THE ORIGIN OF MACROSCOPIC HELICAL STRUCTURE IN THE CHOLESTERIC LIQUID CRYSTALLINE PHASE

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It is very well established that the conformation of the molecular geometry and structure in the crystalline state prefigures the assembly and structure of molecules in the mesomorphic states. A systematic study of the structural aspects of the crystalline phase of mesogenic materials as related to their physical properties gives a clear picture of the origin of these properties at the molecular level as well as their variation with changing structure. Presently, we put forth a plausible origin and requirement for the formation of helical structure in the cholesteric liquid crystalline materials, in their mesogenic phase, in terms of the symmetry and molecular structure of these materials in the crystalline state.

The planar textures of the cholesteric liquid crystalline phase are known for their unique optical properties viz., very high optical rotatory power, circular dichroism, reflection of vivid colours etc. These properties have been theoretically explained very clearly by using two different models: one by solving the electromagnetic equations for the Oseen [1] dielectric continuum model and other by using difference equations [2] for wave propagation in a helical structure of birefringent plates. The essential feature in both models is the helical nature (Fig. 1). For wave propagation along the helical axis, one observes optical rotatory power, circular dichroism and reflection. The plane wave incident normal to the helical axis has been observed to show diffraction patterns which have been fully explained by assuming the very same helical structure [3,4]. Thus the existence of helical structure has been uniquely confirmed by these theories and experiments in the cholesteric liquid crystalline state.

From a quantity of preliminary crystallographic data reported in the literature [5–16], we observe that the crystals of the cholesteric phase forming materials invariably conform to either the monoclinic $P2_1$ space group or orthorhombic $P2_12_12_1$ space group (Table I). The symmetry elements of these two space groups can be resolved into a pure rotation

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and translation, unequivocally unlike the other space groups [17]. The several crystallographic screws or microhelices of the crystalline state together with the steric effects and the planar structure of cholesterol derivatives confer on the cholesteric liquid crystalline phase, obtained on heating the solid, a rotation and a translation which is equivalent to

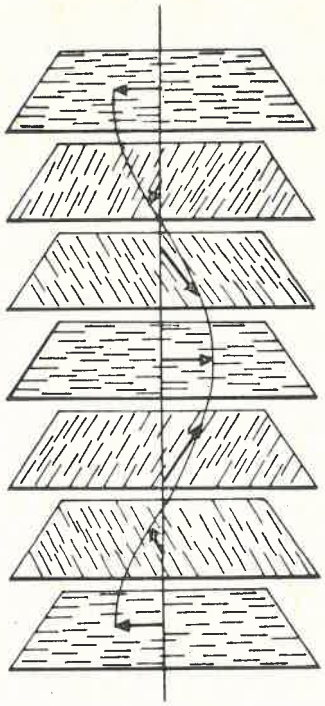

Fig. 1. The cholesteric liquid crystal: Schematic representation of the helical structure

a screw or a helical structure, assumed in the theoretical discussions of optical properties. The general coordinates of infinite micro helices of the crystalline phase can be taken as

$$x_n = r_n \cos\theta, \quad y_n = r_n \sin\theta, \quad z_n = \frac{P\theta}{2\pi},$$

where P is the pitch, r_n is the radius of the n-th helix, and θ is the angular position at height z_n.

As the crystalline phase is heated to the liquid crystalline phase, the micro helices will combine together to give the macro helix as

$$X = \sum r_n \cdot \cos\theta = R\cos\theta, \quad Y = \sum r_n \cdot \sin\theta = R\sin\theta, \quad Z = \frac{P\theta}{2\pi},$$

where $\sum r_n = R$ is the radius of the macro helix, since the pitch is the same. This implies that the cholesteric phase forming materials should normally belong to either the $P2_1$ or $P2_12_12_1$ space group in the solid state. This is further substantiated by consideration of the close

