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The Synthesis of a Cholesterogen with Hydrogen–Deuterium Asymmetry

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Abstract—The uncertainty concerning the factor, steric or polar, that is responsible for the helical molecular arrangement in a cholesteric mesophase is discussed with reference to both thermotropic and lyotropic liquid crystal systems. An attempt has been made to reduce this uncertainty by the study of a mesogen containing in its molecules an hydrogen–deuterium asymmetric centre; hydrogen–deuterium asymmetry is known to give optical activity in a variety of non-mesogens. Steric effects have been reduced to a minimum by the examination of this type of system.

Racemic and optically active 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)-cinnamate have been synthesized. The racemic modification is a nematogen, but the optically active ester gives a cholesteric of very long pitch. This demonstrates that hydrogen–deuterium asymmetry is sufficient to produce a cholesterogen and substantiates the view that the factor mainly responsible for this is polar in nature.

1. Introduction

For many years there has been uncertainty about the factors that are responsible for the helical or twisted molecular arrangement which exists in a cholesteric mesophase, and which is necessary to explain the unique optical properties of the mesophase. It is known of course that all compounds producing cholesteric mesophases consist of asymmetric molecules and are optically active. This indicates that the twisted molecular arrangement is due to either reinforcing steric or polar factors which operate between the molecules with a similar stereochemical configuration. The majority of cholesteric liquid crystals that have been studied are those formed by derivatives of naturally occurring, optically active sterols such as cholesterol and it is to these types that Fergason[1,2,3] refers when he attributes the helical orientation of the molecules to intermolecular steric effects which stem from the " side chain " methyl (10-Me and 13-Me) and

octyl (17-C_8H_{17}) groups of cholesterol, i.e., he proposes that these steric effects rotate the long axes of molecules that lie with their planes one above the other and thus ultimately produce an overall molecular displacement which traces out a helical path. But compounds which are not derived from sterols are also known to be cholesteric. For example, Friedel[4] in 1922 examined the cholesteric phase of active 2-methylbutyl 4-(*p*-cyanobenzylideneamino)cinnamate and recently Leclerq, Billard and Jacques[5] have been able to utilize such non steryl containing cholesterogens in both enantiomorphic forms, e.g., (−) and (+) 4′-(2-methylhexyl)biphenyl-4-carboxylic acid and (−) and (+) 2-methylbutyl 4-(*p*-ethoxybenzylideneamino)-cinnamate. Leclerq *et al.* showed that the racemic modifications are nematic and can be converted to cholesterics by the addition of one of the enantiomers. As the excess of one enantiomer over the other is increased there is a continuous enhancement of the optical properties which characterize cholesteric mesophases. The racemic 2-methylbutyl esters of several 4-(*p*-substituted benzylideneamino)-cinnamic acids have also been shown[6] to be nematic whereas the (−)2-methylbutyl esters are cholesteric.

Turning now to lyotropic systems, Robinson[7,8] was able to justify the description of the liquid, birefringent phase of solutions of the polypeptide poly-γ-benzyl-L-glutamate (PBLG) in various organic solvents as a cholesteric phase and confirmed, by the use of this system, the helicoidal structure postulated for cholesteric mesophases in general. By preparing a solution containing equal amounts of PBLG and the enantiomeric PBDG, he produced a nematic mesophase which corresponded to an "untwisted" cholesteric structure. X-ray data on solutions containing 16.6 to 48.5 ml of PBLG in 100 ml of dioxan, methylene chloride, chloroform or *m*-cresol enabled him to postulate that, since each molecule presents an α-helical arrangement of dipoles and all the helices in a solution are of the same sense, the intermolecular attractions arising from the dipoles may be expected to impose a unidirectional twist on the array of parallel molecules. He suggested that this twisted characteristic of the structure is caused by the arrangement of the dipoles in the PBLG molecules because, knowing the diameter of the cylinder described by a fully extended PBLG molecule, and subtracting this from the intermolecular separation measured at various concentrations, it was found that the side chains

of the molecules overlap only a little at high concentration, but not at all at moderate and low concentrations.

