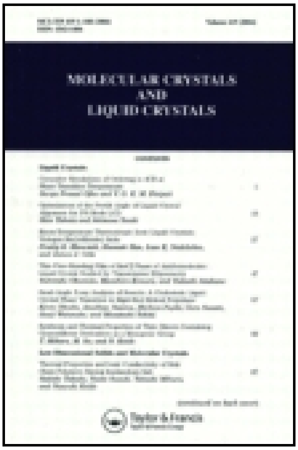

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Helical Twisting Power of Steroidal Solutes in Cholesteric Mesophases. Carbonate Esters of Cholestkerol and Dicholesteryl Compounds

K. Ko [a] , I. Teucher [a] & M. M. Labes [a]

[a] Department of Chemistry, Temple University, Philadelphia, Pa., 19122, USA

Version of record first published: 21 Mar 2007.

To cite this article: K. Ko , I. Teucher & M. M. Labes (1973): Helical Twisting Power of Steroidal Solutes in Cholesteric Mesophases. Carbonate Esters of Cholestkerol and Dicholesteryl Compounds, Molecular Crystals and Liquid Crystals, 22:3-4, 203-210

To link to this article: http://dx.doi.org/10.1080/15421407308083345

Molecular Crystals and Liquid Crystals. 1973. Vol. 22, pp. 203–210

Helical Twisting Power of Steroidal Solutes in Cholesteric Mesophases. Carbonate Esters of Cholesterol and Dicholesteryl Compounds†

K. KO, I. TEUCHER and M. M. LABES

Department of Chemistry
Temple University
Philadelphia, Pa. 19122, USA

Received August 14, 1972; *in revised form December* 4, 1972

Abstract—The alkyl carbonate esters of cholesterol have a helical twisting power P which saturates quickly with chain length, in accord with a model attributing this twist to the effective length of the alkyl chain along the nearest C—O bond. However, compounds having a very small P, such as cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate, appear to change chirality according to the environment. Dicholesteryl compounds have anomalously large P, suggesting a more complex interaction such as structural disarray or bridging of helicoidal arrays.

1. Introduction

In an earlier paper$^{(1)}$ it was reported that it is possible to determine the helical twisting power P of steroidal solutes by dissolving them in a compensated cholesteric liquid crystal solvent consisting of cholesteryl chloride (CC) and cholesteryl myristate (CM). For a series of fatty acid esters of cholesterol, P was found to increase with increasing number of carbon atoms in the chains, showing a zig-zag fine structure with P having higher values for odd-numbered carbon chains. It was also observed that these compounds were left-handed cholesteryl compounds, and that replacing the ester chain by Cl, Br, or OH groups at the 3β position changed the rotational sense to right-handed.$^{(2)}$ Leder$^{(3)}$ has recently discussed this rotatory sense of cholesteric liquid crystals in the following terms: the cholesteryl skeleton is effectively right-handed; additions

---

† Presented at the Fourth International Liquid Crystal Conference, Kent State University, Kent, Ohio, August 21–25, 1972.

at the 3β carbon *reduce* the right-handedness in proportion to the distance to the end of the group or chain in the direction of the 3β carbon bond direction. When that distance is > 2.08 Å, the compound becomes left-handed.

In the present work, a series of cholesteryl alkyl carbonate esters is examined which confirm some of these views. Three additional compounds are reported which have unusual twisting power not directly predictable from their structural characteristics.

2. Experimental

A complete discussion of the method employed in determining the helical twisting power P of solute molecules dissolved in a 1.75 : 1.00 CC : CM solvent has been presented.⁽¹⁾ Briefly, P is, determined from the equation:

$$P \equiv Z_s^{-1}(c = 1) = -m\Delta T_{\text{nem}}(c)/c$$

where $Z_s^{-1}(c)$ is the change in wave number (inverse of the pitch) of the cholesteric solvent matrix when a concentration (c) of a solute (s) having a twisting power $P = Z_s^{-1}(c = 1)$ is added. When the compound forms a cholesteric phase itself, P is identical with the inverse pitch Z^{-1} of the pure compound, with an accuracy of about 20%. The measurement itself involves the determination of the shift $\Delta T_{\text{nematic}} = T_{\text{nematic}}(c) - T_{\text{nematic}}(c = 0)$ of the temperature at which perfect compensation occurs—T_{nematic}—as one adds solute molecules. It is performed by determining the optical rotatory power $r (= 3.9 \times 10^7 Z(T))$ as a function of temperature and observing the discontinuity and inversion of sign of the optical rotatory power.⁽¹⁾ m is the slope of Z^{-1} vs. T.

