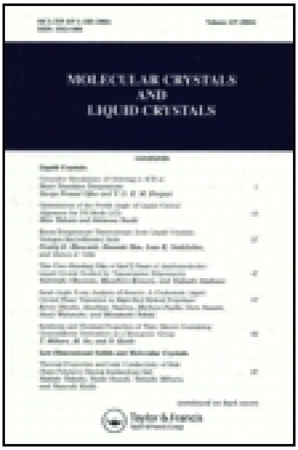

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New DI Cholesteryl Imide Esters (I) and Carbamates (II) with Flexible Spacers

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New Di Cholesteryl Imide Esters (I) and Carbamates (II) with Flexible Spacers

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Two homologous series having dicholesteryl moiety are synthesized and their mesogenic properties are studied.

Dicholesteryl esters of N,N′-alkane-α,ω-diyl bis(Trimellitimides) (series-I) exhibit cholesteric phases. The flexibility is increased from two to eight methylene units in the central linkage. Overall molecule is very large where different steric, repulsive and attractive forces would be operating. However, the net result of all these forces is that all derivatives but one exhibit cholesteric phases of high thermal stabilities.

Dicholesteryl carbamates are synthesized by changing α,ω diamino alkanes (series-II). The series exhibits smectic phases with one exception. The dicholesteryl carbonates studied by us having flexible spacers exhibit cholesteric phases indicating that carbamate linkage is more conducive to smectic mesomorphism. The effect of increase in spacer length on mesomorphic properties is discussed by comparing their mesogenic behaviour with other related mesogens. The study extends the structural gambit for obtaining cholesteric mesophases and provides new materials for application at higher temperatures in non-destructive testing.

Keywords: flexible spacers, odd-even effect, cholesteryl imide esters

INTRODUCTION

Di-cholesteryl esters and carbonates with flexible spacers are known.[1] Some of them exhibit mesomorphism predominantly monotropic in nature. It was thought quite interesting if dicholesteryl esters are synthesized with imide group and flexible spacers. Polyesters of N,N′-alkane α,ω-diyl bis(trimellitimides) are known to exhibit mesomorphism.[2] With this in view compounds of series I were synthesized. Series II is also important as it has two carbamate linkages. The study of mesogens with amide linkages has shown that amido central linkage is highly conducive to mesomorphism and enhances smectic mesophases more than nematic phases and the effect of carbamate linkage should be comparable with such mesogens.

EXPERIMENTAL

Series-I: N,N′-Alkane-α,ω-diyl bis(trimellitimides) and their acid chlorides were synthesized by known methods.[2] The esterification was carried out by condensing diacid chloride with cholesterol following the procedure of Dave and Vora.[3] The dicholesteryl imide esters were crystallized from chloroform-acetone mixture till constant transition temperatures were obtained. The transition temperatures are reported in Table I.

Series-II: Dicholesteryl carbamates were synthesized by condensing different diamines with cholesteryl chloroformate as per the literature method.[4] The carbamates were crystallised from chloroform-acetone mixture till constant transition temperatures were obtained, Table II.

TABLE I

Series-I

Transition temperatures

Sr. No.	X No. of CH_2 Units	Transition Temperatures °C Cholesteric	 Isotropic
1.	2	-	294 (D)
2.	3	221	247 (D)
3.	4	256	277 (D)
4.	5	221	259 (D)
5.	6	224	264 (D)
6.	8	215	262 (D)

D - Decomposition

TABLE II

Series-II

Transition temperatures

Sr. No.	X No. of CH_2 Units	Transition Temperatures °C Smectic	 Cholesteric	 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

RESULTS AND DISCUSSION

Series-I: Six compounds are synthesized by varying the methylene spacers from 2 to 8. First member with two methylene spacer is non-mesogenic. The other members exhibit cholesteric phases at higher temperatures. The solid-mesogenic transition temperatures are above 200°C. The graph of transition temperatures against the number of methylene spacers exhibit odd-even effect (Figure 1) for cholesteric-isotropic transition temperatures as well as for solid-cholesteric transition temperatures. The odd-even effect is much pronounced in solid-cholesteric or isotropic

