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Cholesteric helix inversion: Novel nitro compounds showing unusual changes of the cholesteric helical pitch

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Cholesteric helix inversion: Novel nitro compounds showing unusual changes of the cholesteric helical pitch

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We present a homologeous series of liquid crystalline trioxadecalin compounds having a terminal alkoxy chain and a nitro group. The (1*S*,3*R*,6*R*,8*R*)-3-(4″-nitrophenyl)-8-(4′-octoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decane **2c** shows a temperature-dependent inversion of the cholesteric helix at lower temperatures. For higher temperatures, the reciprocal helical pitch reaches a minimum, then it increases, tending to a second inversion point just above the clearing point. An additional chiral centre in the side chain leads for nitro compounds **3** to non-mesomorphic behaviour. For the cyano compounds **4**, the change in the cholesteric helix is suppressed, for the *R* configuration, but for the *S* configuration helical inversion occurs at high temperatures and selective reflection above the transition to the TGB_A phase.

1. Introduction

The cholesteric mesophase is formed by chiral molecules. Their chiral centres each possess a helical twisting power and are responsible for the resulting helical structure of the mesophase. In some cases, the helical twist changes on heating leading to a nematic phase formed by a single chiral compound.

An inversion of the helical twist sense in a single compound was first reported in 1989 [1]: a norcholesterol ester showed a temperature-dependent change of the helical pitch. This was explained in terms of different chiral centres with different twisting powers and twist senses that compete for the resulting helical twist sense. Another example arose through the examination of chiral liquid crystalline epoxides with two chiral centres in the side chain next to each other [2]. The effect of two chiral centres, one in each side chain of the molecules investigated, was discussed as a linear addition of the effects of the chiral centres [3]. However, a propiolate ester with only one single chiral centre was then shown to give the same effect [4]. This was explained by the assumption of two sterically preferred conformations of the chiral end chain with different twisting senses so that there is a temperature-dependent domination of either the left- or right-twisting conformation.

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We have synthesized a homologous series of cyano compounds with a trioxadecalin ring bearing four conformationally fixed chiral centres. The four-step synthesis is based on commercially available tri-*O*-acetyl-D-glucal which is simply derived from glucose [5]. Some of the derived (1*S*,3*R*,6*R*,8*R*)-3-(4″-cyanophenyl)-8-(4′-alkoxyphenyl)-2,4,7-trioxabicyclo[4.4.0]decanes **1** (see figure 1) with a *trans*-decalin ring system in the core of the molecule show a cholesteric helix inversion [6].

It was of interest to see how changes in the molecular substitution pattern would influence the cholesteric helix. The elimination of the one chiral centre, by replacing the carbon atom in the 3-position by a boron atom leads to molecules that do not show an inversion of the cholesteric helix [7]. This means that this chiral carbon atom

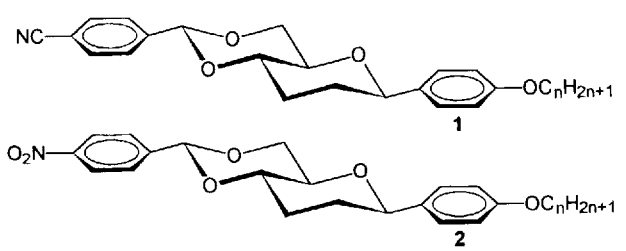

Figure 1. Compounds **1** and **2** showing a cholesteric helix inversion.

Table 1. Transition temperatures of compounds **2a–2g** and temperatures of inversion.

Compound	*n*	Transition temperatures/°C							Inversion
2a	6	Cr	111·4			Ch	159·5	I	80
2b	7	Cr	108·0			Ch	152·0	I	107
2c	8	Cr	104·8			Ch	149·1	I	113
2d	9	Cr	102·9			Ch	143·9	I	129
2e	10	Cr	101·3			Ch	140·7	I	133
2f	12	Cr	101·1	S_A	132·8	Ch	138·6	I	133
2g	14	Cr	98·8	S_A	137·5			I	

has a major effect on the macroscopic chirality of the molecule.

2. Results and discussions

We then changed the achiral polar terminal group near this chiral centre by introducing a nitro group instead of the cyano group (**2**, figure 1). The derived compounds (see table 1) with shorter alkyl chains up to $n=10$ only form cholesteric phases. Compound **2f** with $n=12$ shows a smectic A and a cholesteric phase, and **2g** with $n=14$ only has a smectic A phase. Compounds **2a–2e** ($n=6$–10) exhibit an inversion of the pitch of the cholesteric helix which is manifested by the conversion of the cholesteric cell texture to a schlieren texture which means a change in the helical pitch.