It is also noted that nematogens, e.g., *p*-azoxyanisole, containing cholesteryl acetate[9] or propionate[10] (as little as 1%) give phases with the optical properties of long pitch cholesterics. Moreover, nematic mesophases can be transformed into cholesterics by the addition of 10% or more of an optically active yet non-mesogenic compound, e.g., (+)2-octanol.

All these observations imply strongly that polar effects are a cause of the twisting in the cholesteric phase. A further relevant consideration is the phenomenon caused by applying an electric field at 90° to the long axes of the cholesteric helices formed by cholesteric materials of relatively weak negative or positive dielectric anisotropy diluted with nematic compounds having a strong positive dielectric anisotropy. The field readily rotates the molecules of strong positive dielectric anisotropy so that their long axes are aligned with the field, and the overall result is equivalent to an unwinding of the helices and the generation of a nematic mesophase. Removal of the field results in regeneration of the helices and cholesteric properties.

Particularly in the cases mentioned above in which the cholesterogen is diluted with non-optically active material (solvent or nematogen), it seems unlikely that steric factors would be able to propagate through the diluting medium between the asymmetric molecules, especially as so little of the cholesterogen or other optically active compound is required to produce the twisting in a nematic medium (although the resulting pitch would then be long).

From a more theoretical standpoint, a nematic mesophase may be considered as a statistically parallel orientation of rod-like molecules. The molecules will undoubtably oscillate about a position of strict parallelity (an angular displacement as high as 20° has been proposed by Keating), but the average situation will amount to a parallel distribution. With asymmetric molecules, the asymmetry of the molecular polarizability and the intermolecular force field could lead to a weighting of this oscillation to the right or left, resulting in an average situation in which the long axes of the molecules are displaced to the right or left (depending on the sign of the molecular asymmetry) producing a twisted structure. Keating[11] suggests

in a more quantitative manner a similar theory for the cholesteric phase, demonstrating that polar factors can be used to explain the twisting phenomenon.

However, no conclusive evidence which clearly separates the polar and steric factors has been experimentally achieved on typically cholesteric compounds. It seemed of interest therefore to consider whether an experiment could be designed which would distinguish as clearly as possible which of these two effects is responsible for the unique cholesteric structure.

Now it is known that H–D asymmetry causes optical activity. This was conclusively and unambiguously shown by Eliel[12] on an experimental basis using only one H–D asymmetric centre in α-deuterioethylbenzene; earlier attempts had merely shown that a slight change in rotatory power was associated with H–D asymmetry. Fickett[13] has also explained theoretically why H–D asymmetry appreciably affects optical activity as a consequence of the disymmetric vibrational wave functions of C–H and C–D. Thus we have in deuterium, a substituent which has been shown to produce an asymmetric centre in conjunction with hydrogen, and yet the " sizes " or average vibrational amplitudes for C–H and C–D are very similar. The difference is in fact within the limits within which the bonds vibrate, as shown by the fact that interpretation of spectroscopic data on CH_4 and CD_4 using harmonic equations gives values of 1.094 Å and 1.091 Å for the C–H and C–D bonds, respectively. When anharmonic equations are used the values of the two bond lengths obtained are in fact the same (1.085 Å).[28]

The proposed experiment was therefore to prepare a mesogen whose optical activity was due solely to H–D asymmetry and to examine the liquid crystalline behaviour of the compound.

To eliminate steric effects completely from the experimental study would of course require the use of two different substituents which have different electrical properties (and hence different electrical interactions on the intermolecular level), but exactly the same " effective " size (size in this context being a compound of zero point size and average vibrational amplitude). Such an experiment in practise is not possible and related problems in designing experiments to distinguish absolutely between steric and polar factors are encountered frequently in studies of reaction mechanisms. Similar

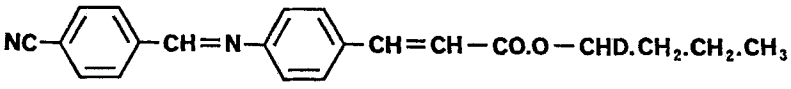
problems of separating closely related factors are encountered too in NMR spectroscopy when attempts are made to account for isotopic shifts in terms of changes in bond length, bond angle, population of excited vibrational states etc.