TABLE I

Crystal data for some cholesteric compounds

	Space group	a(Å)	b(Å)	c(Å)	β(°)	Molecules per unit cell
Cholesteryl methanoate	[a] Monoclinic $P2_1$	15.65	6.06	13.53	96.0	2
Cholesteryl ethanoate	[a] Monoclinic $P2_1$	17.51	9.44	16.4	105.5	4
	[b] Monoclinic $P2_1$	16.537	9.289	17.640	106.95	4
Cholesteryl butanoate	[a] Monoclinic $P2_1$	25.36	9.55	23.60	95.0	8
Cholesteryl pentanoate	[a] Orthorhombic $P2_1\ 2_1\ 2_1$	21.45	21.5	6.40	—	4
Cholesteryl hexanoate	[a] Monoclinic $P2_1$	13.67	9.30	12.19	92.0	2
Cholesteryl heptanoate	[a] Monoclinic $P2_1$	14.02	9.23	12.54	92.0	2
Cholesteryl octanoate	[a] Monoclinic $P2_1$	13.95	9.20	12.67	94.0	2
	[c] Monoclinic $P2_1$	12.80	9.20	14.12	93.81	2
Cholesteryl nonanoate	[a] Monoclinic $P2_1$	14.44	9.33	12.81	95.5	2
Cholesteryl decanoate	[a] Monoclinic $P2_1$	30.00	9.05	12.85	92.0	4
Cholesteryl dodecanoate	[a] Monoclinic $P2_1$	31.80	8.92	12.92	93.0	4
	[d] Monoclinic $P2_1$	12.989	9.008	32.020	91.36	4
Cholesteryl tetradecanoate	[a] Monoclinic $P2_1$	50.30	7.50	10.18	92.5	4
Cholesteryl hexadecanoate	[a] Orthorhombic $P2_1\ 2_1\ 2_1$	25.53	34.9	9.00	—	8
Cholesteryl octa decanoate	[a] Monoclinic $P2_1$	57.50	7.55	10.20	96.0	4
	[e] Monoclinic $P2_1$	12.65	9.13	18.79	93.3	2
Cholesteryl chloride	[f] Monoclinic $P2_1$	10.60	7.55	21.70	132.0	2
	[g] Monoclinic $P2_1$	16.333	7.553	10.691	102.95	2
	[h] Monoclinic $P2_1$	10.82	7.61	21.46	131.8	2
Cholesteryl bromide	[f] Monoclinic $P2_1$	11.00	7.55	21.60	134.0	2
	[h] Monoclinic $P2_1$	11.10	7.56	21.83	133.9	2
Cholesteryl iodide	[f] Monoclinic $P2_1$	11.00	10.42	21.80	149.0	2
	[i] Monoclinic $P2_1$	12.57	9.04	21.89	149.0	2
Cholesteryl methyl carbonate	[j] Monoclinic $P2_1$	16.50	7.43	10.22	103.2	2
Cholesteryl ethyl carbonate	[k] Monoclinic $P2_1$	17.89	11.34	13.11	105.2	4
Cholesteryl benzoate	[l] Orthorhombic $P2_1\ 2_1\ 2_1$	10.14	10.06	26.00	—	4

a — Barnard et al. [5] d — Sawzik et al. [8] g — Ohrt et al. [11] j — Rajalakshmi et al. [14]
b — Sawzik et al. [6] e — Craven et al. [9] h — Vani et al. [12] k — Shivaprakash et al. [15]
c — Craven et al. [7] f — Bernal et al. [10] i — Carlisle et al. [13] l — Shivaprakash et al. [16]

packing of molecules having the molecular symmetry 1 in the crystal [18]. The possible closest packed space groups are P1, $P2_1$, $P2_1/c$, P*ca*, P*na* and $P2_12_12_1$. Groups $P2_1$ and $P2_12_12_1$ without a symmetry center are quite logically to be found where molecules are in either their right-handed or left-handed configurations, which in the liquid crystalline state impose either the left or the right handedness. A smooth transition to the helical structure of the mesomorphic state can be expected to occur on melting from the solid state preferentially for those crystals with space groups $P2_1$ and $P2_12_12_1$, since they have pure screw axes for their symmetry. The screw axes of the crystalline phase determine the optic axis in the mesophase.

On transition from the solid to the liquid crystalline phase the crystallographic screw axes may exist as micro helices in the cholesteric phase or as a macro helix which accounts for the large form optical rotation. This is confirmed by the studies of Galanov [19] and

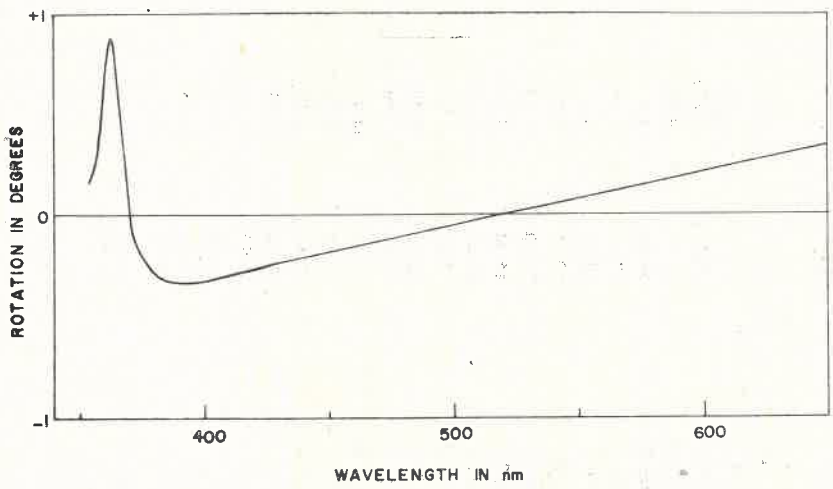

Fig. 2. Rotation dispersion of a mixture of l-menthol and n-p-methoxybenzylidene-p′-butylaniline (MBBA) (thickness 10 μm)

Galanov et al. [20] and Chandrasekhar and Shashidhara Prasad [21, 22, 2]. The optical rotatory power expression obtained by Galanov, based on a set of micro screw axes, the phases of the helices in the plane perpendicular to the screw axis randomly distributed, shows two zeros, similar to the one obtained by Chandrasekhar et al. [2] using a single macro helix. The existence of two zeros has been confirmed by experiment (Fig. 2) which in turn confirms the proposed twists occurring in cholesteric phase from solid state.

Based on this we can explain the necessity of applying small pressures to get a mono-domain plain texture for the cholesteric phase, as the requirement to align the micro helices into the same line.

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