Compound **2c** with $n=8$ presents the phenomenon of a nearly double inversion of the helical twist sense. On heating, the crystals melt showing a cholesteric cell texture which changes to a typical nematic schlieren texture. This nematic texture changes again, giving the cholesteric cell texture. At higher temperatures, the cholesteric texture changes again to a nematic schlieren texture just below the clearing point. In general, for shorter chain lengths, the lower inversion point is readily observable, but for longer chain lengths only the approach to the higher inversion point is seen.

Investigations on **2c** (for methods see [1]) show that there is a right-handed helix at lower temperatures which changes to a left-handed helix at higher temperatures; an inversion temperature of 110·5°C was measured (see figure 2). At approximately 130–140°C, there is a minimum of the reciprocal pitch, meaning a nearly constant pitch of the helix. Above 140°C, the pitch changes again and should approach the second helical inversion point at an extrapolated temperature of 150°C, but the clearing point of 149·1°C is too low for direct observation of this point. We suppose that this is not a pre-transitional effect of the isotropic phase involving an unwinding of the cholesteric helix; compounds of the same basic structure, for example, with a methoxy group instead of the nitro group, possess higher clearing points and a blue phase,

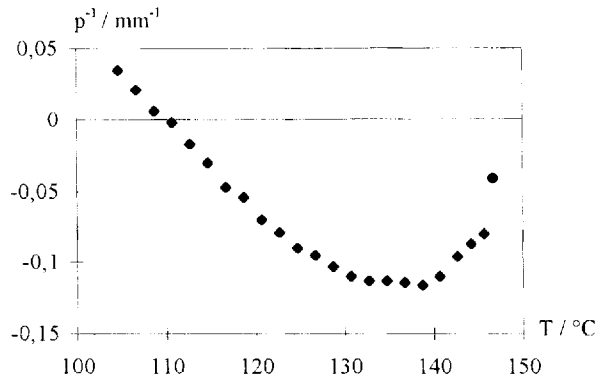

Figure 2. Pitch of the cholesteric helix of compound **2c**.

but they do not show any change of the helix either near this temperature or near their clearing points.

To our knowledge, this is the first time that a single compound has been found to show a minimum of the reciprocal pitch, followed by increasing values tending to a second inversion of the cholesteric twist sense.

We then introduced a further chiral centre to study the scope and the limitations of the changes of the cholesteric helix. This fifth chiral carbon atom was introduced into the alkyl chain of the molecule in both the *R* and *S* configurations yielding structures **3** and **4** (see figure 3).

The expected effect on the cholesteric helix is not observable for the nitro compounds **3**. The structural

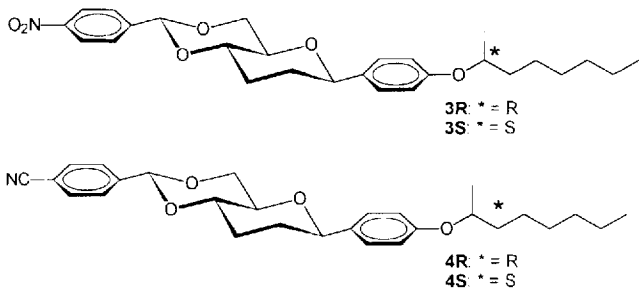

Figure 3. Compounds **3–4** with lateral substituents in the end chain.

disturbance by the lateral methyl group is too large, causing only a crystalline–isotropic transition.

The behaviour of the cyano compounds is different. They can be compared with the previously described [6] compounds, exhibiting for side chains with $n=7$, 8 and 9 a cholesteric helix inversion.

Compound **4S** possesses only monotropic phases. On cooling down, a blue phase occurs with a pitch in the UV and then a cholesteric phase which does not change the helix. At 55·0°C, a TGB_A phase and at 53·5°C a smectic A phase is exhibited. The diastereomeric compound **4R** shows an enantiotropic cholesteric phase, but in this case a helical inversion at 76°C (nematic texture) is observed, followed by a sharply increasing pitch. After the inversion, the cholesteric texture changes its colour over a small temperature range from blue and green to red and yellow. Then there follow the transitions to a TGB_A and smectic A phase. Similar observations were made by Goodby *et al.* [8], but they observed the increase in pitch of the helix at higher temperatures.

A contact preparation of **4R** and **4S** shows a linear decrease of the helical pitch, demonstrated by a fan texture changing to a finger print texture. At low temperatures, the helical twist sense of both compounds is the same.

In admixture with 4-*n*-butyl-4′-methoxyazoxybenzene (Cr 20 N 76 I), both the **4R** and **4S** compounds exhibit an induced blue phase.