With H–D asymmetry, we would however have reduced the steric effect to the lowest conceivable level, although it was recognized that it would not be possible to say that any property of the liquid crystal was due exclusively to *either* a difference in size (i.e., average vibrational amplitude) *or* a change in atom or bond polarizability, since the latter is a consequence of the former when one is concerned with isotopic substitution.

However it was thought of interest to try an experiment using H–D asymmetry in a mesogen, for at least it would show whether such asymmetry is sufficient in itself to produce cholesteric properties. Also other cholesterogens involve at least a methyl group at the asymmetric centre and thereby introduce quite large steric effects; yet the resulting angles of rotation are less than 10 minutes of arc. On this basis, the very small steric difference between H and D might be expected to have a negligible effect on the molecular orientation in the mesophase. If therefore the optically active deuterio- substituted mesogen were cholesteric, it would seem reasonable to ascribe its behaviour predominantly to polar effects and not to steric factors.

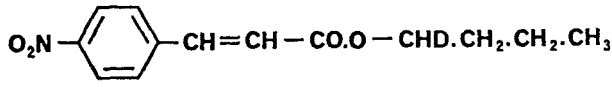
Selection of the Mesogen

Streitwieser[14] has shown that 1-butanol-1-*d* forms optically active isomers, and Gray and Harrison[15] have prepared 1-butyl 4-(*p*-cyanobenzylideneamino)cinnamate and found it to be a stable mesogen with strong nematic tendencies. 1-Butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate (I) seemed therefore a suitable compound to study. The method of preparation was *via* the ester of

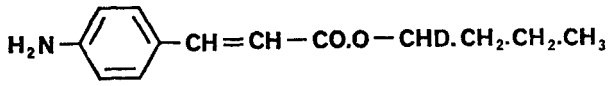


I

p-nitrocinnamic acid which was prepared from *p*-nitrocinnamoyl chloride and active 1-butanol-1-*d* in pyridine as solvent. The last step has the essential feature that the asymmetry of the C_1 carbon of 1-butanol-1-*d* cannot be changed during the reaction because no carbonium ion intermediate is formed. Subsequent reduction of the nitro-ester (II) with iron powder and 20% aqueous acetic acid in



II



III

ethanol yielded the amine (III) which was then condensed with *p*-cyanobenzaldehyde. These steps cannot affect the asymmetry of the C_1 carbon in the butyl group. The programme also included preparation of the racemic modification of the deuterio-ester, so that a comparison of its behaviour with that of the optically active analogue would be obtained.

2. Experimental

2.1. Materials

The preparation of 1-butyl 4-(*p*-cyanobenzylideneamino)cinnamate and thermodynamic data for the transition temperatures have previously been reported.[15] The constants obtained here corresponded and were C–N, 108°C; ΔH 8.68 kcal mol^{-1} and N–I, 133°C; ΔH 0.10 kcal mol^{-1}. Crystal polymorphism occurs in the compound,[15,16] and there is a lower melting crystal form having C–N, 90°C, but it does not predominate.

Racemic 1-*butyl*-1-*d* 4-(p-*cyanobenzylideneamino*)*cinnamate*

Racemic 1-butanol-1-*d* (b.p. 117 °C) was prepared by a standard procedure[14] from butyraldehyde by reduction with $LiAlD_4$. The yield was 50%. NMR spectroscopy showed an unresolved complex peak at 6.4 τ due to –CHD–O–; integration showed that the area under this peak and the area under the –OH peak observed at 6.05 τ were in the ratio of 1.1:1. IR spectroscopy gave no evidence for an –OD stretching frequency, and therefore the 1-butanol-1-*d* was 90 ± 5% of the type –CHD–OH. The compound showed no optical rotation.

