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Compounds of the formula 3(β)-cholesteryl—O—$\overset{\overset{O}{\|}}{C}$—X—Ar—N=N—Ar′ where X = O or NH, Ar = 1,4-phenylene or 3-hydroxy-1,4-phenylene, and Ar′ = phenyl, 4′-cyanophenyl, 4′-nitrophenyl, or 4′-N,N-diethylaminophenyl were prepared which have broad liquid crystalline ranges as determined by differential scanning calorimetry. Changes were found in the characteristics of the parent azobenzene compounds following carbonate or carbamate formation. The pitch and order parameters of the title compounds were determined in several nematic hosts. In addition, a method for assessing the alignment of the cholesteryl moiety in liquid crystalline hosts is presented.

INTRODUCTION

We have been investigating classes of compounds which are liquid–crystalline dyes, and have found that condensation of cholesteryl chloroformate with phenyl azo dyes containing an hydroxyl or amine group leads to colored cholesteryl derivatives having a broad liquid–crystalline range. Compounds we have prepared are of the general formula

$$3(\beta)\text{-cholesteryl—O—}\overset{\overset{O}{\|}}{C}\text{—X—Ar—N=N—Ar}'$$

where X = O or NH, Ar = 1,4-phenylene or 3-hydroxy-1,4-phenylene, and Ar′ = phenyl, 4′-cyanophenyl, 4′-nitrophenyl, or 4′-N,N-diethylaminophenyl. Cholesteryl 4-phenyl-azophenyl carbonate (I: X = 0; Ar = 1,4-phenylene, Ar′ = phenyl) had been previously prepared and was found to be liquid crystalline.[1] While numerous liquid-crystalline derivatives of cholesterol are known,[2] and several nematogenic homologous series containing azobenzene linkages have been prepared,[3] no report of the preparation and characterization of the title compounds has appeared. We were particularly

interested in the guest–host interactions of these cholesterics in nematic solvents.

EXPERIMENTAL

Synthesis

Compounds I–IV shown in Table I were prepared in a similar manner. A 300 ml round-bottom flask equipped with a magnetic stirrer and a reflux condenser was charged with 10 mmoles of the appropriate hydroxy- or amino-azo-aromatic compound, an equimolar amount of cholesteryl chloroformate, and 125 ml benzene. The mixture was heated in an oil bath until a homogeneous solution formed, then 2 ml of pyridine was added. The reaction mixture was refluxed for 18 hours, and then cooled. To isolate the product, the mixture was heated, deposited on a short column of silicic acid, and eluted with chloroform. The chloroform was removed under vacuum. The chromatographic procedure was repeated until the desired compound was obtained, as shown by thin layer chromatography. The product was then recrystallized from a chloroform methyl ethyl ketone solution to a constant melting point range. Compound V was prepared similarly except that the reaction solvent was toluene which contained 1% by volume of pyridine.

Yields on purified compounds as well as their analytical data are shown in Table I.

Measurements and materials

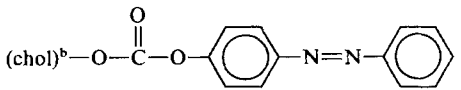
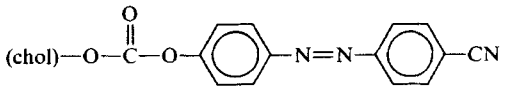
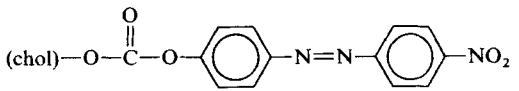
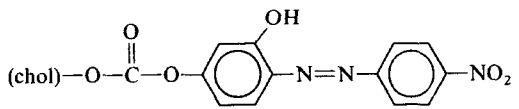
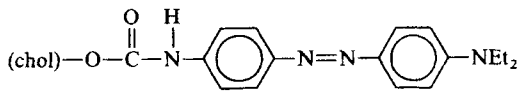
Melting points were determined on a Thomas–Hoover melting point apparatus. Thermal transition enthalpies and temperatures were obtained using a DuPont 900 thermal analyzer. Optical spectra were recorded on a Cary 14 spectrophotometer.

