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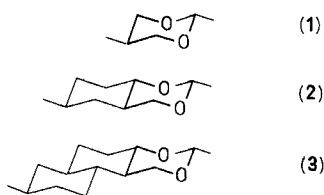
The mesomorphic properties of 2,7-disubstituted 1,3-dioxaperhydrophenanthrenes

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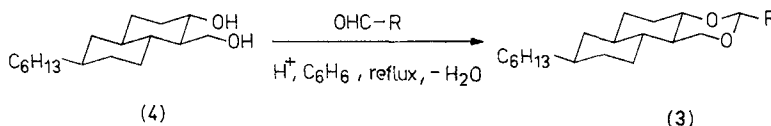
The mesomorphic properties of a new class of heteroalicyclic compounds are reported. The liquid-crystalline behaviour of these substances is compared with that of related materials.

In several papers we have reported the liquid-crystalline properties of 2,5-disubstituted 1,3-dioxane derivatives (1) and 2,6-disubstituted 1,3-dioxadecalin derivatives (2) [1-3]. Now we have been successful in synthesizing liquid-crystalline derivatives of the all-*trans*-1,3-dioxaperhydrophenanthrene (3) (scheme 1).



Scheme 1.

These compounds have been prepared in a rather simple manner by acid catalysed acetalization of different aldehydes with 6 α -*n*-hexyl-1 α -hydroxymethyl-(4 $\alpha\beta$,8 $\alpha\alpha$)-decalin-2 β -ol (4), whereby almost exclusively the desired all-*trans* isomers (3) have been obtained (scheme 2). They were further purified by recrystallization from ethanol.

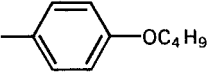
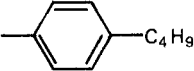
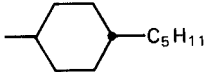
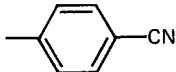
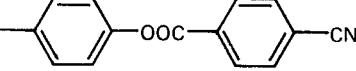


Scheme 2.

The purity was checked by careful inspection of the $^1\text{H-N.M.R.}$ spectra of these compounds. The signal of the H-2 proton is well separated from others and its chemical shift indicates, by comparison with reference data [1, 3, 4], the axial arrangement of the H-2 proton. No signal for the equatorial H-2 proton was detected. The synthesis of compound (4) will be reported in a separate paper.

The liquid-crystalline properties have been observed by polarizing microscopy (see table 1). Compound (3a), which has two alkyl chains attached to the 1,3-dioxaperhydrophenanthrene framework, exhibits no stable mesophase. We were not

Table 1. Mesomorphic properties of the 2,7-disubstituted 1,3-dioxaperhydrophenanthrenes (3a)–(3f).

Compound	R	C	S _A	N	I			
(3a)	–C ₆ H ₁₃	●	61.5	–	–	–	–	●
(3b)		●	87	–	–	●	154	●
(3c)		●	80	●	111	●	127	●
(3d)		●	83	●	134	●	168	●
(3e)		●	111.5	–	–	●	187.5	●
(3f)		●	174	–	–	●	305	●

† Decomposition.

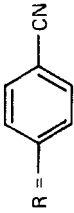



able to detect a monotropic mesophase, because the compound crystallizes rapidly if it was cooled only few degrees below the melting point. All of the other compounds synthesized exhibit broad mesomorphic ranges, whereby the nematic and the smectic A phase predominate.

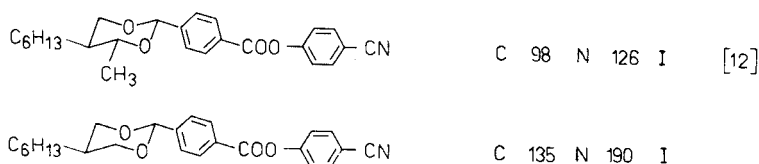
A direct comparison between the mesomorphic properties of the 1,3-dioxaperhydrophenanthrenes and analogous perhydrophenanthrene derivatives [5–10] is presently possible only in one case, since other appropriate materials have not yet been synthesized. The 2,7-di-*n*-hexylperhydrophenanthrene [8] exhibits a stable nematic mesophase between 70/75°C and 87.5°C, whereas none has been detected for the analogous compound (3a). We can conclude therefore that the mesophase stability of the 1,3-dioxaperhydrophenanthrenes is significantly lower than the mesophase stability of the parent perhydrophenanthrene derivatives. Presumably, this is a result of slight deviations from molecular linearity caused by the folding of the 1,3-dioxaperhydrophenanthrene framework in the O–C–O region due to the smaller O–C–O bond lengths and bond angles.

Table 2 compares the liquid-crystalline behaviour of the compounds (3d) and (3e) with the similar 1,3-dioxane and 1,3-dioxadecalin derivatives [3].

It is observed that the clearing temperatures increase in the order 1,3-dioxane \lesssim 1,3-dioxadecalin \ll 1,3-dioxaperhydrophenanthrene, due to the increasing molecular length. However, the difference between the 1,3-dioxanes and the 1,3-dioxadecalins is rather small, because the breadth of the molecule is also increased by the annulation of the cyclohexane ring. The annulation of a second cyclohexane ring to the 1,3-dioxadecalins (2) increases the molecular length but not the diameter of the rotational cylinder, thus the mesophase stability increases significantly on going from 1,3-dioxadecalin to 1,3-dioxaperhydrophenanthrene derivatives.

Table 3. Comparison of the liquid-crystalline properties of 2-substituted 5-(*trans*-4-*n*-hexylcyclohexyl)-1,3-dioxanes and 2-substituted 7-*n*-hexyl-1,3-dioxaperhydrophenanthrenes.

	R = 		R = 								
	C	N	I	C	S _B	S _A	N	I			
	●	95	●	214	●	<20	●	236	-	-	●
	●	111.5	●	187.5	●	83	-	-	134	●	168



Scheme 3.

The 2-substituted 5-(*trans*-4-*n*-hexylcyclohexyl)-1,3-dioxanes [11] and the 2-substituted 1,3-dioxaperhydrophenanthrenes which are compared in table 3, have exactly the same length but the clearing temperatures of the former are significantly higher. This difference should be attributed to the increased molecular diameter of the compounds (3). That is, the ethylene bridge between the cyclohexane ring and the 1,3-dioxane ring acts like a lateral substituent. Indeed, a methyl group in the equatorial position 4 of the 1,3-dioxane ring causes a clearing temperature depression which is of the same order of magnitude (scheme 3).

As another important effect, the smectic B phase, readily exhibited by cyclohexane and heterocyclohexane derivatives, is strongly suppressed in the 1,3-dioxaperhydrophenanthrene derivatives. Finally, the melting points of the condensed 1,3-dioxane derivatives are generally higher than those of the parent 1,3-dioxanes.

These results should be principally transferable to other liquid-crystalline structural units. In this way the synthesis of heteroalicyclic compounds gives new insights into the complex relationship between molecular structure and mesomorphic properties. In particular the 1,3-diheterocyclohexane derivatives are easily prepared in a pure state and are easily studied by spectroscopic methods, so they are especially valuable materials.

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