Liquid Crystalline Norcholesterylesters: Influence of the Axial Methylgroups on the Phase Transitions and the Cholesteric Helix

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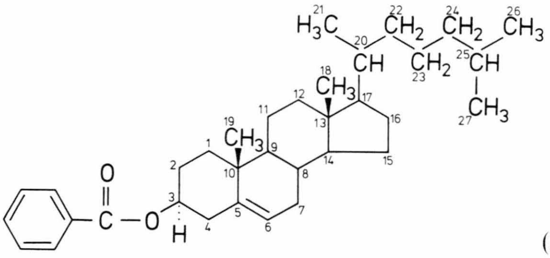
Z. Naturforsch. **44a**, 1127–1130 (1989); received August 21, 1989

In commemoration of the deceased W. J. A. Goossens

Liquid crystalline norcholesteryl anisic esters were prepared in which the methylgroups 19, 21, 27, and 18 are removed successively from the cholestene skeleton. The influence of the axial methylgroups on the phase transition temperatures and the choleric helical structure has been investigated. On heating the 18.19.21.27-tetranorcholesteryl ester, at 155 °C an inversion of the helical screw sense from left to right was observed.

Introduction

More than 100 years ago the liquid crystalline properties of the bencoic ester Ia of cholesterol (5-cholesten-3-ol) have been described by Reinitzer [1]. Meanwhile, a large number of cholesterol esters have been synthesized [2], all forming so-called cholesteric mesophases with outstanding optical properties: i) selective reflection of circularly polarized light, ii) anomalous optical rotatory power [3]. These properties result from a helical superstructure of the molecules which are locally parallel aligned with their molecular long axes [4]. This helical structure is determined by the pitch p after which the local director of the molecules has turned by 2π and a screw sense which can be left- or right-handed. It should be emphasized that cholesteric mesophases can only be formed by optically active molecules, a fact which can be understood by means of the molecular statistical theory of Goossens [5]. A further requirement for the mesogenity of cholesteryl esters is an all-trans conformation of the steroid skeleton and an equatorial position of the substituents in 3- and 17-position. Shortening of the alkyl chain in 17-position does not influence the liquid crystalline properties, but branching of the chain decreases the mesomorphic behaviour [6, 7]. Elimination of the methyl group in position 21 destroys the mesogenity [7].



(Ia)

Less information is available about the effect of the axially positioned methyl groups in positions 18 and 19 of the steroid skeleton. As the introduction of those axial methyl groups into the skeleton of nematogenic trans-perhydrophenanthrenes has been demonstrated to decrease the temperature range of the nematic phase considerably [8] it can be expected that the elimination of the 18 and 19 methyl groups from the cholestene skeleton would enhance the mesomorphic behaviour. This was indeed first verified in the case of 19-norcholesteryl esters [9].

It is the aim of this paper to study the effect of the several methyl groups in different positions of the 5-cholesten skeleton on the stability of the cholesteric phase as well as on its helical structure. For this purpose the anisic esters of four norcholesterols with methyl groups successively eliminated from positons 19, 21, 27, and 18 have been investigated.

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Experimental

19-Norcholesteryl anisic ester (II)

Starting from cholesteryl acetate, 19-norcholesterol was prepared on a known route via 19-hydroxycholesteryl and the corresponding aldehyde which yields 19-norcholesterol acetate by photochemical decarbonylation. The acetate was saponified and the resulting 10-norcholesterol treated with anisic acid chloride [9].

19.21.27-Trinorcholesteryl anisic ester (III)

Starting from oestrone methylether the anisic ester III was prepared in a seven step synthesis as described in detail elsewhere [10].

18.19.21.27-Tetranorcholesteryl anisic ester (IV)

Analogously to the preparation of III the seven step synthesis of the anisic ester IV started from 18-noroestrone methylether which was prepared from the oestrone methylether [10]. For details cf. [10].

Purification

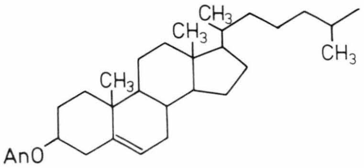
The norcholesterols were purified by column chromatography on silica gel 60 (Merck) with a solvent mixture of petroleum ether/dichloromethane/diethyl ether 50:35:15. The anisic esters were chromatographed also on silica gel 60 with petroleum ether/dichloromethane 80:20 and finally recrystallized from alcohol. The purity has been tested by thin layer chromatography and by gaschromatography (Varian Aerograph Series 2400) with a 25 m glass capillary column (Se 52). All compounds have been characterized by IR spectroscopy, mass spectroscopy, by their NMR spectra (^{1}H, ^{13}C) and by optical rotation (for details cf. [10]). The phase transition temperatures were determined by thermomicroscopy (polarizing microscope Leitz SM Lux Pol and heating stage Mettler FP 5/52). The helical pitch of the cholesteric phasse was measured in wedge-shaped samples between a convex lense and a plane glass plate by means of the resulting Cano lines [11]. In the same sample the screw sense of the cholesteric helix was determined by observation of the shift of the interference lines in monochromatic light on rotation of the analyser as described by Gerber [12].

