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Synthesis, spectroscopic and mesomorphic studies on heterocyclic liquid crystals with 1,3-oxazepine-4,7-dione, 1,3-oxazepane-4,7-dione and 1,3-oxazepine-1,5-dione cores

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ABSTRACT

Three series of newly derived 3-substituted-phenyl-2-(4-(tetradecyloxy)phenyl)-2,3-dihydro-1,3-oxazepine-4,7-diones, 3-substituted-phenyl-2-(4-(tetradecyloxy)phenyl)-1,3-oxazepane-4,7-diones and 4-substituted-phenyl-3-(4-(tetradecyloxy)phenyl)-3,4-dihydrobenzo[*e*][1,3]-oxazepine-1,5-diones have been synthesized from the reactions of 4-substituted-N-(4-(tetradecyloxy)benzylidene)aniline derivatives with maleic, succinic and phthalic anhydride. All structures were elucidated by physical measurements and the bonding characteristics of the resulting compounds were substantiated by FT-IR spectroscopy. Their molecular structures are supported by the ¹H and ¹³C NMR spectra along with two-dimensional COSY, NOESY, HMQC and HMBC. The effect from different substituents upon thermal and mesomorphic behaviour has been investigated by differential scanning calorimetry and polarizing optical microscopy, respectively. All compounds possess relatively high phase transition temperatures with only 4-phenyl-3-(4-(tetradecyloxy)phenyl)-3,4-dihydrobenzo[*e*][1,3]oxazepine-1,5-dione exhibited the texture characteristics of the nematic phase.

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1. Introduction

It has been documented that benzoxazepines are important in the diverse fields of heteroatom chemistry and biochemistry owing to its wide range of biological activities [1–4]. One of the factors in determining the nature of these compounds can be attributed to the presence of the Schiff base or imine group. The advantage of incorporating Schiff base into benzoxazepines can be ascribed to the possibility of exhibiting liquid crystalline behaviour as that shown by 4-methoxybenzyliden-4'-butylaniline [5]. In relation to this, the mesomorphic properties of aromatic Schiff base esters with substituents varying in their polarities have been reported [6–8].

A large number of these analogues containing heterocyclic units have hitherto been synthesized [9–17]. In principle, the heterocyclic unit is of great importance as core particularly in the thermotropic liquid crystals and this can be due to their ability to impart lateral and/or longitudinal dipoles coupled with the changes in molecular shape [18,19]. In this paper we reported the preparation of the new compounds derived from 3-substituted-phenyl-2-(4-(tetradecyloxy)phenyl)-2,3-dihydro-1,3-oxazepine-4,7-diones, 3-substituted-phenyl-2-(4-(tetradecyloxy)phenyl)-1,3-oxazepane-4, 7-diones and 4-substituted-phenyl-3-(4-(tetradecyloxy)phenyl)-3,4-dihydro-benzo[*e*][1,3]-oxazepine-1,5-diones. The structures for all the title compounds were characterized by FT-IR and NMR (¹H, ¹³C, COSY, NOESY, HMQC and HMBC). The phase transition temperatures and enthalpy values of the title compounds were measured by differential scanning calorimetry (DSC) and the textures of the mesophases were studied using polarizing optical microscope (POM).

2. Experimental

Whilst 4-hydroxybenzaldehyde, maleic anhydride, succinic anhydride and phthalic anhydride were obtained from Aldrichm, the aniline, 4-nitroaniline 4-phenylenediamine, 4-bromoaniline and 1-bromotetradecane were obtained from Merck. They were used without further purification. Thin-layer chromatography (TLC) was performed on silica-gel plates. Benzene and THF were dried by standard method.

2.1. Synthesis

2.1.1. Synthesis of 4-(tetradecyloxy)benzaldehyde

4-(Tetradecyloxy)benzaldehyde was prepared following the method described by Catanescu [20]. *p*-Hydroxybenzaldehyde (0.1 mol, 12.2 g) in 25 ml of DMF was placed in a 250 ml two-necked

