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Mesophase behaviour of 1, 3-diacyloxy and 1,4-diacyloxy esters

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ABSTRACT

Methods of synthesis of 1,3-diacyloxy benzene and 1,4-diacyloxy benzene derivatives are discussed. The compounds of first series was synthesized by different acid chlorides (Lauric, myristic, palmitic, heptadecanoic and steric) on treatment with resorcinol in presence of triethyl amine we can get 1,3-diacyloxy benzene derivatives and it was characterized by I.R and NMR data. The compounds of second series was synthesized by different acid chlorides on treatment with hydroquinone in presence of triethyl amine, resulting the formation of 1,4-diacyloxy benzene derivatives and characterized by I.R and NMR. The above two series of compounds was purified and crystallized from alcohol as shining needles. Further the liquid crystalline properties were studied for the above two series of compounds by using DSC and all the compounds possess pronounced L.C. Properties and showed the mesophase at two transition temperature regions. The mesophases were photographed and respective thermograms were recorded during heating rate 5^o/min and 10^o/min on cooling. The results are presented.

Keywords: Synthesis, flavonoid esters, Liquid crystals, Mesophase.

INTRODUCTION

Approximately 5% of all organic compounds exhibiting LC behavior have important characteristic properties like anisotropy, magnetic and electric susceptibility [1]. The molecule shows mesomorphic behavior because of increased dipolar forces acting along the long molecular axis, by the electronic substituents. Habes and coworkers [2] have found that the presence of an ortho hydroxy group in benzylidene aniline stabilizes the resulting unit due to intramolecular hydrogen bonding. The temperature - dependent variation in the color of cholesteric liquid crystals has led to the use of these substances in the measurement of temperature gradients [3-5]. Nematic liquid crystals are useful research tools in the application of magnetic resonance [6-10]. Molecules that are dissolved in nematic liquid crystal solvent give a very highly resolved NMR spectrum exhibiting inter molecular dipole-dipole fine structures. Analysis of the spectra of molecules in liquid crystal solvents yields information regarding the anisotropy of chemical shifts, direct magnetic dipole-dipole interaction, in direct spin-spin couplings, bond angles, bond lengths, molecular order and relaxation process.

Now a days liquid crystals are widely used in cosmetic industry in manufacturing of liquid crystal make up removers [11], lipsticks and lip glasses [12] containing cholesteric liquid crystal and also used in the manufacture of vaginal fluids. Liquid crystals are used extensively in pharmaceutical industries. In addition to this development, L.C's were found to be useful laboratory tools for GLC and absorption spectroscopy. Films of microencapsulated [13]. LC's can be prepared by specifying, draw-bar coatings or silk screening.

Novel families of cholesteric liquid crystals [14] have been developed by dupont (USA) for the decorative market. These materials, which are still in the experimental stage, may be used to provide attractive decorative effects on opaque, translucent and transparent surfaces. In contrast to most commercial liquid crystals, these materials exist as