The compounds used in our nematic hosts were EBBA (4-ethoxybenzylidene-4′-butylaniline) and MBBA (4-methoxybenzylidene-4′-butylaniline) which were purified by molecular distillation, and PEBAB (4-ethoxybenzylidene-4′-aminobenzontrile) which was purified by repeated recrystallization. The 1:1 molar mixture of EBBA and MBBA is designated EM. A mixture of EBBA, MBBA, and PEBAB described by Tarry[4] was used as the positive nematic host (PNH). It consists of 85 wt% of a 70 : 30 molar mixture of MBBA–EBBA and 15 wt% PEBAB.

The pitch of the cholesteryl derivatives in nematic hosts was determined by use of a Cano wedge.[5] The procedure used in our laboratory has been previously described.[6] Two glass slides were coated with SiO_x by evaporation

TABLE I

Analytical data for cholesteryl azo compounds

No.	Compound	Yield (%)	Analysis[a]			
			C (% calc)	C (% found)	H (% calc)	H (% found)
I		85	78.65	78.81	8.91	8.74
II		83.4	77.44	77.34	8.40	8.57
III		23.2	73.25	73.30	8.15	8.05
IV		59.5	71.51	71.89	7.95	7.77
V		58	77.60	77.33	9.47	9.40

[a] Analyses performed by Micro-Analysis, Inc., Wilmington, DE.
[b] chol = 3(β)-cholesteryl.

at an angle of 30° from the surface of the glass.[7] The slides were washed with acetone and then methanol in an ultrasonic bath for 3 minutes each. The wedge was prepared using a Mylar spacer with the two evaporated surfaces aligned parallel to one another. The cell was then filled with the heated, isotropic cholesteric mixture. On cooling, distinct lines were observed on viewing the cell with plane polarized light with each separation between two consecutive lines corresponding to a 180° rotation. The pitch was obtained from the equation

$$\text{Pitch} = \frac{td}{l} \tag{1}$$

where t = thickness of spacer, d = distance between two consecutive lines, and l = distance between spacer and end of cell.

The order parameters were obtained using a procedure described elsewhere.[8] The cell used consisted of two 2.5 × 2.5 cm glass plates, each having a transparent, conductive layer of tin-doped indium oxide onto which a SiO_x layer was evaporated at an angle of 30° to the horizontal to give parallel alignment.[7] The top plate had two diagonally-placed holes (1 mm diameter) to allow flow filling. The plates were separated by 12 μm spacers and epoxy-sealed together. The cells were flushed with acetone, methanol, and nitrogen prior to filling. The dye concentration was *ca.* 0.3 wt%.

The optical density was measured on a Cary 14 spectrophotometer equipped with a Glan–Foucoult calcite polarizer using a modified sample holder which has been previously described.[9] Corrections were made for host and cell absorption, reflection, and scattering.

RESULTS AND DISCUSSION

Thermal analysis

The results of thermal analysis of compounds I–V using differential scanning calorimetry are shown in Table II (C = crystalline, Ch = cholesteric, I = isotropic). All transitions were found to be diatropic with some supercooling observed. The enthalpies found for the Ch→I transitions are within the range determined for other cholesteryl derivatives.[10] There appears to be some correlation between molecular structure and the C→Ch and Ch→I transition temperatures. In general, addition of substituents which cause the azobenzene moiety to become more electron deficient leads to higher transition temperatures. Furthermore, addition of the electron-donating diethylamino group causes a decrease in the C→Ch transition temperature. However, no corresponding change occurs in the Ch→I transition temperature. An explanation for this apparent substituent effect on transition temperatures

TABLE II

Liquid crystalline transitions of cholesteryl azo compounds

Compound	Crystalline(C) → cholesteric(Ch) transition (°C)	Ch → Isotropic(I) transition (°C)	Liquid crystalline range (°C)	ΔH_{Ch-I} (cal/mole)
I[a]	169	214	45	65.4
II	226	250	24	389.2
III	219	256	37	150.9
IV	213	243	30	41.5
V	137	215	78	70.8

[a] Schadendorff and Verdino[1] report a C → Ch transition temperature of 166°C and a Ch → I transition temperature of 208°C.

would be that the molecules are arranged in a manner which allows intermolecular donor-acceptor interactions to occur, with a more electron deficient azobenzene moiety enhancing these interactions. In the crystal structure of cholesteryl iodide,[11] the molecules pack in a head-to-tail manner. Such an interaction with our compounds might occur even if all molecules are parallel and would facilitate intermolecular donor-acceptor interactions. The trends in transition temperatures do not carry over to $\Delta H_{Ch \to I}$ or in the temperature span of the liquid crystalline range. Trends found in homologous series of liquid crystals have often been found to correlate with isotropic transition temperatures, but not with transition enthalpies.[10]

