhydrophenanthrene-2-carboxylates

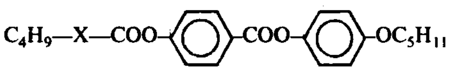


No.	R^6	K	S	N	I
3.1.	C_6H_{13}	liquid at room temperature			
3.2.		● 83	(.64)	● 110	●

The clearing points are lower than those of the analogous 9, 10-dihydrophenanthrene carboxylates, but so also are the melting points.



X	K	S	N	I
	● 92-93	—	● 171	●[5]
	● 76	● 136	● 144	●



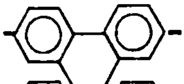
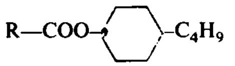
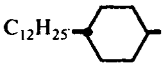
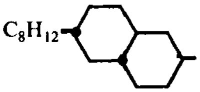
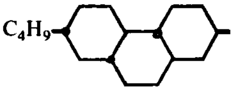
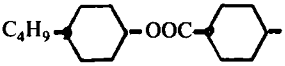
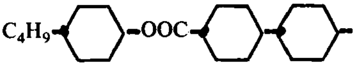
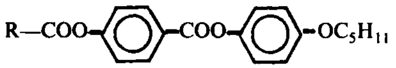
X	K	S	N	I
	● 138	● 202	● 316	●[5]
	● 70	● 224	● 288	●

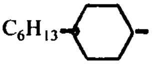
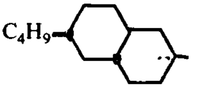
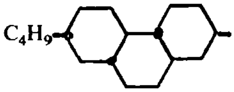
TABLE IV

Comparison of transition temperatures of compounds with alicyclic ring systems



R	K	S	N	I
	● 47	● 76,5	—	●
	● 52	(● 46)	● 76	●^{4}
	● 83	(● 64)	● 110	●
	● 119	● 143	● 160	●^{3}
	● 95	● 217	● 248	●^{3}



R	K	S	N	I $\Delta T_{K\text{-}I}$
	● 69	● 162	● 201	● 132
	● 70	● 149	● 230	● 160^4
	● 70	● 224	● 288	● 218

EXPERIMENTAL

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

7--*n*BUTYLPERHYDROPHENANTHRENE-2-CARBOXYLIC ACID

7-*n*-Butyl-9, 10-dihydrophenanthrene-2-carboxylic acid[5] (0.075 mol) in 10% aqueous KOH (200 ml) and 30 g of Raney Nickel were shaken in a 1 l autoclave at a hydrogen pressure of 15 MPa and at 260–270 °C for about 120 h. The catalyst was filtered off and the hot solution acidified with concentrated HCl. Then the viscous product was separated and recrystallized from methanol/toluene.

ESTERFICATION

A solution of the phenolic ar alcoholic components in dry pyridine was added to an equimolar amount of the crude acid chloride. After allowing to stand at room temperature for about 15 h, the reaction mixture was heated at 60–70 °C for 4 h. After being cooled, the mixture was poured into crushed ice mixed with sulfuric acid. The product was isolated by ether extraction. The ether solution was washed with 10% aqueous $NaHCO_3$ and water and dried with Na_2SO_4. After this, the solvent was removed. Recrystallization from pure methanol until constant transition temperatures gave the pure esters.

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