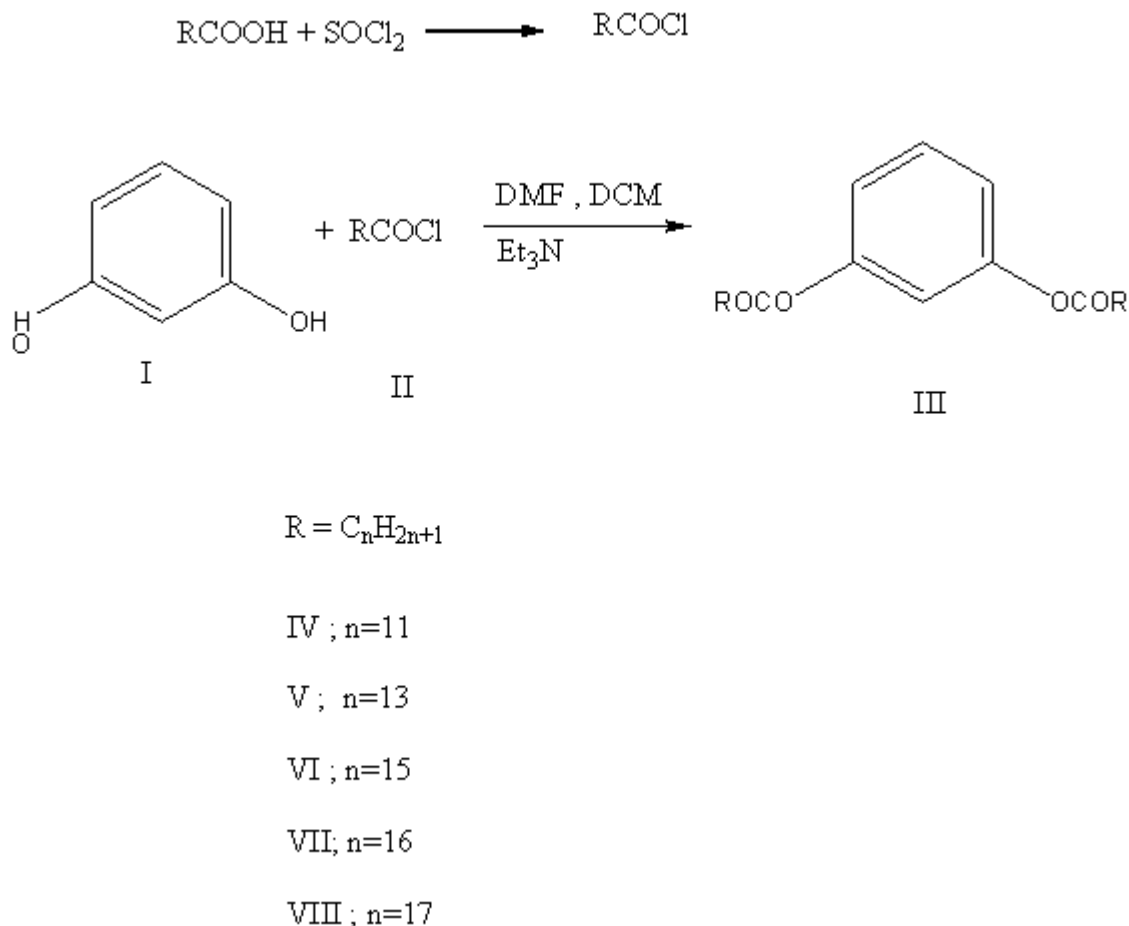
solid glasses at ambient temperature. Asymmetric molecules usually have a boarder mesophase range than their symmetric analogues mainly due to lowering of the melting points. According to Miczkowski *et al*, [15] this also has a strong influence on the polar structure of the mesophase; asymmetric compounds have a tendency to form ferroelectric phases instead of anti-ferroelectric phases.

RESULTS AND DISCUSSION

In this paper five new 1,3-diacyloxy benzene and five 1,4-diacyloxy benzene derivatives were synthesized and the structure of the ten compounds are detailed below;

Compound IV, XII	R = C _n H _{2n+1}	n=11
Compound V, XIII	R = C _n H _{2n+1}	n=13
Compound VI, XIV	R = C _n H _{2n+1}	n=15
Compound VII, XV	R = C _n H _{2n+1}	n=16
Compound VIII, XVI	R = C _n H _{2n+1}	n=17

All the present compounds, viz IV, V, VI, VII, VIII and XII, XIII, XIV, XV, XVI are found to exhibit liquid crystalline phases as identified by polarized optical microscope and by DSC. The compounds commonly exhibiting characteristic broken conic smectic G [16] phase stands as an evidence to claim the mesomorphism by the 1,3-diacyloxy benzene(IV,V,VI,VII,VIII) and 1,4-diacyloxy benzene(XII,XIII,XIV,XV,XVI) homologous series of compounds.



Scheme-I

MATERIAL AND METHODS

In continuation of our investigations, it is proposed to synthesize new banana shaped(Bent) liquid crystals and further characterize their LC properties. 1,3-di(acyloxy) benzene and 1,4-di(acyloxy) benzene derivatives were synthesized and structures were confirmed by spectral data. All the newly synthesized compounds exhibited liquid crystalline properties, which were examined employing polarizing microscope equipped with hot stage and also by

differential scanning calorimeter. The mesophases were photographed and respective thermograms were recorded during heating at a rate 5⁰ c/min and 10⁰ c/min on cooling.