From the racemic 1-butanol-1-*d* were prepared, by standard synthetic methods and purification procedures, 1-butyl-1-*d* *p*-nitrocinnamate, m.p. 67.5–68 °C, 1-butyl-1-*d* *p*-aminocinnamate, m.p. 86 °C, and finally the Schiff's base. The lower melting form of this compound does predominate (C–N, 90°C; ΔH 6.42 kcal mol^{-1}). DTA showed only a very small peak corresponding to the higher melting form, C–N, 108°C, and a small transition peak for the change N–I, 133°C; ΔH 0.08 kcal mol^{-1}. Integration of peaks in the NMR spectrum due to –CHD– and =CH–CO– showed that the protons were in a ratio of 1.06:1, respectively, indicating that 94% of the molecules contained the –CHD– unit. Microanalysis for the Schiff's base gave C, 75.5; H and D, 6.4; N, 8.4%. Calc. for $C_{21}H_{19}DN_2O_2$, C, 75.7; H and D, 6.3; N, 8.4% (Calc. for $C_{21}H_{20}N_{29}O_2$, H, 6.0%). For the nitro-ester, the results were C, 62.4; H and D, 6.5; N, 5.7—calc. for $C_{13}H_{14}DNO_4$, C, 62.4; H and D, 6.4; N, 5.6% and for the amino-ester, C, 71.1; H and D, 8.2; N, 6.7—calc. for $C_{13}H_{16}DNO_2$, C, 70.9; H and D, 8.2; N, 6.4%.

2-*Octanol*-2-d

The preparation of racemic 2-octanol-2-*d* was based on the method of Streitwieser,[14] using freshly distilled 2-octanone (82 g, 99.4% pure by g.l.c.), $LiAlD_4$ (6.5 g) and dry ether (650 ml); the product boiling at 176–178 °C was collected and found, by IR spectroscopy, to contain about 20% of a carbonyl-containing impurity, presumably the ketone. Fractional distillation using a spinning band column was necessary to effect a separation and yielded 2-octanol-2-*d*, 67 g (80%), b.p. 177–178 °C. IR spectroscopy showed negligible contamination with carbonyl impurity, and NMR spectroscopy showed no signal attributable to the methine proton of 2-octanol.

Resolution of 2-*octanol*-2-d

The racemic 2-octanol-2-*d* was resolved in the manner described by Ingersoll[18] with the exception that about five times more acetone than that recommended was required to attain complete solution of the phthalate half ester and brucine. It is interesting to note that when the literature is followed back to the method used by the original authors,[19] about seven times the amount of acetone stated in later procedures was used for the same step.

Both enantiomers of 2-octanol-2-*d*, with specific rotations $[\alpha]_D^{22} = +8.46°$ and $-9.23°$, were finally produced in overall yields of about 45%; the b.p.s. were 177–178°C. Streitwieser[14] obtained specific rotations $[\alpha]_D^{25}$ between $-7.76°$ and $+9.76°$.

Optically active 1-*butanol*-1-d

The method used for this preparation was based on a procedure described by Streitwieser.[14] 2-Octanol-2-*d* ($[\alpha]_D^{22} = -9.23°$) was used in two separate runs. A period of 24 hrs was chosen for the reaction time between equal molar amounts of 2-octanol-2-*d*, which had been converted to 2-octyloxy-2-*d* magnesium bromide, and butyraldehyde. Following Streitwieser's isolation procedure, the fractions of b.p. 118–122°C were collected in an average yield of 22% and had $[\alpha]_D^{22} = +0.208°$ and $+0.171°$. These specific rotations were obtained from values of $\alpha_D^{22} = +0.017$ and $+0.014°$ (neat, $l = 0.1$), respectively. By this method, Streitwieser[14] obtained values for α_D^{25} up to $-0.226 \pm 0.008°$ (neat, $l = 4$), which is equivalent to $[\alpha]_D^{25} = -0.069°$. Subsequently, Streitwieser[17] obtained (+) 1-butanol-1-*d* from butyraldehyde-1-*d* and (−)isobornyloxy magnesium bromide with $[\alpha]_D^{25} = +0.185°$. Mosher,[20] by reducing butyraldehyde-1-*d* with actively fermenting yeast, obtained optically pure (+) 1-butanol-1-*d* having a specific rotation $[\alpha]_D^{27.5} = +0.471°$. This means that the average optical purity of the 1-butanol-1-*d* prepared in the present work was 40%.