The methyl, ethyl, propyl, butyl and nonyl carbonates were purified samples obtained from Dr. M. J. Vogel of IBM Corporation. The other solutes were obtained from commercial sources. The decyl and dodecyl carbonates were purified by crystallization from amyl alcohol. Cholesteryl-2-(2-ethoxyethoxy)ethyl carbonate (CEEC) was purified as previously described.⁽³⁾ Dicholesteryl carbonate and dicholesteryl sulfite were recrystallized from amyl alcohol. Microanalysis gave for them C = 82.83%; H = 11.45%; O = 6.16% and C = 79.34%. H = 11.30%; O = 6.15%; S = 3.76% respectively. The calculated numbers are C = 82.63%; H = 11.35%; O = 6.01% and C = 79.15%. H = 11.01%; O = 5.86%; S = 3.91% respectively.

3. Results

The temperature dependence of the optical rotation of a series of cholesteryl alkyl carbonates was measured in the CC : CM mixture, and typical results are shown in Fig. 1 for the butyl carbonate. The dependence of $\Delta T_{\text{nematic}}$ on the number of carbon atoms in the alkyl chain of the alkyl carbonate is compared with the results previously obtained for the alkyl esters of cholesterol in Fig. 2. Whereas $\Delta T_{\text{nematic}}$ depends markedly on the chain length of the alkyl esters, the alkyl carbonates are characterized by a helical twisting power that approaches saturation very quickly as the chain length increases. The order of magnitude of $\Delta T_{\text{nematic}}$ is the same for both series.

To explain this independence, one has only to extend the analyses previously advanced.(1,3) The size and structural arrangement of the side chain at the 3β carbon are of prime importance to P. For the alkyl esters, the ester chain makes an angle with the central molecular plane, and its projection into the plane forms an angle with the long axis of the steroid ring system; its effective left-handed twisting power reflects the length of the lever arm extending from the 3β carbon. Leder(3) gives a diagram for an alkyl ester of cholesterol from which he determines the projection of the —OCOR group along the 3β-carbon bond direction. For the acetate, for example, this distance d is 2.22 Å. This value is actually an average of the projection distance from 3β-carbon to carbonyl oxygen, and the projection distance from 3β-carbon to the end of the alkyl chain. For the alkyl carbonate esters it is possible to draw a similar diagram to that of Leder's, and Fig. 3 presents this diagram for cholesteryl propyl carbonate. Here, d has a value of 2.27 Å. For the carbonate esters, d is almost constant for C_3 and above, and completely saturates at C_5. The twisting power of the carbonate esters observed is consistent with these values. $\Delta T_{\text{nematic}}$ for the propyl was found to be higher than expected. To calculate the twisting power $P = Z_s^{-1}$, one must multiply $\Delta T_{\text{nematic}}$ by $m/c = 5 \times 10^3$.