General synthetic procedure of 1,3-diacyloxy benzene derivatives:

The reaction of resorcinol(I)(1 mole) with acid chlorides (lauryl chlorides, myristoyl chloride, palmitoyl chloride, heptadecanoyl chloride, stearoyl chloride)(II)(2 moles) in presence of tri ethyl amine (Et₃N) stirred at room temperatures(6-10 hours); results in the formation of 1,3-diacyloxy benzene(III).. Purification of compound(s) III by column chromatography (eluent; Hexane: Ethylacetate 90:10) resulted the formation of pure product. The product was recrystallised from methanol. The ¹H NMR spectrum of III showed resonances at δ6.89-6.97, δ7.3 (aromatic protons) confirmed the structures of 1,3-diacyloxy benzene(III). The synthetic work is presented in scheme I. All these compounds were confirmed by Spectral data (I.R and NMR).

Preparation of acid chlorides (III):

Long chain fatty acids (0.1 mol, lauric, myristic, palmitic, heptadecanoic and stearic acids) were reacted with freshly distilled SOCl₂ (0.3 mol). The contents were refluxed for 4 hours. Adding formic acid into the flask until no smell of SOCl₂ is observed destroyed excess SOCl₂. The crude acid chlorides were distilled at reduced pressure and used immediately for esterification.

Synthesis of 1,3-dilauroyloxy benzene (IV):

Resorcinol (0.01 mol) was dissolved in 5 ml of Dichloro methane, dimethyl formaamide and lauroyl chlorides (0.02 mol) were stirred in the presense of triethyl amine at room temperature under anhydrous conditions. The reaction mixture was stirred 6-10 hours at room temperature. The reaction mixture is poured into ice cold water and extracted with ethyl acetate repeatedly. After the above usual work up, the organic layer was then dried over anhydrous MgSO₄ and evaporated, it yielded a crude ester. Purification of the ester by a column chromatography eluent with n-hexane: ethyl acetate (90:10) collecting 50ml fractions afforded 1,3-di lauroyloxy benzene(IV) and thus formed was crystallized twice from MeOH-CHCl₃. Purity of the compound is checked by TLC. This is a low melting solid.

IR (ν_{max}): 2926, 2854, 1753, 1442, 1413; ¹H NMR (CDCl₃ /TMS): 0.9(t, 2xCH₃), 1.2-1.4(br.s, CH₂Protons), 1.7(Pentet, CH₂), 2.5(t, OCOCH₂), 6.8-6.9(Ar.Protons), 7.3(Ar protons)

Synthesis of 1,3-dimyristoyloxy benzene (V):

Resorcinol (0.01mol) was dissolved in 5 ml of DCM , DMF and myristoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography , was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

IR (ν_{max}): 2918, 2847, 1750, 1467, 1433; ¹H NMR (CDCl₃ /TMS): 0.86-0.89(t,2xCH₃), 1.2-1.4(br.s, CH₂Protons), 1.7(Pentet,CH₂), 2.5(t, OCOCH₂), 6.8-6.9(Ar.Protons), 7.3(Ar protons)

Synthesis of 1,3-dipalmitoyloxy benzene (VI):

Resorcinol (0.01mol) was dissolved in 5 ml of DCM , DMF and Palmitoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

IR (ν_{max}) : 2918, 2848, 1755, 1602,1466,1408; ¹H NMR (CDCl₃ /TMS): 0.86-89 (t,2xCH₃), 1.2-1.4(br.s,CH₂Protons), 1.69-1.77(Pentet ,CH₂), 2.5(t, OCOCH₂), 6.8-6.9(Ar.Protons), 7.3(Ar protons)

Synthesis of 1,3-diheptadecanoyloxy benzene (VII):

Resorcinol (0.01mol) was dissolved in 5 ml of DCM , DMF and heptadecanoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

IR (ν_{max}) : 2918, 2840, 1751,1450, 1430; ¹H NMR (CDCl₃ /TMS): 0.86-0.89(t, 2xCH₃), 1.2-1.4(br.s, CH₂Protons), 1.63-1.77(Pentet ,CH₂), 2.5(t, OCOCH₂), 6.8-6.9(Ar. Protons), 7.3(Ar protons)

Synthesis of 1,3-distearoyloxy benzene (VIII):