Optically active 1-*butyl*-1-d 4-(p-*cyanobenzylideneamino*)*cinnamate*

Optically active 1-butanol-1-*d* (2.4 g, 1.2 mol. $[\alpha]_D^{22} = +0.189°$) was interacted in dry pyridine (45 ml) with *p*-nitrocinnamoyl chloride (5.8 g, 1.0 mol) by stirring at room temperature overnight and then at 90–100°C for 1 h. The ester was separated by pouring the reaction mixture into water and extracting into ether. Successive

washing of the extract with dilute sulphuric acid, water and aqueous sodium bicarbonate, followed by drying over anhydrous $MgSO_4$, filtration and rotary evaporation gave a yellow solid. Successive recrystallizations from a mixture of petroleum ether (b.p. 40–60 °C) and benzene yielded the nitro-ester, 3.86 g (57%), of m.p. 68 °C which was the same as that of the racemate.

Reduction with iron and 20% aqueous acetic acid[21] in ethanol produced the amino-ester. The crude amino-ester was decolorized using activated carbon and purified by crystallization from a mixture of petroleum ether (b.p. 40–60 °C) and benzene and had m.p. 86°C which was the same as that of the racemate. A yield of 2.0 g (64%) was obtained. Since the amine is a solid, a 10% solution in chloroform had to be used to obtain the optical rotation which was very small, but apparently negative ($\alpha_D^{22} = -0.005 \pm 0.002°$ ($l = 0.1$)). A mass spectrum showed a major peak at 220 and a breakdown peak at 58 corresponding to C_4H_8D. An accurate determination of the molecular weight of the amino-ester by mass spectrometry gave 220.1324 ($C_{13}H_{16}DNO_2 = 220.1336$). Integration of peaks in the NMR spectrum due to –CHD– and =CH–CO– showed that the protons were in a ratio of 1:1, indicating that 100% of the molecules contained the –CHD– unit.

When condensed with *p*-cyanobenzaldehyde (1.1 mol) in hot ethanol the amine (1.0 mol) yielded the required Schiff's base which was purified by crystallization from ethanol and from a mixture of petroleum ether (b.p. 40–60 °C) and benzene until constant melting and clearing points (C–'N', 108 °C; ΔH 9.37 kcal mol^{-1} and 'N'–I, 133 °C; ΔH 0.08 kcal mol^{-1}) were obtained. The compound was again dimorphic with a less stable solid having C–'N' 90 °C, which, in time became the more predominant form. NMR spectroscopy showed, by the same principle as before, that 100% of the molecules contained the –CHD– unit. Micro-analytical data for the deuterio-Schiff's base ester† were again satisfactory, as were those for the intermediate nitro‡ and amino§ deuterio-esters. The deuterio–

† Found; C, 75.4; H and D, 6.2; N, 8.6. Calc. for $C_{21}H_{19}DN_2O_2$: C, 75.7; H and D, 6.3; N, 8.4%

‡ Found; C, 62.3; H and D. 6.5; N, 5.8. Calc. for $C_{13}H_{14}DNO_4$: C, 62.4; H and D, 6.4; N, 5.6%.

§ Found: C, 71.0; H and D, 8.0; N, 6.4. Calc. for $C_{13}H_{16}DNO_2$: C, 70.9; H and D, 8.2; N, 6.4%.

Schiff's base ester ($C_{21}H_{19}DN_2O_2$) produces an ion of mass 332.1520 which corresponds to the loss of a proton giving $C_{21}H_{18}DN_2O_2$, which has a calculated mass of 332.1508. Presumably the azomethine proton is lost. A similar accurate mass determination of the normal ester ($C_{21}H_{20}N_2O_2$) shows it to produce an ion of mass 331.1437 ($C_{21}H_{19}N_2O_2 = 331.1446$). This demonstrates that proton loss occurs here also.