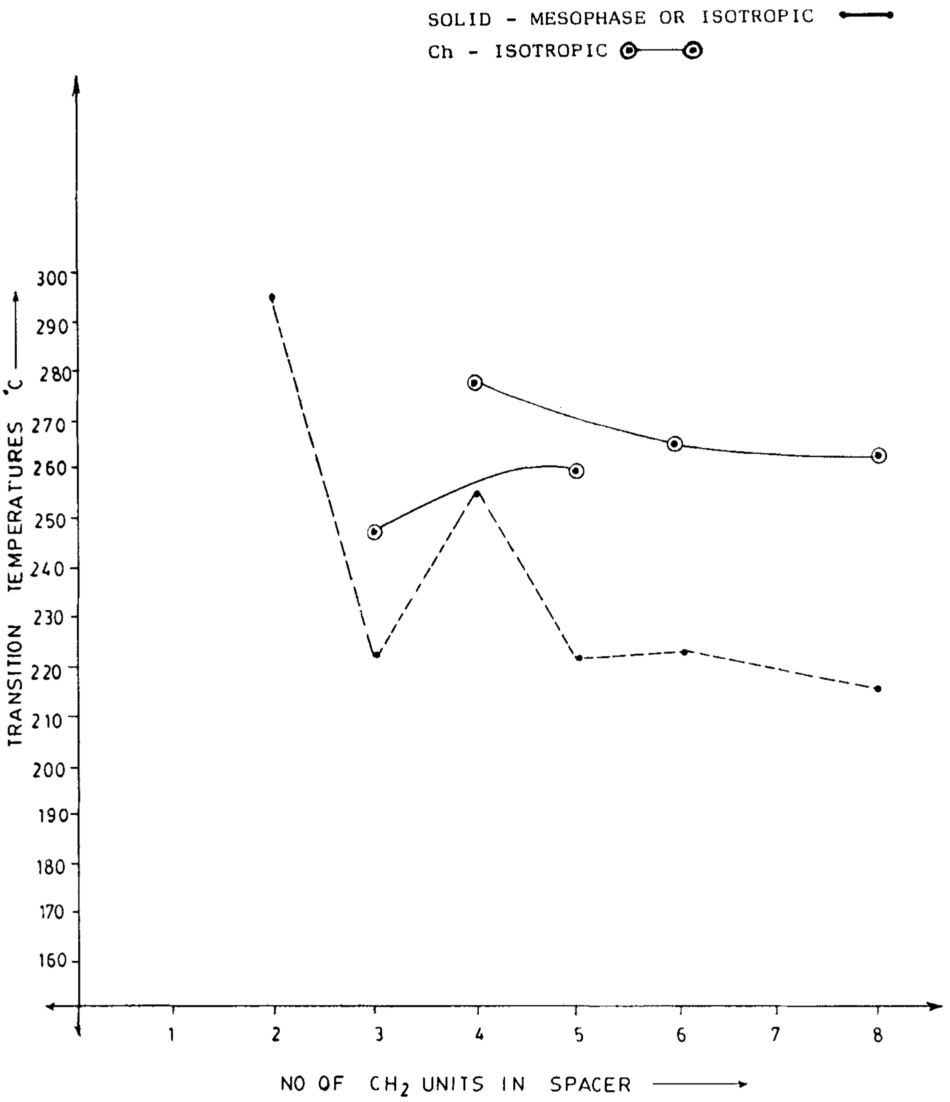
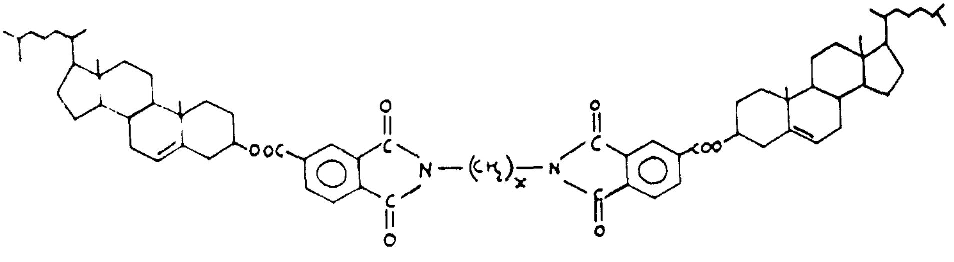


FIGURE 1

transition temperatures, compared to cholesteric-isotropic transition temperatures. This indicates that number of the methylene spacer plays an important role in the structure of crystals of these compounds. The geometry of series-I is as under:



X = 2 to 6,8

The geometry shows very complex structure. It incorporates two imide linkages where carbonyl groups contribute to the lateral attractive forces. Two ester linkages add to the flexibility of the molecules over and above the methylene spacers. The higher thermal stability of cholesteric phases can be attributed to the presence of two imide linkages and two cholesteryl units. Cholesteryl derivatives with other aromatic units are known to exhibit mesomorphism of higher thermal stability. The non-mesomorphism of first compound with two methylene spacers can be attributed to high melting point of the compound originating from less flexibility due to short spacer length. Some of the mesogens exhibit vivid colours in cholesteric phase. Blue phase is not detected in these mesogens.