Spectroscopy

A comparison of the absorption properties of I–V and their phenol or aniline azo precursors are shown in Table III. The limited solubility of 4-nitro-4′-hydroxyazobenzene (VI) and 4-nitro-2′,4′-dihydroxyazobenzene

TABLE III

Absorption properties of cholesteryl azo derivatives and their precursors

			Precursor hydroxy- or amino-azo compound			
Compound	$\lambda^{max}_{CHCl_3}$ (nm)	log ε	$\lambda^{max}_{CHCl_3}$ (nm)	log ε	λ^{max}_{DMF} (nm)	log ε
I	322	4.39	344	4.10	354	4.39
II	332	4.47	363	4.47	540	4.44
					371	3.97
III	340	4.45	—	—	601	4.51
IV	343	4.31	—	—	436	4.41
V	425	4.55	420	4.51	446	4.55
	430[a]	4.55[a]			426	4.53

[a] DMF.

(VII) in $CHCl_3$ as well as the insolubility of I–IV in more polar solvents such as DMF hindered direct comparisons. Compounds such as VI, VII, and 4-cyano-4′-hydroxyazobenzene (VIII) are solvatochromic, and their charge-transfer absorption bands shift to longer wavelengths in polar solvents which can stabilize the separated charges. For the phenol precursor of I–IV, there is a shift in the absorption maximum to shorter wavelengths when the corresponding cholesteryl carbonate is formed. The electron withdrawing nature of the carbonyl group interferes with the longer-wavelength charge transfer contributions of the free phenols. The modest shift to longer wavelengths absorption maxima on going from I through IV is consistent with the concept that there is charge-transfer stabilization involving interactions between the two phenyl groups of the azobenzene moiety.

For V there is a small increase in the wavelength of the absorption maximum compared to that for the corresponding aniline. The electron withdrawing nature of the carbonato group would tend to enhance charge transfer contributions involving the diethylamine phenyl group.

Helical twist

The helical twist (pitch) of I–V in several hosts was determined with results summarized in Figure 1. The hosts are similar in that they consist entirely or in large part of MBBA and EBBA. Regardless of the cholesteryl derivative, there is a trend toward longer pitch with lower concentration. Cano found that the pitch varied inversely with the concentrtion of a cholesteric in a nematic host.[12] All the cholesterics we have described contain pendant

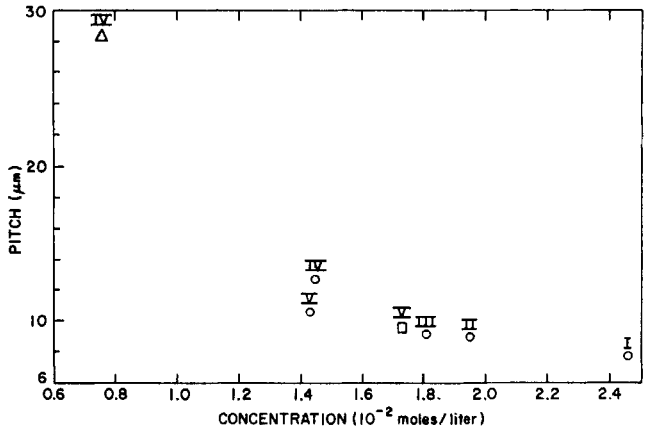


FIGURE 1 Concentration vs. pitch for azobenzene derivatives of cholesteryl in various nematic hosts: ○ = PNH, □ = EM, △ = MBBA.

groups at the 3(β)-cholesteryl position of approximately the same length, and our observed inverse relationship is in line with the results of others.[13] For IV in PNH, the minor deviation from linearity may be a result of the concentration used being near the solubility limit. For all solutions, the sense of the pitch is left-handed.

Order parameter

The order parameters, S, of a dye in a nematic liquid crystalline host is given by the expression[14]

$$S = \tfrac{1}{2}(3\cos^2\theta - 1) \tag{2}$$

where θ is the angle by which the optic axis of the dye is imperfectly aligned with the liquid crystalline host. If the optic axis corresponds to the molecular axis of the dye which is aligned with the nematic host, then the equation for S simplifies to