We propose that there are two effects that cause this mesogenic behaviour. The nitro compounds, like the cyano compounds, form temperature-dependent aggregates. These aggregates have been discussed as the reason for re-entrant behaviour, but they can also cause a change in the cholesteric helix. Also, there is an increasing flexibility of the end chains and an increasing rotation of the aromatic rings at higher temperatures. The conformational effects are the basis of the explanation of Goodby *et al.*, for the inversion in a compound with only one chiral centre. Both effects influence the chiral centres and their effect on the resulting chiral properties of the mesophase. At lower temperatures, the aggregation effects the helical changes, and at higher temperatures, the flexibility has a greater influence. This causes the second inversion for the nitro compounds, and for the cyano compounds this inversion could be far in the isotropic region and, hence, is not observable.

Every chiral centre possesses its own distinct helical twisting power. Compounds **4R** and **4S** possess an additional chiral centre that is known for its high twisting power. The mixed system of both compounds shows at low temperatures an equal twist sense and equal pitch for both diastereomers, but a linear addition of the chiral centres would result in a different helical twist, caused by the additional centre. Hence, the resulting chirality is a combination of the effects of the chiral centres, but it cannot be explained by a linear addition for this class of compounds; the observed properties are an effect of the whole chirality of the whole molecule.

3. Experimental and analysis

The compounds **2–4** were synthesized according to the procedure described in [4]. The compounds **2** differ only in the number of methylene groups in the end chain. The elemental analyses obtained for all the compounds were in the same range (C ± 0·25, H ± 0·6, N ± 0·8 per cent). Thus, the data for **2c** given below are representative for all the compounds **2**.

3.1. *Analytical data for* **2c**

^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta=3{\cdot}69$ (ddd, 1 H, H-1), 5·60 (s, 1 H, H-3), 4·34 (dd, 1 H, H-5eq), 3·80 (dd, 1 H, H-5ax), 3·59 (ddd, 1 H, H-6), 4·49 (dd, 1 H, H-8), 1·87 (m_c, 2 H, H-9ax, H-10ax), 2·05 (m_c, 1 H, H-9eq), 2·23 (m_c, 1 H, H-10eq), 7·70 (d, 2 H, H-2′, H-6′), 8·23 (d, 2 H, H-3″, H-5″), 7·26 (d, 2 H, H-2″, H-6″), 6·87 (d, 2 H, H-3′, H-5′), 3·94 (t, 2 H, α-CH_2), 1·76 (m_c, 2 H, β-CH_2), 1·44 (m_c, 2 H, γ-CH_2), 1·32 (br. s, 8 H, -CH_2-), 0·90 (t, 3 H, CH_3); $^3J_{1,6}=8{\cdot}5$, $^3J_{1,10a}=10{\cdot}3$, $^3J_{5a,5e}=10{\cdot}1$, $^3J_{5a,6}=10{\cdot}1$, $^3J_{5e,6}=5{\cdot}1$, $^3J_{8,9a}=10{\cdot}9$, $^3J_{8,9e}=2{\cdot}0$, $^3J_{Aryl}=8{\cdot}3$ Hz; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta=73{\cdot}8$ (C-1), 100·0 (C-3), 69·6 (C-5), 78·6 (C-6), 79·8 (C-8), 31·6 (C-9), 33·0 (C-10), 133·3 (C-1′), 127·4, 127·2 (C-2′, C-6′, C-2″, C-6″), 114·5 (C-3′, C-5′), 123·5 (C-3″, C-5″), 158·0 (C-4′), 144·2 (C-4″), 68·1 (α-CH_2), 29·3, 29·2, 25·7, 22·6 (-CH_2-), 14·0 (CH_3); $[\alpha]_D^{20}=+23{\cdot}0$ ($c=0{\cdot}5$, $CHCl_3$); elemental analysis: calculated for $C_{27}H_{35}O_6N$

Table 2. Transition temperatures of compounds **3–4**.

Compound	Transition temperatures/°C								
3R	Cr	81·5							I
3S	Cr	110·9							I
4R	Cr	71·7	(S_A	59·9	TGB_A	60·5)	Ch	86·1	BP
4S	Cr	93·7	(S_A	53·5	TGB_A	55·0	Ch	82·3)	I

Parentheses denote a monotropic transition.

(469·6): C 69·05, H 7·53, N 2·98, found C 69·20, H 7·48, N 2·95 per cent.