Resorcinol (0.01mol) was dissolved in 5 ml of DCM , DMFand Stearoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column

chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

IR (ν_{\max}): 2926, 2854, 1753, 1447, 1413; $^1\text{H NMR}$ (CDCl_3/TMS): 0.9(t, 2XCH₃), 1.2-1.4 (br.s, CH₂Protons), 1.7(Pentet,CH₂), 2.5(t, OCOCH₂), 6.8-6.9(Ar. Protons), 7.3(Ar protons)

In order to study the liquid crystalline properties, the compound VI is repeated crystallized from ethanol as flakes. The liquid crystalline behavior of the compound (VI) was evaluated by differential scanning calorimeter and polarizing microscope. The compound (VI) was studied for differential scanning calorimetric data at heating rate 10⁰c/min. The phase transition temperatures and enthalpy changes (ΔH) were recorded. To check reproducibility, the experiments were repeated for the sample. The mesophase was observed between 51.97-56.00⁰C(K→ smectic), $\Delta\text{H}=2.42$ mJ and 60.41-65.85⁰C (smetic to isotropic), $\Delta\text{H}= 377.56$ mJ respectively(Fig 1).

In order to further confirm the mesophase, compound(VI) was studied by employing polarizing microscope at the rate of 2⁰C/min. The observed textures were photographed during the mesophase and was presented in the fig 2. The texture was identified as broken conic smectic G phase. The DSC thermographic data i.e phase transition temperatures, enthalpy changes (ΔH) were recorded for the above esters (IV to VIII) and presented in table I.

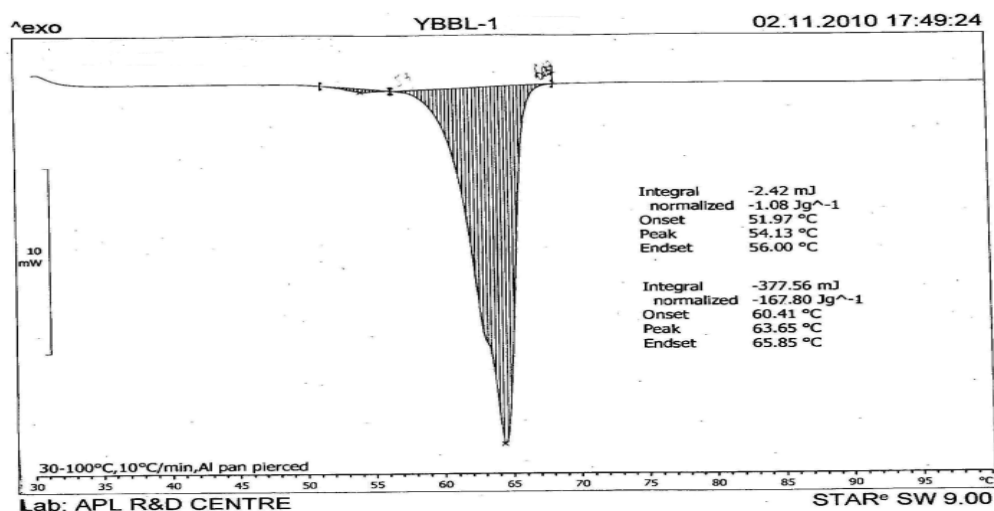


Fig1.DSC Thermogram of 1,3 – dipalmitoyloxy benzene(VI)