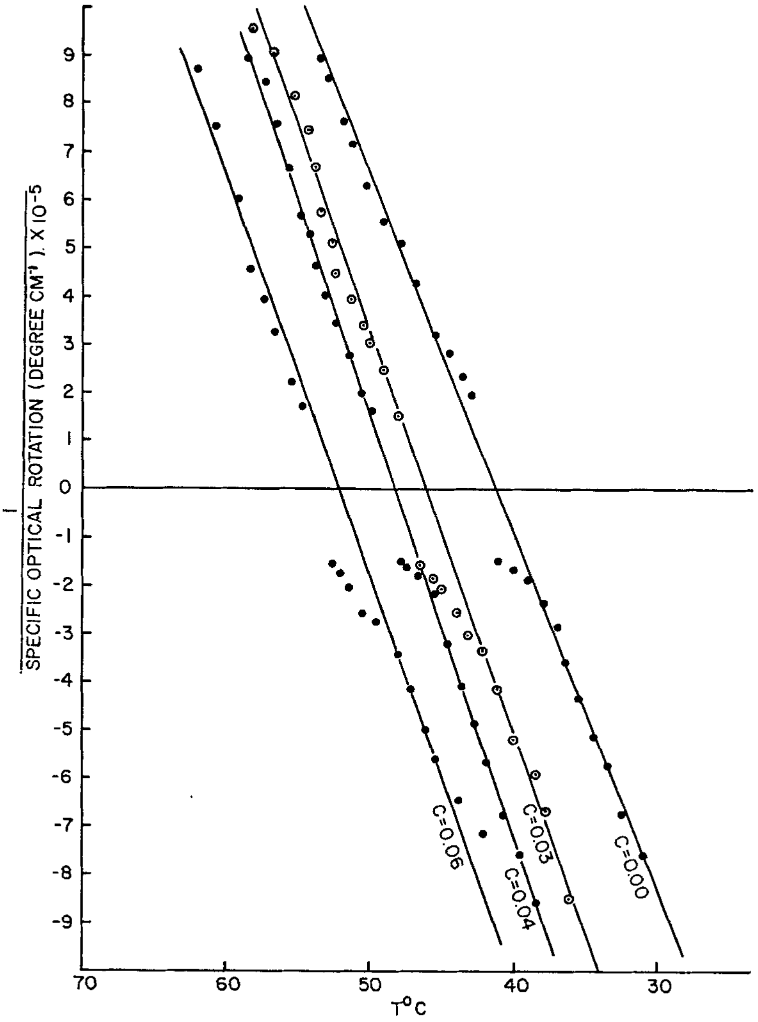

Figure 1. Temperature dependence of specific optical rotation of a 1.75 : 1.00 CC : CM mixture at different relative molar concentrations of cholesteryl *n*-butyl carbonate.

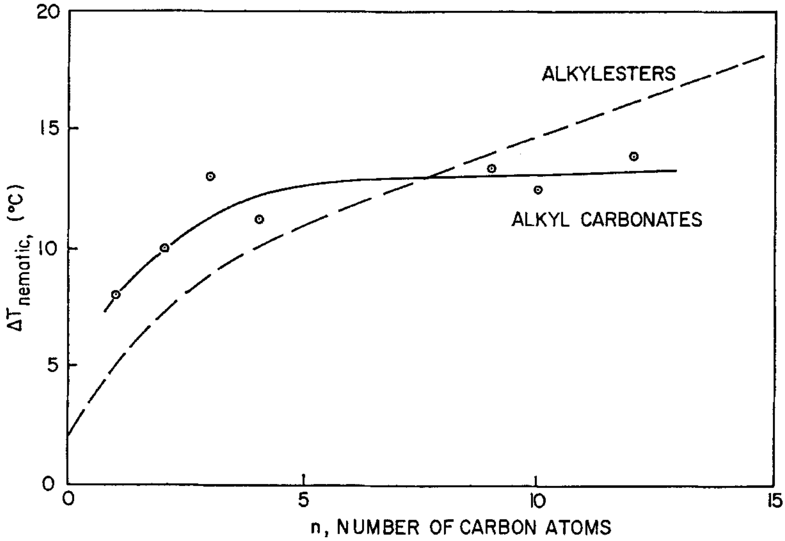

Figure 2. Dependence of the shift in the nematic temperature of a 1.75: 1.00 CC:CM mixture as a function of added alkyl carbonate (full line) and alkyl esters of cholesterol (broken line). n = length of alkyl chain only. Relative molar concentration of all solutes = 0.055.

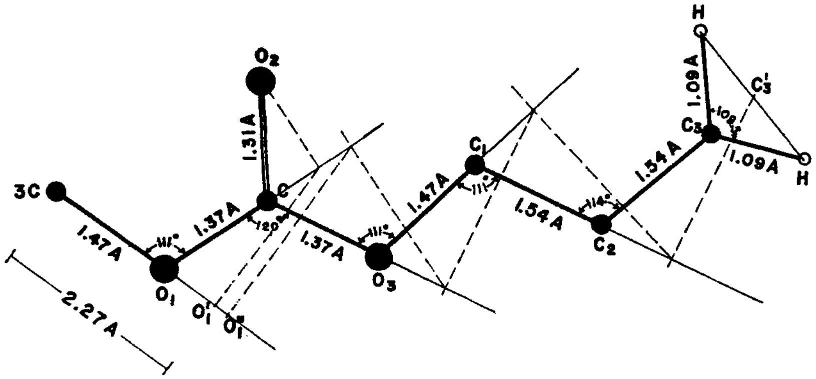

Figure 3. Projection diagram of cholesteryl propyl carbonate.