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Compounds	m.p. °C	Yield%	Molecular formula	Elemental analys	is %, found (calcula	ted)
				С	Н	N
2a	131-132	47	C ₃₁ H ₄₀ BrNO ₄	65.85 (65.26)	7.76 (7.07)	2.07 (2.45)
3a	74–75	40	$C_{31}H_{41}NO_4$	75.10 (75.73)	8.04 (8.41)	2.93 (2.85)
4a	104-105	52	$C_{31}H_{40}N_2O_6$	69.12 (69.38)	7.76 (7.51)	5.35 (5.22)
5a	110-111	59	$C_{31}H_{42}N_2O_4$	73.06 (73.49)	8.25 (8.36)	5.67 (5.53)
2b	156-157	61	C ₃₁ H ₄₂ BrNO ₄	65.38 (65.03)	7.60 (7.39)	2.13 (2.45)
3b	123-124	59	C ₃₁ H ₄₃ NO ₄	75.11 (75.42)	8.93 (8.78)	2.14 (2.84)
4b	82-83	58	$C_{31}H_{42}N_2O_6$	69.58 (69.12)	7.09 (7.86)	5.67 (5.20)
5b	130-131	63	$C_{31}H_{44}N_2O_4$	73.62 (73.19)	8.37 (8.72)	5.19 (5.51)
2c	105-106	61	$C_{35}H_{42}BrNO_4$	67.13 (67.74)	6.17 (6.82)	2.47 (2.26)
3c	98-99	60	C ₃₅ H ₄₃ NO ₄	77.16 (77.60)	8.21 (8.00)	2.09 (2.59)
4c	128-129	40	$C_{35}H_{42}N_2O_6$	71.37 (71.65)	7.02 (7.22)	4.25 (4.77)
5c	133-134	53	$C_{35}H_{44}N_2O_4$	75.11 (75.51)	7.68 (7.97)	5.21 (5.03)

 Table 1

 Physical and analytical data of compounds 2a-5a, 2b-5b and 2c-5c.



R= Br, H, NO₂ and NH_2

Scheme 1. General synthetic procedure for all compounds 1a-1d, 2a-5a, 2b-5b and 2c-5c with atom numbering scheme.

Table 2		
Acquisition	parameter used in the NMR measurements	

Parameters	Experiment							
	¹ H NMR	¹³ C NMR	2D COSY	2D NOESY	2D HMQC	2D HMBC		
SF	400.1 MHz	100.6 MHz	400.1 MHz	400.1 MHz	$F_1 = 100.6 \text{ MHz}$ $F_2 = 400.1 \text{ MHz}$	$F_1 = 100.61 \text{ MHz}$ $F_2 = 400.1 \text{ MHz}$		
SW	10 ppm	180 ppm	10 ppm	10 ppm	$F_1 = 180 \text{ ppm}$ $F_2 = 10 \text{ ppm}$	$F_1 = 180 \text{ ppm}$ $F_2 = 10 \text{ ppm}$		
PW	8.3 μs (30° flip angle)	20.0 μs (90° flip angle)	8.3 μs (90° flip angle)	8.3 μs (90° flip angle)	8.3 μs (90° flip angle)	8.3 µs (90° flip angle)		
AQ	4.0 s	1.3 s	0.3 s	0.3 s	0.09 s	0.4 s		
D1	1.0 s	2.0 s	2.0 s	2.0 s	1.0 s	1.0 s		
NS	16	20,000	16	32	88	92		
TD	66 k	66 k	$F_1 = 256$	$F_1 = 256$	$F_1 = 512$	$F_1 = 512$		
			$F_2 = 2048$	$F_2 = 2048$	$F_2 = 1024$	$F_2 = 4096$		

Abbreviations: F₁, ¹³C channel (except 2D COSY where F₁ and F₂ are 1H channel); SF, spectrometer frequency; SW, spectral width; AQ, acquisition time; DI, relaxation delay; NS, number; TD, number of data point .

flask equipped with a condenser and magnetic stirring bar. A solution containing anhydrous sodium carbonate (0.25 mol, 27.2 g) and 1-bromo-tetradecane (0.1 mol, 26.9 g) in 25 ml DMF was added to the reaction flask. The mixture was refluxed (rf) for 4 h at 150 °C under continuous stirring. After cooling, the reaction mixture was poured into 1 L of cold water (approx. 5 °C) and then filtered. The precipitate was washed once with KOH and then with water. It was dried and finally recrystallized from ethanol.

2.1.2. General procedure for the synthesis of imines 1a-1d

Since the synthesis of compounds **1a–1d** was based on the same method as described by Yeap et al. [21], therefore, the description in relation to the synthesis of whole series will be represented by compound **1a**.

An equimolar amount of 4-(tetradecyloxy)benzaldehyde with 4-bromoaniline dissolved in absolute ethanol was refluxed (rf) for 3 h and the precipitate thus formed upon cooling to room temperature was filtered. The solid residue was recrystallized from methanol and dried under reduced pressure. The analytical and FT-IR data for compounds **1a–1d** are summarized as follows:

1a: Yield 66%. m.p. 122–123 °C. Anal. for $C_{27}H_{38}BrNO$ (%): Found (%) C 68.97, H 8.49, N 2.96; Calc. (%) C 68.63, H 8.11, N 2.96. IR: v_{max} (KBr) (cm⁻¹) 2945, 2918, 1630, 1606, 1580, 1254.

