

Novel Nematic all-*trans*-Perhydroanthracenes, -naphthacenes, and -benz[*a*]anthracenes

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Abstract: Hydroxy derivatives of the title compounds were prepared, two of them via regioselective formation of enamines. Some nematic acyl derivatives of the alcohols are described and their phase transition data recorded.

Liquid crystalline alicyclic compounds like bicyclohexyl^[1] or all-*trans*-perhydrophenanthrene^[2,3] derivatives may be considered as segments of the cholesterol or cholesterol skeleton. Cyclohexyldecalins^[4] and all-*trans*-perhydrochrysenes^[5] can be looked at as parts of D-homocholestane. It seemed of interest to us to which extent the liquid crystalline behaviour would be changed when the ring pattern of cholesterol was abandoned in aliphatic examples like those given in the title.

The unsaturated ketone **1**, earlier used in other syntheses^[2,5], was subjected to a Birch reduction^[6], to give the saturated decalone **2** (Scheme 1). Enamine formation of **2** with morpholine proceeded regioselectively. The product **3** was not isolated but subsequently alkylated with 2-buten-3-one^[7]. The resulting diketone **4** was cyclized in an intramolecular aldol condensation to give the unsaturated ketone **5**^[8]. Over-reduction according to Birch^[9] yielded the all-*trans*-perhydro-2-anthracenol **6a**^[10], which was esterified with some acids^[11]. While the esters with aliphatic carboxylic acids are not mesogenic^[12,13], the benzoate **6e** and the anisate **6f** (see Table 1) show nematic behaviour^[12,13].

The unsaturated ketone **5** could also be used to attach a further cyclohexane ring. Birch reduction gave the all-*trans*-perhydroanthrone **7**^[14]. This was regioselectively transformed to the enamine **8**^[15], alkylation of which gave the diketone **9**^[15] (Scheme 1). Treatment with sodium me-

thoxide induced the ring closure to the unsaturated ketone **10**^[16], which was subjected to an over-reduction according to

Birch^[9] to give the all-*trans*-perhydro-2-naphthacenol **11a**^[17]. Only the hexanoate and the anisate were prepared^[18] and proved both to be nematic (see Table 1)^[13].

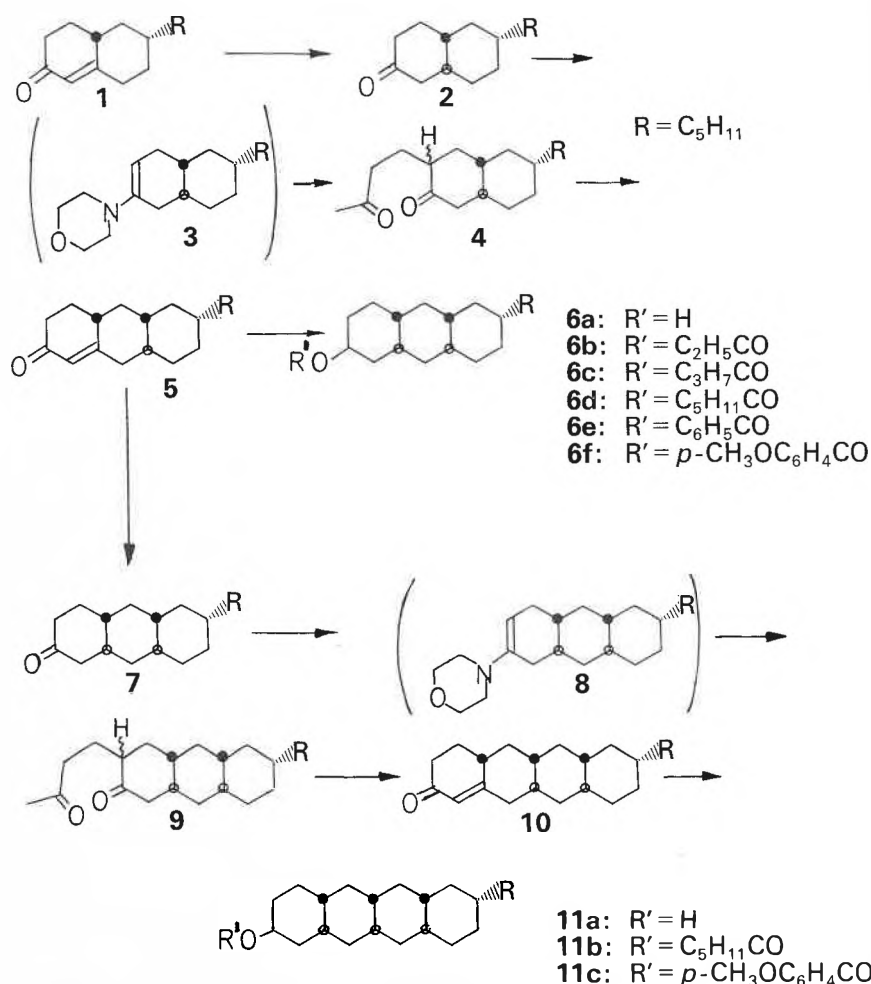
Table 1. Melting and clearing points and nematic ranges (°C) of the hexanoates **6d**, **11b**, **15b** and the anisates **6f**, **11c**, **15c**.

