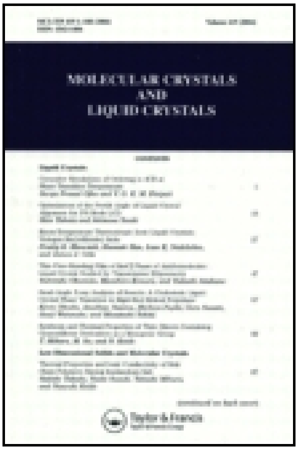

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Cholesteryl Dicarbonates with Rigid and Flexible Spacers

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Cholesteryl Dicarbonates with Rigid and Flexible Spacers

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Eleven cholesteryl dicarbonates have been synthesized with rigid and flexible spacers by reacting cholesteryl chloroformate with glycols, oxyglycols, aromatic dihydroxy and amino hydroxy compounds. The mesogenic properties are evaluated by microscopic and calorimetric methods. Ten of the dicarbonates synthesized exhibit mesomorphism. The dicarbonates with rigid structures exhibit higher thermal stabilities compared to those having flexible spacers. Dicarbonates having lateral substituent exhibit lower thermal stabilities. Increase in breadth and steric repulsion is not conductive to mesomorphism even in the dicarbonate system. It is quite interesting to observe mesomorphism in glycols with shorter chain length and flexibility having two bulky cholesteryl moiety at the ends. Many of the compounds exhibit vivid colours in cholesteric phase at definite temperatures. The calorimetric results are in conformity with optical results for solid cholesteric transitions. The enthalpy and entropy changes are correlated with structural changes in the molecules. The thermal stabilities are compared with related members to correlate mesomorphic behaviour of the dicarbonates with structural changes.

Keywords: Cholesteryl dicarbonates, oxy-glycols, flexible spacers

INTRODUCTION

Cholesteryl carbonates and thio carbonates are known to exhibit mesogenic behaviour.[1,2] An attempt has been made in the present study to synthesize Cholesteryl dicarbonates having flexible and rigid spacers to understand effect of chemical constitution on mesomorphism.

EXPERIMENTAL

Dicarbonates are synthesized by reacting glycols, oxyglycols, aromatic dihydroxy and amino hydroxy compounds with cholesteryl chloroformate as per the method reported in the literature.[1] The dicarbonates were purified by crystalising them from chloroform-Acetone mixture till constant transition temperatures were obtained. The transition temperatures (Table I) were determined by using laborlux 12 POL microscope. The compounds were characterised by elemental analysis

TABLE I

Transition temperatures and calorimetric data

Code No.	Transition State	Transition Temperature °C (Microscope reading)		ΔH J/G	ΔS J/G.K.
CC-1	Solid$_{I}$-Solid$_{II}$	145		—	—
	Solid$_{II}$-Iso	162	(160)	—	—
	Iso-Ch	122.7	(126)	3.227	0.008
CC-2	Solid-Ch	179.7	(172.0)	41.781	0.092
	Ch-Iso	263.2	(252.0)	0.918	0.002
CC-3	Solid-Iso	121	(122)	52.575	0.133
	Iso-Ch	100.9	(111)	1.117	0.003
	Ch-Sm		(90)	—	—
CC-4	Solid$_{I}$-Solid$_{II}$	103.7		0.451	0.001
	Solid$_{II}$-Solid$_{3}$	122.2	(126)	22.841	0.058
	Solid$_{3}$-Iso	169.6	(178)	40.096	0.09
	Iso-Ch	160.7	(177)	1.449	0.003
CC-5	Solid-Ch	148.5	(160)	30.103	0.0714
	Ch-Iso	190.5	(188)	0.532	0.001
CC-6	Solid-Ch	181.4	(180)	67.399	0.148
	Ch-Iso	252.4	(254)	2.317	0.004
CC-7	Solid-Ch	170.7	(166)	44.239	0.099
	Ch-Iso	—	(204)	—	—
CC-8	Solid$_{I}$-Solid$_{II}$	163.3	(174)	15.828	0.036
	Solid$_{II}$-Ch	236.1	(222)	23.083	0.045
	Ch-iso	266.8	(264)	3.847	0.007
CC-9	Solid-Iso		(230)		—
CC-10	Solid-Ch	165.9	(166)	Total ΔH	
	Ch-Iso	189.4	(197)	30.775*	
CC-11	Solid-Ch	165.7	(169)	23.66	0.054
	Ch-Iso	263.1	(262)	2.609	0.005

* Overlapping peaks for both the transitions.