1b: Yield 75%. m.p. 72–73 °C. Anal. for $C_{27}H_{39}NO$ (%): Found (%) C 82.07, H 9.40, N 3.87. Calc. (%) C 82.39, H 9.99, N 3.56. IR: $v_{max}(KBr)$ (cm⁻¹) 2950, 2916, 1635, 1600, 1585, 1250.

1c: Yield 47%. m.p. 67–68 °C. Anal. for $C_{27}H_{38}N_2O_3$ (%): Found (%) C 73.17, H 8.93, N 6.76. Calc. (%) C 73.94, H 8.73, N 6.39. IR: v_{max} (KBr) (cm⁻¹) 2960, 2923, 1637, 1598, 1583, 1247.

Table 3			
¹ H NMR che	emical shifts (ppn	 of compounds 	1a-1d.

Atom	Chemical shift (ppm)					
	1a	1b	1c	1d		
H1 and H5	7.91	7.86	7.90	7.88		
H2 and H4	7.52	7.58	7.23	7.11		
H7	9.21	8.53	9.26	8.38		
H9 and H13	7.62	7.11	7.41	7.51		
H10 and H12	7.08	7.28	7.22	6.99		
H11	-	7.03	-	4.85		
H1′	4.08	4.06	4.04	4.09		
H2′	1.76	1.74	1.75	1.8		
H4'-12'	1.25	1.26	1.24	1.27		
H13′	1.28	1.28	1.27	1.29		
H14′	0.84	0.87	0.85	0.91		

1d: Yield 58%. m.p. 79–80 °C. Anal. for $C_{27}H_{40}N_2O$ (%): Found (%) C 79.21, H 9.05, N 6.32. Calc. (%) C 79.36, H 9.87, N 6.86. IR: v_{max} (KBr) (cm⁻¹) 2930, 2923, 1635, 1602, 1582, 1248.

2.1.3. Synthesis of compounds 2a-5a, 2b-5b and 2c-5c

All the above mentioned compounds were synthesized by the same method. The synthetic method will be described by based on the compound **2a**.

A solution of maleic anhydride (0.01 mol, 0.8 g) in 10 ml dry benzene was added dropwise to a hot dry benzene solution (20 ml) containing 0.01 mol (4.7 g) **1a** in a round bottom flask equipped with a double surface condenser fitted with calcium chloride guard tube. The reaction mixture was refluxed (rf) for 3 h and the reaction was monitored by TLC. The solvent was distilled off in vacuo. The solid product thus obtained was filtered and washed with distilled cold water. The resulting solid was recrystallized twice from dioxane. Physical and analytical data of **2a–5a**, **2b–5b** and **2c–5c** are listed in Table 1.

 Table 4

 ¹³C NMR chemical shifts (ppm) of compounds 1a–1d.

Carbon no.	Chemical shift (ppm)						
	1a	1b	1c	1d			
C1	130.42	130.01	130.78	130.08			
C2	115.89	115.11	115.70	115.64			
C3	164.21	164.18	163.22	162.54			
C4	115.89	115.11	115.70	115.64			
C5	130.42	130.01	130.78	130.08			
C6	129.12	130.36	130.21	130.24			
C7	163.67	163.13	163.34	162.95			
C8	138.88	138.65	139.84	139.76			
C9	123.14	122.89	122.21	122.70			
C10	132.70	132.18	132.65	132.80			
C11	122.70	128.86	157.16	143.32			
C12	132.70	132.18	132.65	132.80			
C13	123.14	122.89	122.21	122.70			
C1′	69.13	70.05	69.86	70.15			
C2′	29.33	29.27	29.30	29.27			
C3′	26.45	26.37	26.39	26.37			
C4′	29.59	29.45	29.41	29.45			
C5′	29.64	29.63	29.56	29.63			
C6′	29.72	29.70	29.61	29.70			
C7′	29.84	29.81	29.72	29.81			
C8′	29.89	29.87	29.80	29.87			
C9′	29.90	29.89	29.82	29.89			
C10′	29.90	29.91	29.87	29.91			
C11′	29.92	29.97	29.90	29.97			
C12′	32.17	32.67	32.03	32.67			
C13′	22.96	22.12	23.09	23.14			
C14′	14.78	14.70	15.02	14.64			

able 5
'ibrational frequencies (cm^{-1}) and their assignments for compounds 2a–5a , 2b–5b and 2c–5c .

