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Liquid Crystals

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Some novel cholesteric liquid crystals

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A novel series of cholesteric liquid crystals (CNT_n), made by quaternization of the new mesogenic unit cholesteryl isonicotinate (CN) with n -alkyl salts, C_nH_{2n+1} (T) ($n = 2$ to 8, T = 4-MeC₆H₄SO₃) has been prepared. Differential scanning calorimetry and polarizing optical microscopy studies reveal that all of these salts exhibit an enantiotropic cholesteric phase but for the cholesteryl isonicotinate unit the cholesteric phase is monotropic. For all members of the series the cholesteric-isotropic transitions are not reversible as these salts begin to decompose before their cholesteric-isotropic transition point is reached.

1. Introduction

Mesogenic esters linking heterocyclic carboxylic acids and cholesterol have not been studied. We now report the synthesis and liquid crystal properties of a new unit, cholesteryl isonicotinate (CN). We have also prepared and undertaken a study of the liquid-crystalline behaviour of a novel homologous series of amphiphiles, the n -alkyl tosylates of cholesteryl isonicotinate (CNT_n). This is the first example of liquid-crystalline behaviour observed with CN as the mesogenic unit, although there are examples of relevant pyridinium [1] and bipyridinium [2, 3] based amphiphiles that exhibit thermotropic mesophases.

2. Experimental

2.1. Synthesis of materials

Isonicotinyl chloride hydrochloride was synthesized [4] by dissolving 0.15 mol of isonicotinic acid in 15 ml of dry benzene and the mixture was brought to the boil on a water bath. Freshly distilled thionyl chloride (0.15 mol) was then added dropwise with stirring, under nitrogen. Stirring was continued for a further 3 h at the reflux temperature. The white crystalline product was isolated by filtration and washed with dry light petroleum (bp 60–80°C) to yield white crystals of isonicotinyl chloride hydrochloride (14.46 g, 82 per cent) melting at 164°C.

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Cholesteryl isonicotinate was synthesized by adding a mixture of 80 mmol of cholesterol and 50 ml of dry pyridine to 80 mmol of isonicotinyl chloride hydrochloride; the mixture was heated under reflux with stirring under nitrogen. Stirring was continued under reflux for a further 3 h when only one spot was shown by thin layer chromatography (TLC) [5] ($R_f=0.3$, elution with 1:9 methanol/chloroform mixture), indicating completion of the reaction. The reaction mixture was then poured with stirring into 300 ml of ice-water and the resulting precipitate was filtered off. The crude product was washed with water and acetone. The solid was recrystallized from light petroleum (bp 60–80°C) to yield white crystals of CN (30.6 g, 76.3 per cent). Calculated for $C_{33}H_{49}O_2N$: C, 80.60 per cent; H, 10.04 per cent; N, 2.85 per cent. Found: C, 80.41 per cent; H, 10.15 per cent; N, 2.44 per cent.

The *n*-alkyl tosylates, $C_nH_{2n+1}T$ ($T=4\text{-MeC}_6\text{H}_4\text{SO}_3$, $n=2$ to 8) were synthesized by dissolving 0.1 mol of the appropriate alcohol in 50 ml of dry pyridine and cooling the mixture in an ice bath. A solution of 0.11 mol of $4\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ in 50 ml of dry pyridine was added dropwise with stirring under nitrogen, and the temperature was maintained between 0 and 10°C. Stirring was continued for a further 2 h at this temperature. The reaction mixture was then poured into 400 ml of ice-water, with stirring, and the resulting product was extracted with benzene. The crude product was dissolved in 50 ml of benzene, and washed successively with 10 per cent HCl (2 × 100 ml) and 100 ml of saturated NaHCO_3 . The benzene extract was dried over anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator. The concentrate was applied to a silica gel column and the pure tosylate was eluted with 1:1 benzene/ Et_2O .