2.2 Method

IR, NMR and mass spectroscopic data were obtained using a Perkin Elmer 457 spectrophotometer, a J.E.O.L., JNM-4H-100 MHz spectrometer and an A.E.I. M.S. 902 spectrometer, respectively. Optical rotations were measured to an accuracy of $\pm 0.002°$ using a Bendix N.P.L. 143A automatic polarimeter.

The melting points and liquid crystal transition temperatures for the Schiff's bases and the associated enthalpies of transition were measured using a low temperature differential thermal analyser (Stanton Redcroft Ltd., London—model LDT 671). These transition temperatures were also checked using a polarizing microscope in conjunction with a heated stage (C. Reichert, Optische Werke A.G., Wien, Austria); this equipment was also used to examine the textures of the nematic and cholesteric phases of the Schiff's bases. The photomicrograph of the Grandjean terraces of the cholesteric phase of the active 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate was obtained using a Leica camera.

3. Discussion and Results

Comparison of crystal–mesophase transition temperatures of the normal butyl, and the racemic and optically active deuterio-substituted butyl Schiff's base esters shows that they are the same and that the three compounds exhibit the same crystal polymorphs. The racemic deuterio–Schiff's base ester, however, gives the form melting at 90 °C most predominantly. The enthalpies of these transitions are also of the same order for the three esters. Any differences in the enthalpies could be attributed to the fact that

different proportions of the material melt at different temperatures depending on the proportion of the two polymorphic forms present. All three compounds have the same mesophase–isotropic liquid transition temperatures with comparable enthalpies of transition; for the two deuterio-substituted compounds, the enthalpies of these transitions are identical.

The textures of the liquid crystalline phases obtained from the racemic deuterio- and active deuterio–Schiff's base esters differ considerably. The racemic compound, when viewed between crossed polars showed small homogeneous areas of varying birefringence and contained the black thread-like lines typical of nematics. The active compound was consistently different; it was of a more uniform birefringence and contained both thread-like lines and ribbons which approached in their appearance the alignment discontinuities typical of cholesteric plane textures. When viewed, by reflection, in normal light, the phase was not coloured.

3.1. Grandjean Terraces

Grandjean[22] found that when a little (−)2-methylbutyl 4-(*p*-cyanobenzylideneamino)cinnamate was melted in a freshly cleaved mica wedge and viewed under a microscope, a series of regularly spaced bands separated by sharp lines could be seen either with polarized light or between crossed polars. On rotating the preparation between crossed polars, no change in the position of the lines in the specimen occurred. The appearance of these bands was explained by de Vries,[23] who proposed that the mica imposes a certain orientation on the molecules in contact with the surfaces. Only when the thickness of the wedge is equivalent to a whole number of half turns of the helix will the structure " fit "; elsewhere there will be competition between the orientating influence of the mica and the tendency of the structure to twist at its normal pitch. Consequently in the latter areas, the structure will be disturbed. Thus a succession of disturbed and undisturbed regions will be formed, giving the banded image when viewed through a microscope.

Only small areas of the preparation are ever in fact orientated in such a way as to exhibit Grandjean terraces, and consequently, the terraces do not manifest themselves over large areas. The optically active deuterio-ester under study here was found not to orientate

itself very readily to exhibit Grandjean terraces, and several preparations had often to be made before they were seen.

Crystals of the optically active 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate were inserted into a freshly cleaved mica wedge and heated on a Kofler hot stage (C. Reichert, Wien, Austria), until the amorphous isotropic liquid was formed. On cooling, small areas showing Grandjean terraces could be seen (Fig. 1). The sample in the wedge was then heated again until it changed to the amorphous isotropic liquid when the terraces disappeared. On cooling into the cholesteric state, the terraces reformed in the same area, showing that the bands were Grandjean terraces, and not due to defects in the mica.