TABLE II

Elemental analysis

	Calculated (%)			Found (%)		
Code No.	C	H	N	C	H	N
CC-1	77.42	10.54	—	77.31	10.67	—
CC-2	76.39	10.47	—	76.01	10.03	—
CC-3	75.44	10.41	—	75.21	10.89	—
CC-5	78.66	10.66	—	78.38	11.04	—
CC-6	78.77	10.72	—	78.36	11.09	—
CC-7	78.77	10.72	—	78.32	11.01	—
CC-8	79.66	10.06	—	79.18	10.50	—
CC-9	79.66	10.06	—	79.91	10.49	—
CC-10	80.99	9.83	—	80.83	10.33	—
CC-11	79.74	10.18	1.5	80.12	10.55	1.06

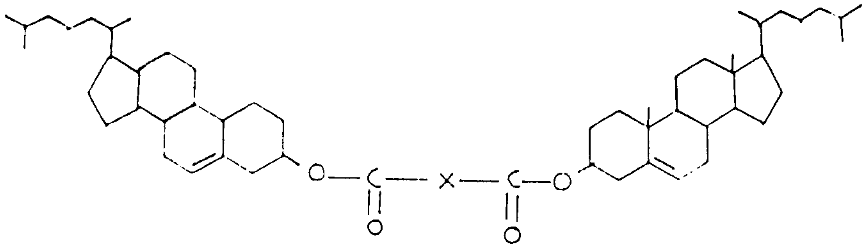
(Table II) and IR spectra. Calorimetric study was carried out by using Mettler TA 4000 DSC equipment.

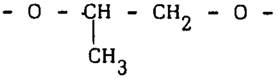
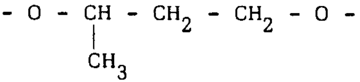
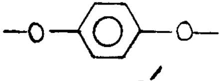
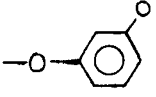
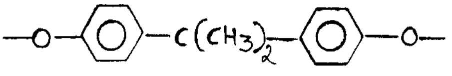
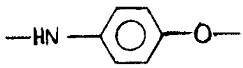
RESULTS AND DISCUSSION

Reference to Table I shows that except for one, all the compounds exhibit mesomorphism. All the mesogenic compounds exhibit cholesteric phase with one exception. Compound no. 3 exhibits smectic phase along with cholesteric phase.

Compound nos. 1–3 are having the difference of $—CH_2—CH_2—O$ flexible

Structure of the Compound



X	Code No.
$-(CH_2CH_2O)_2-O-$	CC - 1
$-O-(CH_2CH_2O)_2-CH_2CH_2-O-$	CC - 2
$-O-(CH_2CH_2O)_3-CH_2CH_2-O-$	CC - 3
$-O-CH_2-CH_2-O-$	CC - 4
 $-O-\underset{\mid \atop CH_3}{CH}-CH_2-O-$	CC - 5
$-O-CH_2-CH_2-CH_2-CH_2-O-$	CC - 6
 $-O-\underset{\mid \atop CH_3}{CH}-CH_2-CH_2-O-$	CC - 7
	CC - 8
	CC - 9
	CC - 10
	CC - 11

spacer increasing from 2 to 4. The reference to Table I indicates that cholesteric phase is monotropic in nature in compounds no. 1 and 3 with lower thermal stabilities whereas compound no. 2 exhibits enantiotropic cholesteric phase of higher thermal stability.