$$S = \frac{A_{\parallel} - A_{\perp}}{2A_{\perp} + A_{\parallel}} \tag{3}$$

where $A_{\parallel}$ is the optical density of the dye at its absorption maximum as measured with plane-polarized light oriented parallel to the liquid crystal director, and $A_{\perp}$ is the optical density of the dye at its absorption maximum as measured by plane-polarized light oriented perpendicular to the liquid crystal director. Although this formula is normally used for dyes in simple nematic hosts, one can make use of this formula for cholesteric materials if one assumes that the light propagates along the twist axis. This assumption is valid for $\lambda \ll$ pitch, a condition used in our experiments. Groups pendant from the 3(β)-cholesteryl position have been shown to be within 19° of the cholesteryl long axis.[11] A schematic drawing of the cholesteryl moiety is shown in Figure 2. If one assumes that the cholesteryl moiety aligns itself with the long axis of the host nematic fluid, then the order parameter of the dye calculated by Eq. (3) is meaningful relative to the non-cholesteric-containing host.

Results for V and some related compounds are shown in Table IV. The order parameters for V in EM and PNH are most like those reported for typical monoazo compounds.[8,14] We can therefore conclude that the azobenzene moiety of V is about as well aligned with the host as the monoazo dyes. It has been previously shown that, if steric factors are nearly equivalent, S for a dye will increase with increasing dye molecule length.[8,14] Despite the great length of the cholesteryl moiety (see Figure 2), no large enhancement of S is observed. Therefore, the dye derivatives of cholesteryl may be useful probes for the alignment of the cholesteryl moiety in the nematic host.

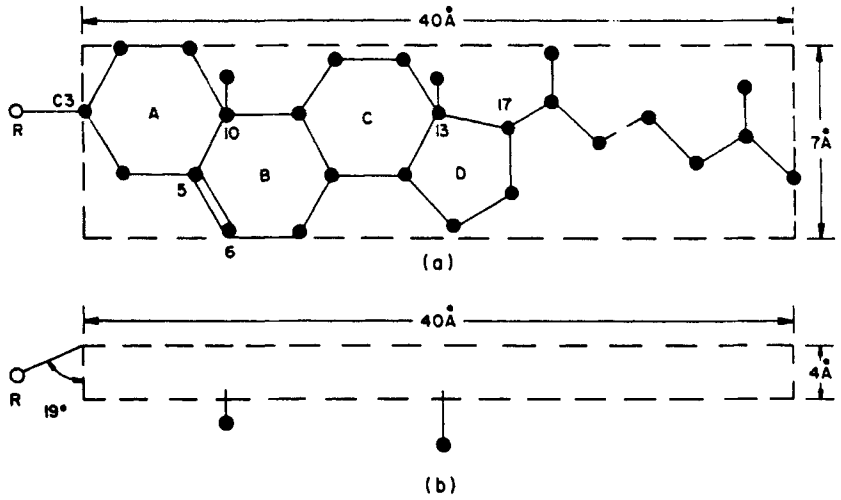
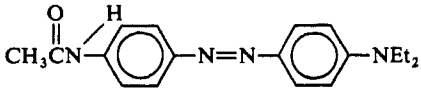
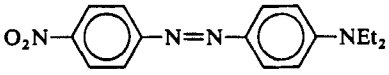
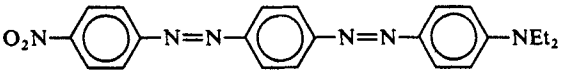


FIGURE 2 Somewhat Idealized Model of Cholesteryl Iodide from the Crystal Structure of Carlisle and Crowfoot.[11] a) Bottom view; b) Side view, R = iodine.

TABLE IV

Order parameters for V and related azo compounds

Dye	Host	λ^{max} (nm)	S	Reference
V	EM	423	0.51	[a]
	PNH	420	0.62	[a]
	PNH	425	0.50	[b]
	EM	505	0.51	[c]
	PNH	506	0.55	[b,c]
	EM	542	0.70	[c]
	PNH	538	0.65	[b,c]

[a] This work.
[b] Ref. 8.
[c] Ref. 15.

There is no decrease in S for the azobenzene chromophore which would be expected if there was a significant deviation of that chromophore from the plane of the cholesteryl group. In cholesteryl iodide, the deviation from planarity for the iodide atom was 19°. The carbamate linkage is apparently flexible enough to allow the azobenzene moiety to lie in the same plane as the cholesteryl group. We conclude that the interactions with the host of the

two methyl groups lateral to the plane of the cholesteryl moiety, as well as other guest-host steric interactions lead to poorer alignment of cholesteryl derivatives in nematic hosts than might be expected from only considerations of the length of the cholesteryl moiety.

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