Cholesteryl isonicotinate-*N*-alkyl tosylates (CNT_n) ($n=2$ to 8 carbon atoms in the alkyl chain and $T=4\text{-MeC}_6\text{H}_4\text{SO}_3$) were synthesized by adding 1.5 mmol of the appropriate *n*-alkyl tosylate to a solution of 1 mmol of CN in 3 ml of *N*-methylpyrrolidone and the reaction mixture was heated, with stirring, under reflux (120°C) for 8 h. The reaction mixture was then cooled to room temperature and acetone was added to precipitate the product. The crude product was filtered off, and purified by recrystallization from the appropriate solvents several times until no impurity spots could be detected by TLC [6, 7] ($R_f(\text{CNT}_7)=0.44$, elution with 4:6 ethanol/chloroform mixture). Calculated for $C_{47}H_{71}O_5\text{NS}$ (CNT_7): C, 74.07 per cent; H, 9.39 per cent; N, 1.83 per cent. Found: C, 73.70 per cent; H, 9.47 per cent; N, 1.96 per cent. Elemental analyses for the remaining compounds were also satisfactory.

2.2. Spectral, optical and thermal characterization

IR spectra (KBr) were recorded on a Pye Unicam SP3-300 spectrometer. UV spectra were recorded on a Pye Unicam SP8-100 UV spectrophotometer. ^1H NMR spectra were recorded on a Bruker WM-250 spectrometer.

The phase transitions were observed with a Leitz Laborlux 12 Pol in conjunction with a Leitz 350 hot stage and equipped with a Vario-Orthomat camera. Differential scanning calorimetry results were recorded at a scan rate of $10^\circ\text{C min}^{-1}$ with a Perkin-Elmer mark II instrument.

3. Results and discussion

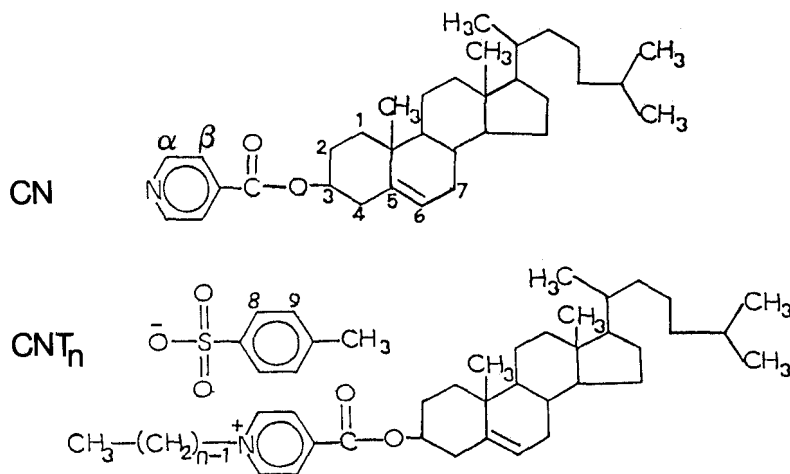
CN exhibited IR absorptions at *c.* 2930 cm^{-1} (C–CH sat, stretch), 1720 cm^{-1} (C=O, stretch), 3080 cm^{-1} (C=C–H, unsat, stretch), 1600 cm^{-1} (C=C aromatic, stretch), 1370 cm^{-1} (C–C stretch) and $820\text{--}850\text{ cm}^{-1}$ (*p*-substituted aromatic ring). All CNT_n salts exhibited intense absorptions at *c.* 1200 cm^{-1} (–CH₂–N) [8] and 1120 cm^{-1} (S=O stretch) in addition to absorptions exhibited by CN. The UV absorption spectra of

CNT_n salts in methanol were identical and contained three bands with λ_{\max} at 274 (log $\epsilon=3.72$), 220 (log $\epsilon=4.45$) and 201 nm (log $\epsilon=4.49$) (ϵ is the molar extinction coefficient). CN revealed two bands with λ_{\max} at 270 (log $\epsilon=4.87$) and 220 nm (log $\epsilon=5.16$). The ¹H NMR spectral data for the compounds studied (see the scheme) are given in table 1. CN exhibited two doublets at $\delta=8.78$ and 7.87 ppm ($J=4.2$ Hz) for α -H and β -H, respectively, in addition to the expected signals for the cholesteryl moiety. The CNT_n compounds showed two broad doublets at $\delta=9.46\pm 0.05$ and 8.34 ± 0.05 ppm for α -H and β -H, respectively, in addition to the expected signals for cholesteryl, the alkyl chain and the tosylate moieties.