Com.	vC—H benzylic	vC_{ph} —H	υCH_3 as υCH_3 s	vCH_2 as vCH_2 s	vC=0	vC=C	vC—H	δC—O lacton	C ₄ 0	Others
2a	3273	3075	2953	2870	1707	1603	1488	1303	1257	611 C—Br
			2918	2810		1572				
2b	3298	3019	2953	2853	1723	1602	1488	1309	1263	652 C—Br
			2940	2795		1569				
2c	3270	3071	2931	2852	1719	1605	1489	1334	1246	645 C—Br
			2914	2801		1588				
3a	3211	3059	2949	2854	1701	1602	1445	1322	1257	-
			2925	2835		1577				
3b	3218	3042	2940	2851	1697	1600	1448	1320	1250	-
			2921	2830		1570				
3c	3235	3071	2936	2852	1719	1605	1489	1334	1246	-
			2918	2821		1588				
4a	3221	3072	2954	2874	1677	1606	1463	1341	1254	1638 NO ₂
			2918	2849		1581				1277
4b	3220	3068	2950	2869	1692	1600	1460	1340	1250	1630 NO ₂
			2915	2838		1580				1290
4c	3217	3051	2955	2860	1701	1602	1461	1348	1252	1645 NO ₂
			2918	2830		1583				1270
5a	3220	3050	2951	2864	1679	1602	1458	1344	1251	3304 NH ₂
			2915	2833		1580				32060
5b	3219	3048	2955	2862	1690	1605	1462	1340	1253	3315 NH ₂
			2918	2849		1584				3218
5c	3222	3053	2951	2861	1689	1601	1460	1339	1253	3312 NH ₂
			2917	2841		1581				3211

v = Stretching, δ = bending, γ = out of plane, s = symmetric, as = symmetric.

The synthetic route used to prepare all the intermediates and title compounds **1a–1d**, **2a–5a**, **2b–5b** and **2c–5c** with numbered atoms are shown in Scheme 1.

2.2. Physical measurements

Melting points were recorded by Gallenkamp digital melting point apparatus. The measurements were carried out by heating up the sample from room temperature. The elemental (CHN) microanalyses were performed using a Perkin Elmer 2400 LS Series CHNS/O analyzer.

Table 6a¹H NMR chemical shifts (ppm) of compounds 2a-5a and 2b-5b.

Atom	Chemical shift (ppm)							
	2a	3a	4a	5a	2b	3b	4b	5b
H2 and H6	7.43	7.48	7.92	7.41	7.45	7.40	7.94	7.48
H3 and H5	7.12	7.09	7.02	7.08	7.05	7.03	7.04	7.06
H13 and H17	7.82	7.62	7.88	6.75	7.86	7.29	7.85	6.76
H14 and H16	7.56	7.28	8.21	6.97	7.57	7.60	8.03	7.01
H15	-	7.18	-	5.25	-	7.31	-	5.28
H7	9.82	9.81	9.25	9.88	9.83	9.86	9.39	9.36
H9	6.34	6.32	6.40	6.43	2.52	2.54	2.48	2.55
H10	6.47	6.41	6.73	6.57	2.56	2.58	2.55	2.59
H1′	4.08	4.07	4.08	4.06	4.08	4.06	4.07	4.09
H2′	1.73	1.73	1.72	1.70	1.80	1.71	1.58	1.68
H4'-12'	1.27	1.26	1.25	1.24	1.28	1.25	1.24	1.23
H14′	0.85	0.87	0.86	0.88	0.83	0.85	0.87	0.88

Table (6Ŀ
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¹H NMR chemical shifts (ppm) of compounds **2c–5c**.

Atom Chemical shift (ppm)				
	2c	3c	4c	5c
H2 and H6	7.23	7.32	7.43	7.25
H3 and H5	6.51	7.03	6.75	6.64
H7	9.82	9.81	9.91	9.21
H12	7.82	8.02	7.75	8.06
H13	7.52	7.50	7.97	7.50
H14	7.63	7.59	7.71	7.58
H15	7.49	7.47	7.48	7.46
H19	-	7.07	-	5.09
H17 and H21	7.94	7.48	7.35	6.98
H18 and H20	7.75	7.70	8.18	6.42
H1′	4.09	4.07	4.04	4.08
H2′	1.73	1.70	1.64	1.71
H4'-12'	1.29	1.26	1.22	1.28
H14′	0.85	0.87	0.82	0.89

Table	7
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¹H⁻¹H correlation from 2D COSY and NOESY for **2a–5a**, **2b–5b** and **2c–5c**.