3.2. *Analytical data for* **3R** *and* **3S**

1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 3{\cdot}70$ (ddd, 1 H, H-1), 5·60 (s, 1 H, H-3), 4·34 (m_c, 2 H, H-5eq, O–CH_{alkyl}), 3·80 (dd, 1 H, H-5ax), 3·59 (ddd, 1 H, H-6), 4·48 (dd, 1 H, H-8), 1·88 (m_c, 2 H, H-9ax, H-10ax), 2·06 (m_c, 1 H, H-9eq), 2·23 (m_c, 1 H, H-10eq), 7·70 (d, 2 H, H-2′, H-6′), 8·23 (d, 2 H, H-3″, H-5″), 7·23 (d, 2 H, H-2″, H-6″), 6·87 (d, 2 H, H-3′, H-5′), 1·28 (m_c, 13 H, $-CH_2-$, OCH–CH_3), 0.87 (t, 3 H, CH_3); $^3J_{1,6} = 8{\cdot}5$, $^3J_{1,10a} = 10{\cdot}3$, $^3J_{5a,5c} = 10{\cdot}1$, $^3J_{5a,6} = 10{\cdot}1$, $^3J_{5e,6} = 5{\cdot}1$, $^3J_{8,9a} = 10{\cdot}8$, $^3J_{8,9e} = 2{\cdot}1$, $^3J_{Aryl} = 8{\cdot}3$ Hz; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 73{\cdot}8$ (C-1), 100·1 (C-3), 69·6 (C-5), 78·5 (C-6), 79·8 (C-8), 33·0 (C-9), 31·6 (C-10), 133·3 (C-1′), 144·2 (C-1″), 127·4, 127·3 (C-2′, C-6′, C-2″, C-6″), 115·8 (C-3′, C-5′), 123·5 (C-3″, C-5″), 158·0 (C-4′), 144·0 (C-4″), 74·0 (O–CH_{alkyl}), 36·5, 29·3, 25·5, 22·6 ($-CH_2-$), 19·8, 14·0 (CH_3); **3R**: $[\alpha]_D^{20} = +13{\cdot}5$ ($c = 1{\cdot}0$, $CHCl_3$); **3S**: $[\alpha]_D^{20} = +15{\cdot}3$ ($c = 0{\cdot}2$, $CHCl_3$).

3.3. *Analytical data for* **4R** *and* **4S**

^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 3{\cdot}65$ (ddd, 1 H, H-1), 5·60 (s, 1 H, H-3), 4·33 (m_c, 2 H, H-5eq, (O–CH_{alkyl}), 3·79 (dd, 1 H, H-5ax), 3·58 (ddd, 1 H, H-6), 4·48 (dd, 1 H, H-8), 1·88 (m_c, 2 H, H-9ax, H-10ax), 2·04 (m_c, 1 H, H-9eq), 2·22 (m_c, 1 H, H-10eq), 7·63, 7·69 (d, 4 H, H-2′, H-6′, H-3″, H-5″), 7·40 (d, 2 H, H-2″, H-6″), 6·87 (d, 2 H, H-3′, H-5′), 1·28 (m_c, 13 H, $-CH_2-$, OCH–CH_3), 0·89 (t, 3 H, CH_3); $^3J_{1,6} = 8{\cdot}5$, $^3J_{1,10a} = 10{\cdot}3$, $^3J_{5a,5e} = 10{\cdot}2$, $^3J_{5a,6} = 10{\cdot}2$, $^3J_{5c,6} = 5{\cdot}1$, $^3J_{8,9a} = 10{\cdot}9$, $^3J_{8,9e} = 2{\cdot}1$, $^3J_{Aryl} = 8{\cdot}3$ Hz; ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 73{\cdot}8$ (C-1), 100·2 (C-3), 69·6 (C-5), 78·5 (C-6), 79·8 (C-8), 31·9 (C-9), 33·0 (C-10), 133·6 (C-1′), 142·5 (C-1″), 127·4, 127·2 (C-2′, C-6′, C-2″, C-6″), 115·7 (C-3′, C-5′), 132·2 (C-3″, C-5″), 158·5 (C-4′), 125·2 (C-4″), 112·5 (CN), 74·0 (O–CH_{alkyl}), 36·5, 29·4, 25·5, 22·7 ($-CH_2-$), 19·8, 14·0 (CH_3); **4R**: $[\alpha]_D^{20} = +14{\cdot}6$ ($c = 1{\cdot}0$, $CHCl_3$); **4S**: $[\alpha]_D^{20} = +18{\cdot}8$ ($c = 1{\cdot}0$, $CHCl_3$).

4. Conclusions

We have shown that the cholesteric helical pitch in this class of compounds depends on the number and configuration of the chiral centres and the substitution pattern in the molecule. The change of a cyano to a nitro group leads from a single inversion of the helical pitch to the sequence inversion–maximal value–second inversion of the helical pitch. An additional chiral centre in the side chain, depending on its configuration, causes either the suppression of the inversion or an extremely rapidly increasing pitch after the inversion. This hardens the theory about different chiral centres having different helical twisting power, competing for the resulting macroscopic chiral effects.

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