The DSC scans carried out on these compounds often showed noisy peaks at high temperatures. This has been attributed to the compounds tendency to thermal decomposition. Evidence of thermal decomposition was often noted before the mesophase–isotropic peak was reached, making their study after the first heating cycle rather difficult.

Polarized optical microscopy study revealed that the salts, CNT_n, all exhibit an enantiotropic cholesteric phase but for the unit CN, the cholesteric phase is monotropic. Estimates of cholesteric–isotropic transition temperatures have been obtained using optical microscopy. These values are given in table 2 and seem to be consistent with those obtained from the DSC traces. When each member of the CNT_n series was studied under the polarizing optical microscope, the compound melted to exhibit planar texture with bright oily streaks. Then, on further heating, the compound becomes black in appearance ($n=2$ to 5) or dark brown ($n=6$ to 8) just before the cholesteric–isotropic transition is reached. For example compound CNT₇, on first heating, melted to a cholesteric phase at 177°C and turned into the isotropic phase at 236°C. On lowering the temperature to 215°C no transitions were observed. The sample was then cooled rapidly to room temperature and on reheating melted to a cholesteric phase at 140°C and then formed the isotropic phase at 165°C. This behaviour was found to be common to all members of the series.

When the transition temperatures are plotted against the number of carbon atoms in the alkyl chain (see the figure), the C–Ch transition temperatures lie on a generally falling curve with some indication of (but not pronounced) an odd–even effect. The lack



Labelling sequence for the compounds studied.

Table 1. ^1H NMR chemical shifts of the alkyl tosylates of cholesteryl isonicotinate, CNT_n , in CDCl_3 (TMS internal standard).

Compounds	Pyridyl protons (d/Hz)		Aromatic protons		CH_3 -protons (tosylate) (s)	Olefinic protons H-6 (d/Hz)	Allylic (H-3), ester (H-7) and $-\text{CH}_2-\text{N}$ (um)	CH_3 and CH_2 protons (um)
	α -H	β -H	H-8	H-9				
CN	8.78 (4.2)	7.87 (4.2)				5.40 (4.0)	4.76	0.68–2.48
CNT_2	9.50 (4.5)	8.34 (4.5)	7.73 (7.3)	7.13 (7.6)	2.33	5.40 (4.0)	5.01	0.70–2.45
CNT_3	9.46 (5.4)	8.34 (5.8)	7.37 (7.9)	7.13 (7.6)	2.33	5.45 (4.0)	4.90	0.70–2.48
CNT_4	9.44 (6.4)	8.36 (6.1)	7.37 (7.9)	7.13 (7.9)	2.33	5.44 (4.0)	4.94	0.70–2.43
CNT_5	9.45 (5.2)	8.34 (5.2)	7.72 (7.9)	7.13 (7.9)	2.33	5.45 (4.0)	4.92	0.70–0.48
CNT_6	9.45 (6.4)	8.34 (6.1)	7.72 (8.2)	7.13 (8.2)	2.33	5.44 (4.6)	4.94	0.70–2.48
CNT_7	9.44 (5.2)	8.35 (5.2)	7.73 (7.6)	7.13 (7.6)	2.33	5.44 (4.6)	4.93	0.70–2.49
CNT_8	9.44 (6.2)	8.32 (6.2)	7.73 (8.2)	7.13 (7.9)	2.33	5.44 (5.0)	4.93	0.70–2.74