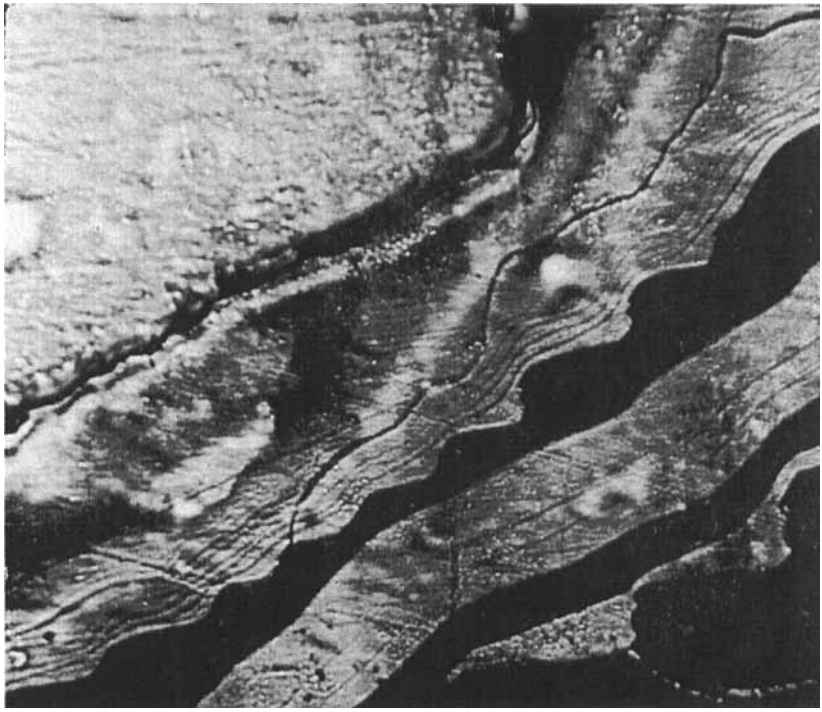


Figure 1. Photomicrograph showing the Grandjean Terraces exhibited by optically active 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate in a mica wedge. Crossed polars (approx. 47×).

3.2. The Pitch of the Helix

The helix arising from the left or right handed molecular displacement in a cholesteric mesophase is of varying pitch length depending upon the compound (or mixture of compounds) and the temperature.

A sample of 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate was introduced by capillarity, in the cholesteric phase, between a microscope-cover slip and a hemispherical lens of radius 4.7 mm. The glass surfaces in contact with the mesogen had been rubbed according to Chatelain's technique.[24] When cooled into the cholesteric phase, the usual optical discontinuities of the Cano wedge formed. From their spacing, the pitch P was found to be 155 ± 5 μm at 120 °C. The temperature dependence of P was weak, i.e., with decreasing temperature, P decreased by 10% throughout the whole cholesteric range.

The pitch length of cholesterics is usually in the range 0.2 μm–20 μm, that for cholesteryl derivatives being nearer to 0.2 μm. Thus 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate has a pitch approx. 10–1000 times longer than that for commonly investigated cholesterogens; this is to be expected when the cholesteric-influencing forces are so small.

These two observations—the Grandjean terraces and the measured pitch—show conclusively that the mesophase of 1-butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate is cholesteric.

4. Conclusion

Although, as has been mentioned earlier, steric and polar factors cannot be conclusively separated by this experiment, it is clear that when steric factors are reduced to a minimum as in the case of the optically active deuterio-ester, the compound still exhibits cholesteric properties, in that Grandjean terraces, which are characteristic of and indeed typify cholesteric mesophases, and a pitch are exhibited by the compound in its liquid crystalline state. This shows conclusively that H–D asymmetry is sufficient to produce a cholesterogen and demonstrates the extreme sensitivity of the nature of the liquid crystal system formed to the intermolecular forces at play.

It must also be remembered that the active butyl-1-*d* 4-(*p*-cyanobenzylideneamino)cinnamate is at most only 40% optically pure.

This in fact makes the evidence that polar factors cause the helicoidal arrangement even more acceptable, because the system is effectively a " diluted " cholesteric, the diluent being racemic butyl-l-*d* 4-(*p*-cyanobenzylideneamino)cinnamate.