Results and discussion

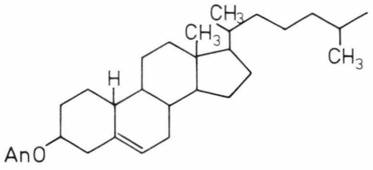
Stability of the cholesteric phase

The phase transition temperatures as well as the range of the cholesteric phase of the cholesterol esters under discussion are given in Table 1.

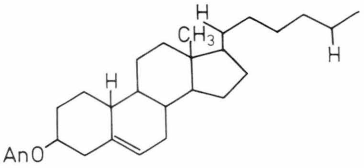
Cholesteryl benzoate (Ia) exhibits a rather narrow temperature range of the cholesteric phase, $\Delta T_{\mathrm{ch}} = 32\,^{\circ}\mathrm{C}$. By the anisic ester Ib it is demonstrated that the phase transition temperatures are very sensitive to changes of the molecular structure: only the introduction of a methoxy group into the benzene ring of Ia enhances the cholesteric range to 88 °C. Thus, in the following we only compare the anisic esters Ib–IV to answer the question how changes within the steroid skeleton influence the phase transitions.



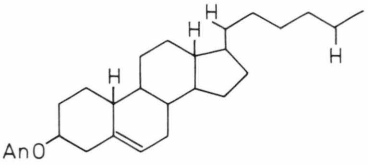
(Ib)



(II)



(III)



(IV)

Table 1. Transition temperatures and helical screw sense of the cholesteric phases of cholesterol and norcholesterol esters.

Compound	T_{F}/°C	T_{C}/°C	ΔT_{ch}/°C	Helical screw sense
Ia	150	182	32	left
Ib	180	268	88	left
II	146	254	108	left
III	72	213	140	left
IV	138	226	88	left/right

T_{F} melting point; T_{C} clearing point; $\Delta T = T_{\mathrm{C}} - T_{\mathrm{F}}$: range of the cholesteric phase.

By elimination of the 19-CH_3 group in the ester II the cholesteric range is broadened to 108 °C. Comparing the phase transition data of Ib and II (cf. Table 1), however, one can see that T_C is not so much changed but the melting point T_F is lowered. As it has been derived from X-ray analysis of cholesteryl esters, the solid crystal lattice is stabilized by the axial methyl groups [13]. Obviously, the molecular packing in the solid state is disturbed after elimination of the 19-methyl group, which leads to a lower melting point. The same result has been observed in several other esters of 19-norcholesterol [9].

As it is known that the elimination of the 21-methyl group leads to a loss of the cholesteric phase [7], in III the two methyl groups in positions 21 and 27 are removed simultaneously. The cholesteric range of III is broadened ($\Delta T_{ch} = 140$ °C), but this results from a still larger lowering of the melting point down to 72 °C. The same packing effects in the solid state as discussed for II may be responsible for the low melting point of III too.

In the tetranorcholesteryl ester IV the 18-methyl group is eliminated in addition to those in positions 19, 21 and 27. Compared with III T_F rised considerably up to 138 °C. By this the cholesteric range decreases ($\Delta T = 88$ °C) whereas the clearing point was not so much influenced. Because in IV both axial methyl groups are removed from the steroid skeleton, a close molecular packing in the solid state is now no longer hindered, explaining the increase of T_F.

Summarizing, one can derive from the data of Table 1 that the melting point is more sensitive to the elimination of the angular methyl groups than the clearing point.

Helical structure

The helical screw sense of the cholesterol esters depends in an unknown way on the molecular chirality of the chemicals used for their preparation.

The screw sense of our cholesterol esters Ia and Ib is left-handed (cf. Table 1). The cholesteric helices of most of the studied cholesterol esters are left-handed: right-handed helices, as e. g. in cholesteryl chloride are rather seldom. The elimination of the methyl groups in positions 19, 21, and 27 of the cholestene skeleton does not alter the helical structure: the anisic esters II and III exhibit left-handed helices, though there is a loss of one chiral centre at the carbon atom 20 by elimination of the methyl group 21.