The system has highly flexible central linkage. The change in mesogenic behaviour of compound nos. 1–3 can easily be attributed to classical odd-even effect observed in number of homologous series.[3] Compounds no. 1 and 3 have seven and thirteen (odd) spacers whereas compound no. 2 has ten spacers. The results indicate that odd-even effect is quite marked comparable to the results of Gray et al.[4]

Compound no. 3 exhibits monotropic smectic phase which is absent in other homologues. This can be attributed to the increased length of spacers.[3]

The mesogenic behaviour of compound nos. 4–7 is quite interesting. The flexible spaces with α-methyl group also exhibit cholesteric phases of comparable thermal stabilities. The geometry of flexible spacers must be getting adjusted in such a way to avoid steric interaction which can only be highlighted by NMR and X-ray study of these compounds.

All these compounds have very high super-cooling tendency. Cholesteric phase persists up to room temperature in some cases. Out of four aromatic rigid spacer carbonates (nos. 8–11), only one (no. 9) does not exhibit mesomorphism. Compounds having 1,4-phenylene substitution (no. 8 and 10) exhibit higher cholesteric-isotropic transition temperatures. The 1,3-phenylene substitution (no. 9) is not conducive to mesomorphism. These findings are in support of accepted effect of chemical constitution on mesomorphism. Compound no. 10 has a breadth increasing non-linear bisphenol moiety. Even than it exhibits enantiotropic cholesteric phases. However, the effect of non-linearity is reflected in its lower cholesteric-isotropic transition temperatures compared to compounds no. 8 and 11 where only one phenylene spacer is present.

The comparison with the mesogenic properties of dicholesteryl carbamates[5] (Table III) indicates that carbamates induce smectic phases whereas carbonates induce cholesteric properties.

Most of the compounds exhibit vivid colours at different temperatures in cholesteric phase. The study has provided host of new cholesteric compounds and has

TABLE III

Dicholesteryl carbamates: $H_{45}C_{27}OOCHN\text{-}(CH_2)_X\text{-}NHCOOC_{27}H_{45}$

	X	Transition Temperatures °C		
Sr. No.	No. of CH_2 Units	Smectic	Cholestric	Isotropic
1.	2	(215)*	—	233
2.	3	195	—	210
3.	4	161	—	209
4.	5	151	—	199
5.	6	169	—	198
6.	8	(134)	152	177

* ( ) Monotropic values.

brought out some unusual effect of molecular structure on cholesteric behaviour of the mesogens.

All the compounds have been studied by calorimetric method (Table I). Some compounds (compounds no. 1, 3, 4, 5 and 7) did not exhibit peaks for the phase transitions cholesteric-isotropic or Isotropic-cholesteric (monotropic). The calorimetric study was repeated for these compounds by increasing the weight of the compound from 5 mg to 15 – 20 mg. and the heating rate was changed to 20°C per minute. With this variation peaks of all the phase transitions could be observed for compounds no. 1, 3, 4 and 5 but it remained undetected in the case of compound no. 7. Due to the size of the sample cup the amount of sample could not be increased to more than 20 mgs. Otherwise compound no. 7 also would have exhibited peaks showing enthalpy changes for all the transitions. The enthalpy change from cholesteric to isotropic transition is very small hence with the less amount of the substance, it is difficult to record them. Either more sensitive DSC apparatus is required or more amount of substance could be used for the study. Compounds no. 1 and 8 exhibit solid-solid transitions in calorimetric study.

The solid-cholesteric transition temperatures of compounds no. 8 and 11 differs markedly (53°C) but the cholesteric-isotropic transition temperatures differ a little. It is a little higher for dicarbonate (compound no. 8) compared to compound no. 11.

The difference between these two compounds can be explained on unsymmetrical molecules of compound no. 11, otherwise it is known that carbamate linkage is more conducive to mesomorphism compared to carbonate linkage. It is known that unsymmetrical linkages results into lowering of mesogenic transition temperatures.[6,7]

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