Thus it would seem that steric effects are not so likely to be as significant as polar factors in determining the cholesteric properties of the deuterio–Schiff's base ester.

Some support for the subordinate role of steric effects in this context can be found in NMR studies of deuteriated methanes dissolved in nematic solvents. It has been shown[25,26] that CHD_3 and CDH_3 are " ordered " when dissolved in a nematic solvent, and there is a problem in deciding whether steric or polar factors are largely responsible. Steric effects can probably be ruled out because a degree of ordering is also observed[26] for CH_4 and CD_4, this being attributed to a slight distortion of the symmetric molecule by " pressure " from the nematic solvent.[27]

In conclusion, it should perhaps be pointed out that the above results do not preclude the possibility that particularly in steroidal cholesterics, steric reinforcement of polar effects may be of some significance in contributing to the angular displacement of the long molecular axes from a statistically parallel orientation.

Acknowledgements

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REFERENCES

1. Fergason, J. L., *Sci. American* **211**, 77 (1964).
2. Fergason, J. L., *Appl. Optics* **7**, 1729 (1968).
3. Fergason, J. L., *Electro-Technology* Jan., 41 (1970).
4. Friedel, G., *Ann. de Physique* **18**, 273 (1922).
5. Leclerq, M., Billard, J. and Jacques, J., *Mol. Cryst. and Liq. Cryst.* **8**, 367 (1969).
6. Gray, G. W., *Mol. Cryst. and Liq. Cryst.* **7**, 127 (1969).

7. Robinson, C., *Tetrahedron* **13,** 219 (1961).
8. Robinson, C., *Mol. Cryst. and Liq. Cryst.* **1,** 467 (1966).
9. Friedel, G., *C. R. Acad. Sc. Paris, Série B.* **176,** 475 (1923).
10. Alexandrov, V. N. and Chistyakov, I. G., *Mol. Cryst and Liq. Cryst.* **8,** 19 (1969).
11. Keating, P. N., *Mol. Cryst. and Liq. Cryst.* **8,** 315 (1969).
12. Eliel. E. L., *J. Amer. Chem. Soc.* **71,** 3970 (1949).
13. Fickett, W., *J. Amer. Chem. Soc.* **74,** 4204 (1952).
14. Streitwieser, A., *J. Amer. Chem. Soc.* **75,** 5014 (1953).
15. Gray, G. W. and Harrison, K. J., *Mol. Cryst. and Liq. Cryst.* **13,** 37 (1971).
16. Leclerq, M., Billard, J. and Jacques, J., *Mol. Cryst. and Liq. Cryst.* **10,** 429 (1970).
17. Streitwieser, A., *Tetrahedron* **6,** 338 (1959).
18. Ingersoll, A. W., *Organic Reactions,* Vol. II, Ed. R. Adams,, Wiley and Sons, New York, 1944, p. 400.
19. Pickard, R. H. and Kenyon, J., *J. Chem. Soc.* **91,** 2058 (1907).
20. Althouse, V. E., Feigl, D. M., Sanderso ı, W. A. and Mosher, H. S., *J. Amer. Chem. Soc.* **88,** 3595 (1966).
21. Semonsky, M. and Kunak, J., *Chem. L sty* **47,** 598 (1953).
22. Grandjean, F., *C. R. Acad. Sc. Paris, S rie B* **172,** 71 (1921).
23. de Vries, Hl., *Acta Cryst.* **4,** 219 (1951).
24. Chatelain, P., *Bull. Soc. fr. Minér. Cris allogr.* **66,** 105 (1943).
25. Yannoni, C. S. *J. Chem. Phys.* **51,** 1682 (1969).
26. Ader, R. and Loewenstein, A., *Mol. Phys.* **24,** 455 (1972).
27. Snyder, L. C. and Meiboom, S., *J. Chem. Phys.* **44,** 4057 (1966).
28. Interatomic Distances Supplement, Special Publications No. 18, The Chemical Society, London, 1965, p. 5 and references contained therein.