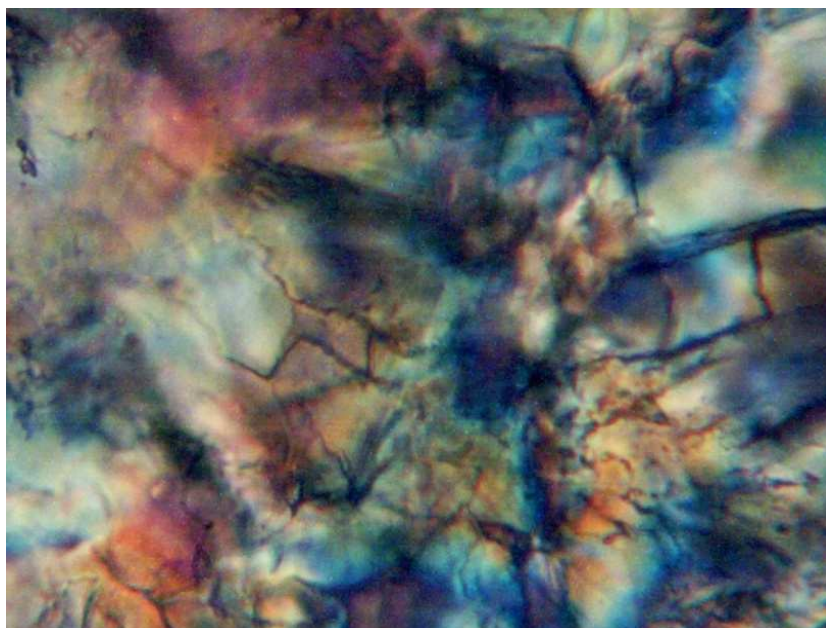
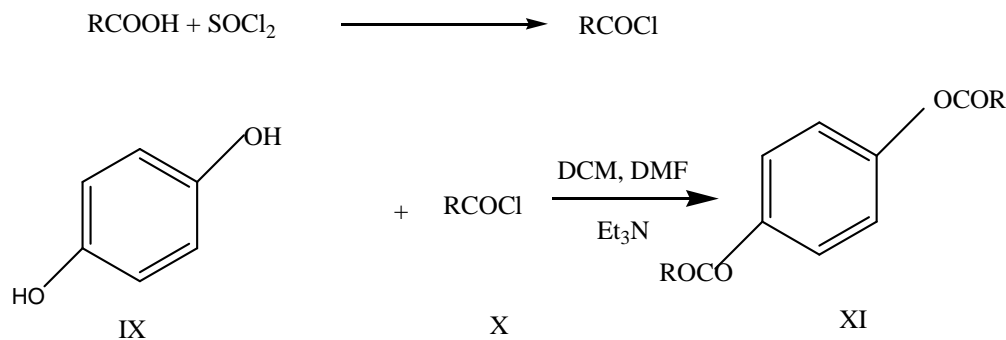


Fig 2. Polarising micrograph of 1,3-dipalmitoyloxy benzene(VI)

Table I Phase transition temperatures (mesophase region) and heat transition of 1,3-diacloxy benzene derivatives

S.No	Compound No.	Temp. in °C crystal K-mesophase	ΔH mJ/mg	Temp in °C Mesophase-isotropic	ΔH mJ/mg
1.	IV	---	----	49.0-52.47	308.48
2.	V	44.46-49.05	2.24	54.32-59.85	352.84
3.	VI	51.97-56.00	2.42	60.41-65.85	377.56
4.	VII	57.37-59.99	2.58	67.07-71.13	458.55
5.	VIII	48.49-51.33	2.30	56.65-59.98	384.48



R = C_nH_{2n+1}

XII ; n=11

XIII ; n=13

XIV ; n=15

XV ; n=16

XVI ; n=17

Scheme II

Synthesis of 1,4-diacloxy benzene derivatives :

The reaction of hydroquinone (IX)(1 mole) with acid chlorides (lauroyl chloride, myristoyl chloride, palmitoyl chloride, heptadecanoyl chloride, stearoyl chloride)(X) (2 moles) in presence of Triethylamine(Et₃N) stirred at room temperatures (6-10 hours) resulted in the formation of 1,4-diacloxy benzene(XI) with 50% yield shown in scheme II. Purification of compound (XI) by column chromatography (eluent : Hexane : Ethyl acetate 90 : 10) resulted the formation of product. The product was recrystallised from methanol. The ¹H NMR spectrum of XI showed at δ7.07 aromatic protons, δ1.2-1.4 showed CH₂ protons confirmed the structure of 1,4-diacloxy benzene(XI). The synthetic scheme presented in scheme II. All the above acid chlorides is treated with hydroquinone and esters were purified by column chromatography with n-hexane and ethyl acetate as eluent. All these compounds were recrystallized from methanol.

Synthesis of 1,4-dilauroyloxy benzene (XII):

Hydroquinone (0.01 mol) was dissolved in 5 ml of Dichloro methane, dimethyl formaamide and lauroyl chlorides (0.02 mol) were stirred in the presence of triethy amine at room temperature under anhydrous conditions. The reaction mixture was stirred 6-8 hours at room temperature. The reaction mixture is poured into ice cold water and extracted with ethyl acetate repeatedly. After the above usual work up, The organic layer was then dried over anhydrous sodium sulphate and evaporated, it yielded a crude ester. Purification of the ester by a column chromatography eluent with n-hexane: ethyl acetate (90:10) collecting 50ml fractions afforded 1, 4-di lauroyloxy benzene (IV) and thus formed was crystallized twice from MeOH-CHCl₃. Purity of the compound is checked by TLC.This is a low melting solid.