Compounds	Atom H	COSY	NOESY
2a-5a	H2 and H6 H3 and H5 H13 and H17 H14 and H16 H7 H9 H10 H10 H11	H3 or H5 H2 or H6 H14 or H16 H13 or H17 - H10 H9 H2′	H14 or H16 H1', H13 or H17 H3 or H5 H2 or H6 - H10 H9 H2', H3 or H5
	H2′	H1′	H1′
	H14′	H13′	H13′
2b-5b	H2 and H6	H32 or H5	H14 or H16
	H3 and H5	H2 or H6	H1', H13 or H17
	H13 and H17	H14 or H16	H3 or H5
	H14 and H16	H13 or H17	H2 or H6
	H7	-	-
	H9	H10	H10
	H10	H9	H9
	H1'	H2'	H2', H3 or H5
	H2'	H1'	H1'
	H14'	H13'	H13'
2c-5c	H2 and H6	H3 or H5	H18 or H20
	H3 and H5	H2 or H6	H1', H17 or H21
	H7	-	-
	H12	H13	H13
	H13	H12, H14	H12, H14
	H14	H13, H15	H13, H15
	H15	H14	H14
	H17 and H21	H18 or H20	H3 or H5
	H18 and H20	H17 or H21	H2 or H6
	H1'	H2'	H2'
	H2'	H1'	H1'
	H14'	H13'	H13'

2.3. FT-IR measurements

The intermediates and title compounds were analyzed in the form of KBr pellets and the spectra were recorded in the range of $4000-400 \text{ cm}^{-1}$ using a Perkin Elmer 2000-FT-IR spectrophotometer.

2.4. NMR measurements

The ¹H and ¹³C NMR spectra were recorded in deuterated chloroform (CDCl₃-d₆) for **1a–1d**, and dimethylsulphoxide (DMSO-d₆) for **2a–5a**, **2b–5b** and **2c–5c** compounds at 298 K on a Bruker 400 MHz UltrashiedTM FT-NMR spectrometer equipped with a 5 mm BBI inverse gradient probe. Chemicals shift were referenced to internal tetramethylsilane (TMS). The concentration of solute molecules was 50 mg in 1.0 ml DMSO. Standard Bruker pulse programs [22] were used throughout the entire experiment. The spectroscopic details of NMR are summarized in Table 2.

2.5. Phase transition temperatures and enthalpy values

The phase transition temperatures and enthalpy values were measured by Perkin Elmer Pyris 1 DSC at heating and cooling rates of 5 °C min⁻¹, respectively.

2.6. Liquid crystalline texture observation

The textural observation was carried out using a Carl Zeiss Axioskop 40 polarizing microscope equipped with a Mettler FP5 hot stage and TMS94 temperature controller. The samples studied by optical microscopy were prepared in thin film sandwiched between glass slide and cover.

3. Results and discussion

All the title compounds **1a–1d**, **2a–5a**, **2b–5b** and **2c–5c** crystallized as stable solids with sharp melting points.

3.1. Physical characterization

3.1.1. ¹H and ¹³C NMR spectral assignment for **1a–1d**

A complete assignment of the imines compounds **1a–1d** can be described by based on a representative compound **1c** (Scheme 1) owing to all of these compounds exhibit similar characteristics as inferred from NMR spectra.

The ¹H NMR data (Table 3) shows that the chemical shifts of the aromatic protons are observed at δ = 7.22–7.90 ppm whilst the proton pairs in both aromatic rings (H1 and H5, H2 and H4) and (H9 and H13, H10 and H12) are equivalent. A singlet is observed at



Fig. 1. ¹H-¹H connectivities in the COSY spectra for compound 2a.

 δ = 9.26 ppm which corresponds to the azomethine proton (H7). The two triplets at δ = 4.04 ppm and δ = 0.85 ppm can be ascribed to the proton H1' and the methyl proton H14', respectively. A quintet at δ = 1.75 ppm attributed to the H2'. The group of protons H4'–H12' are confirmed by the appearance of multipletes at δ = 1.24 ppm.

The ¹³C NMR signals have been substantiated by DEPT135 of which the assignment can be governed by the additive rules and substitution effect. The resonances due to the aromatic carbons in both rings in **1a–1d** can be located at the chemical shift range of δ = 115.89–164.21 ppm, δ = 115.11–164.18 ppm, δ = 115.70–163.22 ppm and δ = 115.64–162.54 ppm, respectively (Table 4). The presence of carbon C7 adjacent to nitrogen atom from imine group (C=N) can be observed at the range of δ = 162.95–163.67 ppm. The chemical shift at δ = 69.13–70.15 ppm range attributed to C1' while C14' assigned at the range of δ = 14.64–15.02 ppm for the respective compounds **1a–1d**.