Series-II: Six members are synthesized by changing α,ω-diamino alkanes. All the members with methylene spacer length 2–8 exhibit smectic mesophase. The texture appears as batonnets and changes to homeotropic texture on further cooling. Marked odd-even effect is not observed in the smectic-isotropic transition temperature curve, when transition temperatures are plotted against number of methylene spacers (Figure 2). The solid-smectic transitions also do not exhibit marked odd-even effect as observed in Series-I. The flexibility in the central linkages is normally deterrent in aromatic systems but Gray and McDonnell[5] have reported that cyclohexane gives better mesogenic properties compared to benzene in such systems. Last member of the series exhibits monotropic smectic phase and enantiotropic cholesteric phase. This is quite unusual. Normally increase in methylene spacers enhance smectogenic tendencies. It seems that increase in flexibility might have affected the smectic phase and would have induced cholesteric phase. Study of some higher homologues will be essential for understanding such behaviour.

The comparison of mesogenic properties of Series-II with Dicholesteryl carbonates with flexible and rigid spacers[6] indicate that Series-II is smectogenic whereas dicholesteryl carbonates exhibit predominantly cholesteric phases.

The two carbamate linkages will enhance polarizability of the molecules which will induce smectic mesophase in Series-II, Vora *et al.*[7,8] have explored the effect of amide linkage on mesomorphism and they have found that high polarizability of amide linkage and its linearity induces smectogenic tendencies and increases the thermal stability of nematic as well as smectic mesophase but enhancement is quite marked in smectic thermal stabilities.

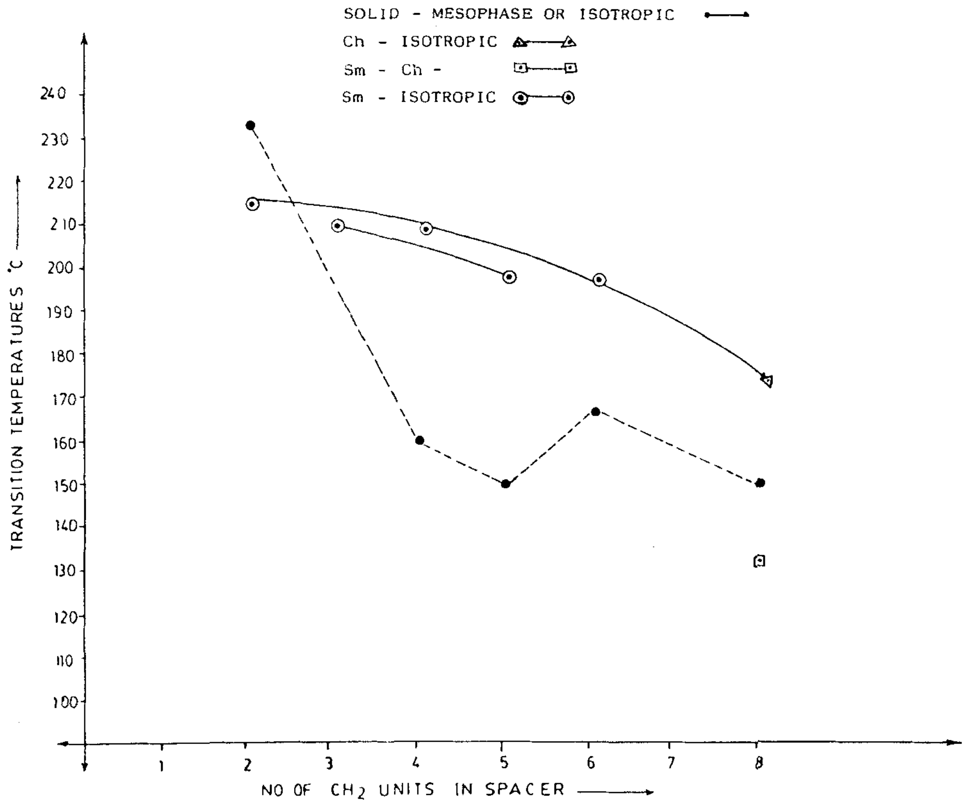


FIGURE 2

The study provided new cholesteric and smectic mesogens with typical structural features.

Acknowledgments

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