¹H NMR (CDCl₃ /TMS): 0.86-0.89 (t, 6H, 2x CH₃), 1.2-1.4(br, S, CH₂ Protons), 1.7(pentet, CH₂), 2.5(triplet, OCOCH₂), 7.077(aromatic protons)

Synthesis of 1,4-dimyristoyloxy benzene (XIII):

Hydroquinone (0.01mol) was dissolved in 5 ml of DCM , DMF and myristoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

$^1\text{H NMR}$ (CDCl_3/TMS): 0.9 (t, 6H, 2x CH_3), 1.2-1.4(br.s, CH_2 Protons), 1.7(pentet, CH_2), 2.5(triplet, OCOCH_2), 7.077(aromatic protons)

Synthesis of 1,4-dipalmitoyloxy benzene (XIV):

Hydroquinone (0.01mol) was dissolved in 5 ml of DCM , DMF and Palmitoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

$^1\text{H NMR}$ (CDCl_3/TMS): 0.86-0.895 (t, 6H, 2x CH_3), 1.2-1.4(br.s, CH_2 Protons), 1.7-1.77(pentet, CH_2), 2.5(triplet, OCOCH_2), 7.076(aromatic protons)

Synthesis of 1,4-diheptadecanoyloxy benzene (XV):

Hydroquinone (0.01mol) was dissolved in 5 ml of DCM , DMF and heptadecanoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography, was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

$^1\text{H NMR}$ (CDCl_3/TMS): 0.86-0.89 (t, 6H, 2x CH_3), 1.2-1.4(br.s, CH_2 Protons), 1.74(pentet, CH_2), 2.5(triplet, OCOCH_2), 7.07(aromatic protons)

Synthesis of 1,4-diStearoyloxy benzene (XVI):

Hydroquinone (0.01mol) was dissolved in 5 ml of DCM , DMF and Stearoyl chloride (0.02mol) and 3 ml of triethyl amine was added and stirred 6 hours at room temperature . After usual workup, the ester obtained by using column chromatography , was crystallized from methanol. It is low melting solid and Purity of the compound is checked by TLC.

$^1\text{H NMR}$ (CDCl_3/TMS): 0.9 (t, 6H, 2x CH_3), 1.2-1.4(br.s, CH_2 Protons), 1.7(pentet, CH_2), 2.5(triplet, OCOCH_2), 7.077(aromatic protons)

In continuation of our studies, compound XIV is repeated crystallized from ethanol as flakes. The liquid crystalline behavior of the compound (XIV) was evaluated by differential scanning calorimeter and polarizing microscope. The compound (XIV) was studied for differential scanning calorimetric data at heating rate $10^0\text{C}/\text{min}$. The phase transition temperatures and enthalpy changes(ΔH) are recorded and presented in fig 3. The data is presented in table II. In order to further confirm the mesophase, compound (XIV) was studied using polarizing microscope at the rate of $10^0\text{C}/\text{min}$. The observed textures were photographed during the mesophase and were presented in the fig 4. The DSC thermographic data i.e phase transition temperatures, enthalpy changes (ΔH) were recorded for the above esters (XII to XVI) shown in table II.

Table II Phase transition temperatures (mesophase region) and heat transition of 1,4-diacyloxy benzene derivatives

S.No	Compound No.	Temp. in ^0C crystal K-mesophase	ΔH mJ/mg	Temp in ^0C Mesophase-isotropic	ΔH mJ/mg
1.	XII	---	----	66.0-70.5	98.57
2.	XIII	64.0-67.5	0.74	71.6-74.5	110.84
3.	XIV	82.06-84.45	0.82	93.98-96.12	136.63
4.	XV	77.5-80.5	0.78	84.0-91.0	124.14
5.	XVI	78.49-80.33	0.80	85.40-90.34	148.24