	R' = C ₅ H ₁₁ CO			R' = <i>p</i> -CH ₃ OC ₆ H ₄ CO		
	m.p.	c.p.	ΔT	m.p.	c.p.	ΔT
6(d,f)	90	90	0	119.6	200.2	80.6
11(b,c)	174.4	194.5	20.1	194.5	271.0	76.5
15(b,c)	126.1	138.8	12.7	125.5	271.5	146

Finally, **5** was alkylated with 1-bromo-3,3-ethylene-dioxybutane to give **12**^[19] (Scheme 2). Birch reduction of **12** led to **13**^[20], which after hydrolysis was cyclized to the unsaturated ketone **14**^[21]. Over-reduction of **14** according to Birch^[9] gave the all-*trans*-perhydro-3-benz[*a*]anthracenol **15a**^[22]. Only the hexanoate and the anisate were prepared^[18] which proved to be nematic, too (see Table 1)^[13].

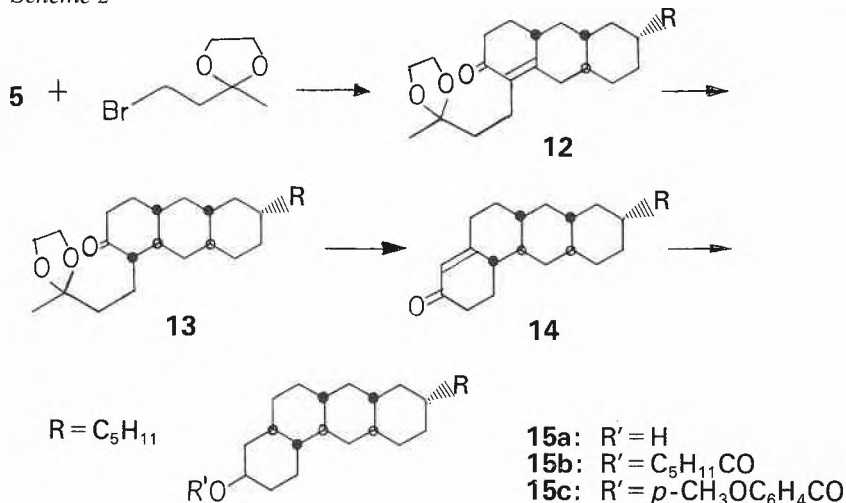
As a result, Table 1 shows that the melting points of the perhydronaphthacenol esters **11b** and **11c** are expectedly high, the nematic range of the hexanoate **11b** compares with those of the perhydrophenanthrenes^[2], while the anisate falls short^[23].