3.2. Physical characterization of 2a-5a, 2b-5b and 2c-5c

3.2.1. FT-IR spectral data

It is clearly shown from the FT-IR spectra of **2a–5a**, **2b–5b** and **2c–5c** that they exhibit similar characteristics. The strong band ob-

servable at 1677–1723 cm⁻¹ corresponds to the stretching of carbonyl group (C=O). The other major band observed at 1303-1348 cm⁻¹ can be assigned to bending of C–O mode. A weak absorption band at 3019-3075 cm⁻¹ can be assigned to the stretching vibration of aromatic C–H bond [23]. Two bands which appear at respective frequency ranges of 1600–1606 cm⁻¹ and 1569–1588 cm⁻¹ can be attributed to the C=C stretching in phenyl ring [21]. The band with weak intensity at the range of 3211-3298 cm⁻¹ can be assigned to the benzylic C–H. The band with strong intensity in the spectra of all compounds at the range of 1246–1263 cm⁻¹ can be ascribed to the ether group (vC_4 –O) [24]. In addition to these bands, there is another band observed at the range of $1445-1489 \text{ cm}^{-1}$ which can be ascribed to the bending of C-H [25]. On the other hand, the infrared spectra exhibit different bands assignable to different substituents X (Br, NO₂ and NH₂) [26] in respective compounds **2**, **4** and **5** (Table 5).

3.2.2. NMR spectroscopy

In order to substantiate the conformation of title compounds **2a–5a**, **2b–5b** and **2c–5c** in the solution state, the conventional ¹H, ¹³C NMR and DEPT135 for all compounds along with COSY, NOESY, HMQC and HMBC were applied.



3.2.2.1. 1D and 2D NMR study of**2a–5a**, **2b–5b** and **2c–5c**. The values of the ¹H NMR chemical shifts for compounds **2a–5a**, **2b–5b** and **2c–5c** in DMSO solution are listed in Tables 6a and 6b, respectively. A complete assignment for the title compounds can be described

by based on a representative compounds as shown in Scheme 1 in which three types of compounds have been differentiated by **a**, **b** and **c**. Inspection from the ¹H NMR spectra for **2a–5a** compounds shows two doublets in the down-field region

Table	8
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¹³C NMR chemical shifts (ppm) of compounds **2a-5a**, **2b-5b** and **2c-5c**.

Carbon no.	Chemical shift (ppm)											
	2a	3a	4a	5a	2b	3b	4b	5b	2c	3c	4c	5c
C1	130.09	130.89	131.07	131.02	130.18	130.06	129.94	130.05	130.25	129.58	128.94	130.55
C2	125.44	126.03	125.63	125.38	125.36	125.32	124.78	125.17	125.47	124.62	124.35	125.52
C3	116.25	116.48	116.90	116.83	116.35	116.46	115.15	115.21	116.54	116.32	115.71	116.28
C4	163.21	162.87	162.67	162.86	164.55	164.33	163.12	164.51	163.18	164.62	164.60	164.12
C5	116.25	116.48	116.90	116.83	116.35	116.46	115.15	115.21	116.54	116.32	115.71	116.28
C6	125.44	126.03	125.63	125.38	125.36	125.32	124.78	125.17	125.47	124.62	124.35	125.52
C7	88.43	88.60	89.14	89.63	88.85	88.62	88.41	88.89	88.54	89.07	88.40	88.85
C8	167.70	168.15	169.52	169.38	174.64	175.83	176.61	176.43	169.87	169.72	169.21	169.41
C9	132.50	132.47	132.69	133.48	32.16	32.28	31.95	31.84	132.25	130.80	132.65	132.34
C10	130.47	130.86	130.18	129.04	29.88	29.78	29.27	29.39	130.68	130.28	129.75	130.66
C11	164.55	165.05	167.16	167.38	171.14	172.01	173.71	173.61	167.31	167.87	167.91	167.23
C12	138.88	138.93	142.67	132.64	139.51	139.29	143.31	130.95	129.69	128.66	128.20	129.85
C13	132.64	132.38	132.85	132.45	132.66	131.76	132.27	132.63	131.54	132.83	132.36	132.65
C14	130.36	130.48	120.58	118.40	130.34	130.54	129.98	118.31	141.35	141.26	135.70	135.30
C15	122.21	121.64	149.26	142.31	121.73	123.43	148.31	142.52	121.57	121.41	121.40	121.36
C16	130.36	130.48	120.58	118.40	130.34	130.54	129.98	118.31	141.35	141.26	135.70	135.30
C17	132.64	132.38	132.85	132.45	132.66	131.76	132.27	132.63	131.54	132.83	132.36	132.65
C18	-	-	-	-	-	-	-	-	130.87	130.52	126.32	118.23
C19	-	-	-	-	-	-	-	-	120.45	120.72	140.56	142.65
C20	-	-	-	-	-	-	-	-	130.87	130.52	126.32	118.23
C21	-	-	-	-	-	-	-	-	138.73	135.71	130.46	132.57
C1′	68.87	66.36	67.62	68.92	68.61	67.39	67.64	67.86	68.45	68.93	68.48	68.77
C2′	29.92	29.47	29.84	29.68	29.55	29.88	29.73	29.85	29.16	29.43	29.83	29.59
C14′	14.78	14.90	15.22	15.23	15.50	15.27	15.01	15.08	15.06	15.31	15.08	15.16

Table 9	
2D ¹ H- ¹³ C HMOC and HMBC correlation for compounds 2a-5a . 2b-5b and 2c-5	ic.