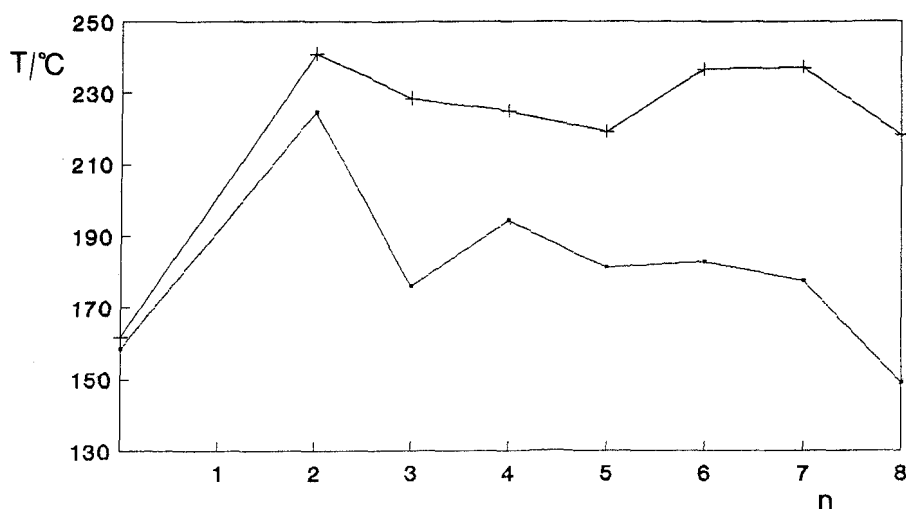
s = singlet, d = doublet, um = unresolved multiplet.

Table 2. Transition temperatures for the alkyl tosylates of cholesteryl isonicotinate, CNT_n.

Compound	T _{Cl} /°C	T _{CCh} /°C	T _{ChI} /°C	ΔH _{CCh} /kJ mol ⁻¹	ΔS _{CCh} /J mol ⁻¹ K ⁻¹
CN	168.8	(158.5)	(161.8)	28.5†	64.54†
CNT ₂	—	224.5	241.0	25.1	50.45
CNT ₃	—	175.5	228.3	—	—
CNT ₄	—	194.0	224.7	31.3	66.96
CNT ₅	—	181.0	219.0	—	—
CNT ₆	—	182.5	236.3	—	—
CNT ₇	—	177.1	236.8	15.8	33.31
CNT ₈	—	148.5	218.1	17.0	34.57

† Values are for the C-I transition.

Monotropic transitions in parentheses. The temperatures were obtained by comparing DSC with optical microscopy values.



Plot of transition temperature against the length, *n*, of the *n*-alkyl chain for the compounds CNT_n. ■ C-Ch, + Ch-I.

of a smooth curve relationship for the compounds studied, in our opinion, is due only to the onset of decomposition of the salts which causes some uncertainty in the Ch-I transition temperatures. It is interesting to note that a very similar curve, revealing the lack of a smooth curve relationship for a homologous series of thiocholesterol *n*-alkyl ethers, has been reported [9] but no reasons were put forward for this. Thermal non-reversibility of the cholesteric-isotropic transitions has also been reported [10] for the early members of the homologous series of aryl esters of cholesterol.

It has not proved possible to determine the enthalpy and entropy changes at the Ch-I transition but the melting enthalpy and entropy changes have been obtained and are listed in table 2. These values show no discernible trend.

The fact that cholesteryl isonicotinate exhibits a monotropic cholesteric phase while that exhibited by cholesteryl benzoate is enantiotropic may be attributed to possible repulsion between the nitrogen lone pair of the heterocyclic ring and the

oxygen of the ester group. However, this repulsion in the CNT_n series does not exist since the nitrogen lone pair is involved in the quaternization process and hence all of the compounds in the series exhibit an enantiotropic cholesteric phase.

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