Scheme 1



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Scheme 2



The melting points of the perhydrobenz[*a*]anthracenol esters **15b** and **15c** are much lower, indicating a less stable packing of the bent molecules in the crystal lattice. The clearing point of **15c**, however, does not differ from that of **11c**. As a consequence, the nematic range of **15c** is rather large and falls between that of the corresponding perhydrophenanthrene^[23] and cyclohexyldecalin^[4] derivatives. The clearing point of the hexanoate **15b** is much lower, probably because the mobile hexanoate group hinders a parallel arrangement of the molecules in the nematic phase. The hexanoate of the perhydroanthracenol (**6d**) is not mesogenic and the nematic range of the anisate **6f** is moderate as that of **11c**.

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- [2] H. Minas, H.-R. Murawski, H. Stegemeyer, W. Sucrow, *J. Chem. Soc. Chem. Commun.* (1982) 308.
- [3] D. Varech, L. Lacombe, J. Jacques, *Nouv. J. Chim.* 8 (1984) 445.
- [4] M. Petzilkka, K. Schleich, *Helv. Chim. Acta* 65 (1982) 1242; W. Sucrow, H. Wolter, *Chimia* 36 (1982) 460.
- [5] P. Geschwinder, H. Minas, W. Sucrow, *Chimia* 39 (1985) 186.
- [6] Li in liq. NH_3 /1 in tetrahydrofuran, 90 min; chromatography (silica gel, petrol ether/ CH_2Cl_2 / Et_2O 50:35:15); 69% yield.
- [7] Water was removed from the mixture of morpholine and **2** with *p*-toluenesulfonic acid in boiling toluene, after evaporation benzene and 2-buten-3-one were added and the mixture was refluxed for 4 h. Chromatography (cf. [6]) gave 49% **4** as a mixture of stereoisomers, that needed not be separated, since the next stage leads to equilibration.
- [8] **4** was refluxed in methanol with sodium methoxide under nitrogen; chromatography (cf. [6]) yielded 98% **5**, *m.p.* 74°C.
- [9] D. Caine, *Org. React.* 23 (1976) 1.
- [10] The unsaturated ketone **5** was reduced with Li in liq. NH_3 , methanol was added, and more lithium for the blue colour to reappear. Chromatography (cf. [6]) gave 57% **6a**, *m.p.* 154°C, with 18 single peaks (expected: 19) in the completely proton decoupled ^{13}C -NMR spectrum.
- [11] The esters were prepared from **6a** and the acid chlorides in pyridine and purified by chromatography (cf. [6]).
- [12] **6b**, *m.p.* 107°C; **6c**, *m.p.* 110°C; **6e**, *m.p.* 122°C; *c.p.* 126.5°C.
- [13] All new compounds gave satisfactory elemental analyses and single peaks in GL chromatography.
- [14] **5** was reduced as **1**, 77% yield.
- [15] Enamine formation of **7** and alkylation with 2-buten-3-one to **9** proceeded as with **2**, 47% yield.
- [16] Cyclization of **9** proceeded as with **4**, 46% yield.
- [17] Birch reduction of **10** proceeded to **11a** as with **5**, 54% yield, *m.p.* 220°C.
- [18] Esters were formed as with **6a**.
- [19] Sodium hydride was warmed in dimethyl sulfoxide, after cooling **5** and 1-bromo-3,3-ethylenedioxybutane were added and the mixture stirred at 70°C under nitrogen. Chromatography (cf. [6]) yielded 31% **12**.
- [20] Birch reduction of **12** proceeded to **13** as with **1**, 50% yield.
- [21] **13** was hydrolyzed with halfconc. HCl in boiling benzene, the cyclization to **14** proceeded as with **4**, 89% yield, *m.p.* 78°C.
- [22] Birch reduction to **15a** proceeded as with **5**, 55% yield, *m.p.* 177°C.
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