Compounds	Atom	HMQC	HMBC [J(C, H)]			
		¹ J	² J	зJ	⁴ J	^{intra} J
2a-5a	H2 and H6 H3 and H5 H13 and H17 H14 and H16 H7 H9 H10 H1' H2' H14'	C2 or C6 C3 or C5 C13 or C17 C14 or C16 C7 C9 C10 C1' C2' C14'	C1, C3 or C5 C4, C2 or C6 C12, C14 or C16 C15, C2 or C6 C1 C8, C10 C9, C11 C1' C2' C14'	C4, C7 C1 C15 C12 C2 or C6, C8 C11 C8 C2' C1', C3' C13'	- - - C9 C7 C12 C3' C4' C12'	C1 ⁻ , C9, C14 or C16 C8, C13 or C17 C10, C3 or C5 C11, C2 or C6 C14 or C16 C2 or C6 C13 or C17 C4' C5' C11'
2b-5b	H2 and H6 H3 and H5 H13 and H17 H14 and H16 H7 H9 H10 H1' H2' H14'	C2 or C6 C3 or C5 C13 or C17 C14 or C16 C7 C9 C10 C1' C2' C14'	C1, C3 or C5 C4, C2 or C6 C12, C14 or C16 C15, C13 or C17 C1 C8, C10 C9,C11 C1' C2' C14'	C4 C1 C15 C12 C2 or C6, C11 C11 C8 C2' C1', C3' C13'	- C7 - C10 - C3' C4' C12'	C10, C13 or C17 C11, C14 or C16 C8, C9, C3 or C5 C9, C2 or C6 C3 or C5 C13 or C17 C2 or C6 C4' C5' C11'
2c-5c	H2 and H6 H3 and H5 H7 H12 H13 H14 H15 H15 H15 H17 and H21 H18 and H20 H1' H2' H14'	C2 or C6 C3 or C5 C7 C12 C13 C14 C15 C17 or C21 C18 or C20 C1' C2' C14'	C1, C3 or C5 C4, C2 or C6 C1 C9, C13 C12 C13, C15 C10, C14 C16, C18 or C20 C17 or C21,C19 C2' C1', C3' C13'	C4 C1 C16 C14 C9 C12 C9, C11 C19 C16 C3' C4' C12'	- C9, C17 or C21 C15 C10 C10 C12 C7 - C4' C5' C11'	C9, C12, C18 or C20 C9, C12, C17 or C21 C13 - - C17 or C21 C3 or C5, C15 C2 or C6 C5' C6' C10'

(δ = 6.32–6.43 ppm and δ = 6.41–6.73 ppm) owing to protons H9 and H10 in heterocyclic ring. However, two triplets at the range of δ = 2.48–2.55 ppm and δ = 2.55–2.59 ppm, respectively, can be assigned to the H9 and H10 in compounds **2b–5b**. The ¹H NMR data for compounds **2a–5a** and **2b–5b** show that the signals of the aromatic protons (H2 and H6) can be observed at the range of δ = 7.41–7.92 ppm and δ = 7.40–7.94 ppm. The signals due to H13 and H17 are observed at δ = 6.75–7.88 ppm and δ = 6.76– 7.86 ppm while the resonances for H14 and H16 occurred at δ = 6.97–8.21 ppm and δ = 7.01–8.03 ppm, respectively.

The ¹H NMR spectrum of compound **3a** shows a triplet at δ = 7.18 due to H15 while the analogue H15 proton appears as a singlet at δ = 5.25 in **5a**. The similar explanation can be inferred from the ¹H NMR spectra of **3b** and **5b** wherein a triplet and a singlet occurred at δ = 7.31 ppm and 5.28 ppm, respectively.

The ¹H NMR chemical shifts for compounds **2c–5c** show that the resonances at δ = 6.42–8.18 ppm (Table 6b) can be ascribed to the presence of aromatic protons (C—H). Whilst the proton pairs (H2 and H6, H3 and H5, H17 and H21, H18 and H20) are equivalent, the aromatic protons H12–H15 are found to be non-equivalent. The signal of H19 appears as a triplet at δ = 7.07 for **3c** and occurred as a singlet at δ = 5.09 for compound **5c**.

All title compounds exhibit signal at the range of δ = 9.21– 9.91 ppm which can be ascribed to H7. The two triplets at the range of δ = 0.82–0.89 ppm and δ = 4.04–4.09 ppm can be assigned to the methyl proton H14' and H1', respectively. A quintet at $\delta = 1.58-1.80$ ppm can be attributed to the H2'. The presence of a group of protons from H4' to H12' can be evidenced by the multipletes which occurred at the range of $\delta = 1.22-1.29$ ppm.