Leder's method(3) of determining pitch of a solute consists of measuring the critical wavelength $\lambda_0 = nZ$ as a function of concentration in a given cholesteric solvent (usually cholesteryl oleyl carbonate) and extrapolating to 100% solute concentration. Results obtained in this way, and by measurement of P in a compensated cholesteric solvent give very similar results. Table 1 shows this comparison for three compounds where pitch data have also been obtained by the direct method of measuring the distance between neighboring Grandjean lines in a wedge-type sample on the pure compounds. It is clear that both methods give accurate results with compounds having reasonably large helical twisting power (small pitch). CEEC is an interesting exception. When dissolved in CC : CM, no change in $\Delta T_{\text{nematic}}$ is observed; i.e., CEEC appears to have an infinite pitch; Leder reports a very large pitch for this compound;(5) however, direct measurement of λ_0 in a 12 μ sample gave, after several attempts, the value of 12,800 Å. Results of direct measurement of the pitch give a value of 6000 Å.(4) The divergent values for the pitch of CEEC are no doubt partly explained by the different methods used for the measurements and reflect the situation that probably neither Leder's method nor that used in the present work is adequate for long pitch cholesterics. All the results do however show that the pitch for CEEC is long. Further, the pure compound forms a right-handed helix, whereas the length of the side chain implies the compound should be left-handed. It is possible that in pure CEEC electrostatic repulsion between the carbonyl oxygen and the oxygens in the chain cause a change in the

TABLE 1 Comparison of Calculated and Experimental Pitch Values

	Pitch (Å)		
Compound	Grandjean-line distance	Critical wavelength extrapolation	Shifts in $\Delta T_{\text{nematic}}$
Cholesteryl chloride	3400^{6}	3250^{8}	3380^{1}
Cholesteryl pelargonate	2400^{1}	1800^{8}	1720^{1}
Cholesteryl 2-(2-ethoxy-ethoxy)ethyl carbonate	6000^{4}	$16{,}600^{5}$ 12,800	∞

bond angle bringing the chain closer to the projection of the long axis of the steroid ring system.

It is obvious that other factors may influence the helical twisting power of a solute molecule; in particular, the solvent phase may influence the orientation of the solute side chain. In fact, Leder(5) has reported that cholesteryl 2-(2-butoxyethoxy)ethyl carbonate appears to adopt the rotatory behavior of the material with which it is mixed. This effect may be expected in those compounds having very small helical twisting power. Adams and Haas(9) have pointed out that cholesteryl iodide (CI), which has a very small helical twisting power, adopts the chirality of its environment in certain cases. Leder(3) reports that CI is slightly left-handed.

Two other compounds have also been examined in the present work: both give anomalously high P. Dicholesteryl carbonate shows a very strong left-handed P, as is shown in Table 2. The compound is not very soluble in CC : CM, the maximum concentration which shows agreement with Cano's rule(10) being a relative molar concentration $c = 0.03$. Dicholesteryl sulfite, on the other hand, gives an anomalously high right-handed twist. This commercial compound was extensively crystallized, but did not give a completely satisfactory analysis. The presence of two steroidal skeletons in these solutes does make possible the involvement of the molecule in a more complex interaction with the solvent, either causing structural disarray or some bridging of helicoidal arrays.

TABLE 2 $\Delta T_{\text{nematic}}$ and Pitch for Dicholesteryl Compounds

Compound	$\Delta T_{\text{nematic}}(c)$ °C	Pitch (Å)
Dicholesteryl carbonate	11.0° (0.02)	1020
Dicholesteryl sulfite	−16.5° (0.06)	1695

Acknowledgement

This work was supported by the National Science Foundation under Grant No. GP–25988. Discussion with Dr. Marcel J. Vogel, who furnished purified samples of several of the alkyl carbonate esters, is gratefully acknowledged.

REFERENCES

1. Baessler, H. and Labes, M. M., *J. Chem. Phys.* **52,** 631 (1970).
2. Friedel, G., *Ann. Physique* **18,** 273 (1922).
3. Leder, L. B., *J. Chem. Phys.* **55,** 2649 (1971).
4. Baessler, H., Malya, P. A. G., Nes, W. R. and Labes, M. M., *Mol. Cryst. and Liq. Cryst.* **6,** 329 (1970).
5. Leder, L. B., *Chem. Phys. Letters* **6,** 285 (1970).
6. Durand, G., *Compt. Rend.* **264B,** 1251 (1967).
7. Kassubek, P. and Meier, G., *Mol. Cryst. and Liq. Cryst.* **8,** 307 (1969).
8. Leder, L. B., *J. Chem. Phys.* **54,** 4671 (1971).
9. Adams, J. E. and Haas, W. E. L., *Mol. Cryst. and Liq. Cryst.* **15,** 27 (1971).
10. Cano, R., *Compt. Rend.* **253,** 1815 (1961).