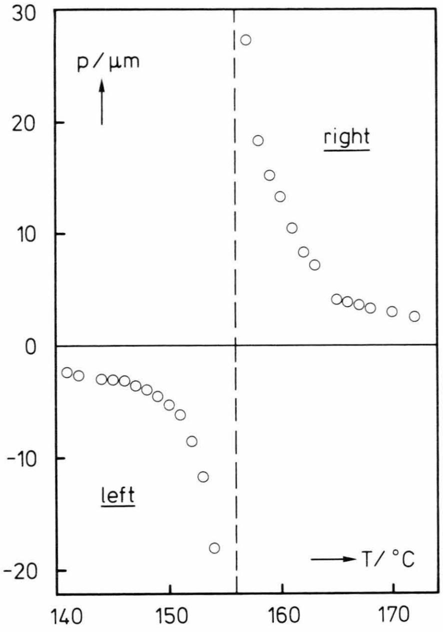


Fig. 1. Helical pitch *p* of the cholesteric phase of the tetranorcholesteryl anisic ester IV as a function of temperature.

An exception was found for the cholesteric phase of the tetranorcholesteryl ester IV: At low temperatures close to above the melting point a left-handed helix has been observed. At 155 °C, however, the screw sense changes to the right and a right-handed helix is preserved up to the clearing point. We have measured the helical pitch p of IV as a function of temperature. As shown in Fig. 1, *p* diverges to infinity indicating that at 155 °C the helix will be unwound and the mesophase becomes nematic. Above 155 °C the director spirals up again but now in a right-handed sense. The pitch changes sign and decreases from higher values to lower ones. As the reciprocal pitch is proportional to the molecular twist in a cholesteric phase we have given p^{-1} versus temperature in Figure 2. The curve cuts the zero line just at the inversion temperature where the sense fo the helix changes sign.

In binary mixtures of cholesterogenic compounds which exhibit a right- and a left-handed helix, respectively, for a given composition an inversion of the helical screw sense with temperature has been observed [14]. This can easily be understood because the tendency of one compound to form a – say – left helix will be overcome by that of the right-handed one on increasing temperature. To our knowledge the ester

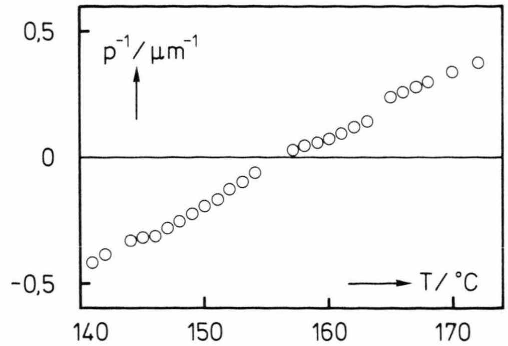


Fig. 2. Inverse helical pitch p^{-1} of the cholesteric phase of the tetranorcholesteryl anisic ester IV vs. temperature. Inversion of helical screw sense at 155 °C.

IV, however, is the first example for a helix inversion with temperature in a single compound.

In principle, one can understand a helix inversion with temperature in a single compound by the following consideration: A chiral cente in a mesogenic molecule tends to twist the local director into a helical superstructure. The relation between the sterical conformation and the twist sense of the resulting helix is not obvious at all, i.e. for a given cholesterogenic chiral molecule one cannot predict the resulting helical screw sense. If a mesogenic molecule possesses more than one chiral centre, as in the case in cholesteryl derivatives, each centre exhibits its own helical twisting power which can result in a right- or left-handed cholesteric helix. If all chiral centres tend to twist the director into the same scew sense only a left- or right-handed helix will be formed independent on temperature. However, there may be chiral centres with twisting powers of opposite sense and different strengths in the same molecule. Both twist tendencies compete with each other. If the range of the cholesteric phase is large enough, like in IV, it may happen that at a given temperature the twist sense of a "left" centre overcomes that of a "right" one and vice versa. By this competition either the left or the right twisting power of different centres wins at different temperatures leading to the helix inversion described above for IV. Obviously, in IV the configuration of the chiral carbon atom 13 from which the 18-CH_3 group has been removed is responsible for the formation of the right handed helix at higher temperatures, for in III, with its 18-methyl group at the chiral centre 13, only a left handed helix was observed up to the clearing point, though III has the largest range of the cholesteric phase*.

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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* *Note added in proof:*

Kuczynski et al. [15] also observed a temperature induced helix inversion as described in the preceding paper in the cholesteric phase of an optically active epoxy derivative with two chiral centres in the molecule.

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