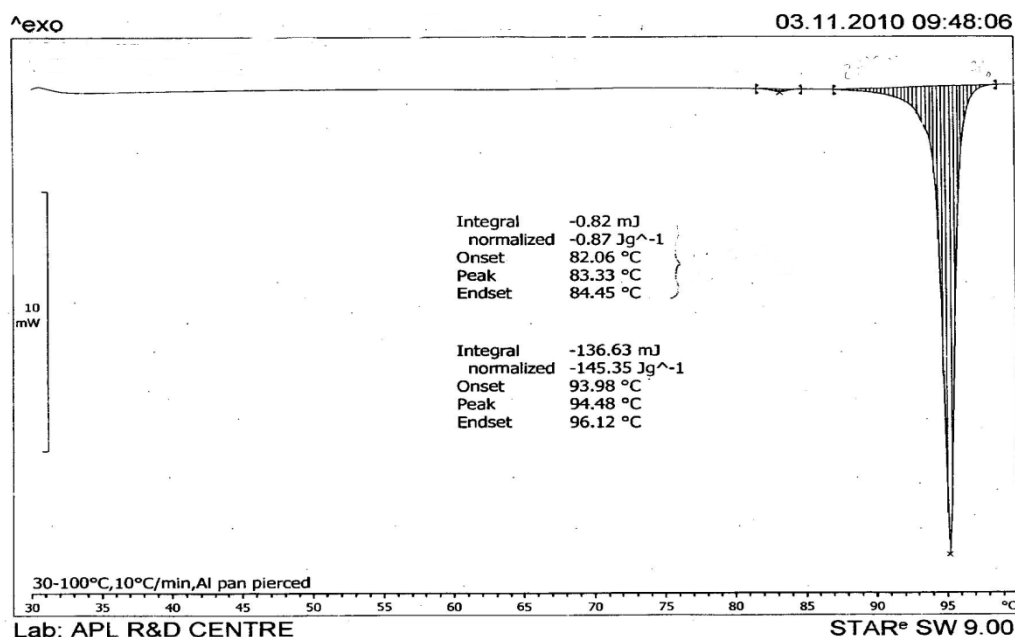


Fig 3. DSC Thermogram of 1,4 – dipalmitoyloxy benzene(XIV) Polarising micrograph of 1,4-dipalmitoyloxy benzene(XIV)

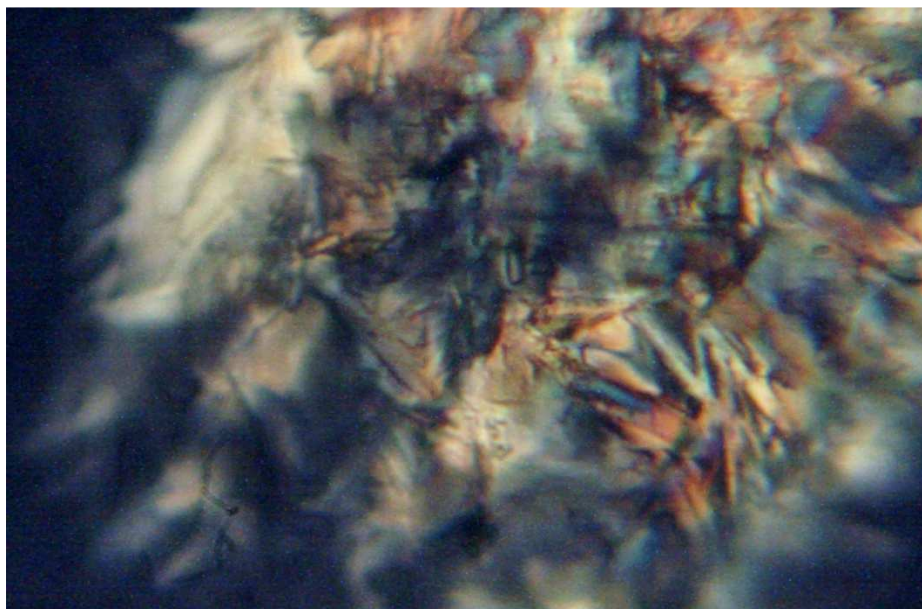


Fig 4. Polarising micrograph of 1,4-dipalmitoyloxy benzene(XIV)

CONCLUSION

The liquid crystalline properties were studied for the above two series of compounds by using DSC and all the compounds possess pronounced L.C. Properties and showed the mesophase at two transition temperature regions. The mesophases were photographed and respective thermograms were recorded during heating rate 5^o/min and 10^o/min on cooling. They showed Smectic phase behavior.

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