The COSY experiments have further substantiated that correlation between the equivalent proton pairs with the adjacent protons wherein the cross peaks resulting from these correlations appear at the same region (Table 7). Inspection from Fig. 1 for compound **2a** exhibits the correlation between H2 (or H6) with the respective protons H3 (or H5) residing at the positions next to earlier atoms. A similar phenomenon can also be found on H13 (or H17) which has correlated with H14 (or H16). The H9 proton for sevenmembered ring is correlated with H10. The correlation by COSY also reveals that the H1' which is adjacent to O atom in ether group correlated with H2'. A similar correlation can also be observed in compounds **2b–5b.** In the COSY spectra of compounds **2c–5c**, it is apparent that more correlations are observed for aromatic protons H12, H13, H14 and H15 (Table 7).

Further investigations on the protons of all compounds were supported by the NOESY experiments (Table 7) of which the selected spectrum for compound **4b** is shown in Fig. 2. Through these techniques, the H3 atom and its equivalent H5 atom are found to be correlated with H13 (or H17). Similarly, the methylene protons at C1' are correlated with H3 (or H5). A similar phenomenon can also be found on H2 (or H6) which correlated with H14 (or H16).





Fig. 4. Long range C—H correlations in the HMBC spectra of compound 4c.

Table 10

The correlation by NOESY also reveals that H7 is not correlated with any other protons in all compounds. While the H9 protons correlated with H10.

The two signals observed at $\delta = 167.70 - 176.61$ ppm and 164.55–173.71 ppm in the respective ¹³C NMR spectra of all title compounds can be attributed to the carbonyl C=O (C8 and C11) in heterocyclic ring. The signal of C7 appears at the range of δ = 88.40–89.63 ppm. The signal appears at high-field (δ = 14.78– 15.50 ppm) can be assigned to C14' of the methyl group in the alkyl chain while a signal at δ = 66.36–68.93 ppm and 29.16–29.92 ppm can be attributed to the C1' and C2', respectively. The resonances due to the aromatic carbons in all title compounds (**a**, **b** and **c**) can be located at δ = 116.25–162.87 ppm, 115.15–164.55 ppm and 115.71-164.62 ppm, respectively (Table 8). The resonance recorded at δ = 121.21–149.26 ppm can be assigned to respective aromatic carbon atoms next to X substituent (Br, NO₂ or NH₂). The signals observed in the spectra of compounds 2a-5a and **2c–5c** at δ = 132.25–133.48 ppm and δ = 129.04–130.86 ppm can be assigned to the respective C9 and C10 in heterocyclic ring. However, the signals at the range of δ = 31.84–32.28 ppm and 29.27–29.88 ppm are due to C9 and C10 in compounds 2b–5b.

The HMQC spectra of compounds **2a–5a**, **2b–5b** and **2c–5c** (Table 9) provide information on the interaction between the protons and the carbon atoms which are directly attached to each other. As a representative, the discussion will be based on the spectrum for **5a** (Fig. 3). It can be deduced from this figure that the H2 (or H6), H3 (or H5), H13 (or H17) and H14 (or H16) in aromatic ring of compounds **2a–5a** and **2b–5b** correlated with C2 (or C6), C3 (or C5), C13 (or C17) and C14 (or C16), respectively. Moreover, the one-bond ¹³C–1H can also indicate the correlations between H1', H2' and H14'

Phase transition temperatures and enthalpy change for compounds **2a–5a**, **2b–5b** and **2c–5c**.

Compounds	Phase transition	Temperature/ °C	Enthalpy change (KJ mol ⁻¹)
2a	Cr–Iso	131.86	71.98
	Iso-Cr	105.85	-57.32
3a	Cr–Iso	74.90	83.44
	Iso-Cr	45.55	-78.71
4a	Cr–Iso	104.13	61.21
	Iso-Cr	79.61	-52.51
5a	Cr–Iso	110.47	79.52
	Iso-Cr	89.48	-62.37
2b	Cr–Iso	156.64	48.21
	Iso-Cr	114.31	-23.43
3b	Cr1-Cr2	32.50	3.99
	Cr2–Iso	123.93	20.62
	Iso-Cr2	109.62	-0.047
	Cr2-Cr1	52.41	-0.32
4b	Cr–Iso	82.98	68.41
	Iso-Cr	47.12	-51.28
5b	Cr–Iso	130.33	88.16
	Iso-Cr	86.24	-38.45
2c	Cr–Iso	105.63	4.22
	Iso-Cr2	74.82	-2.53
	Cr2-Cr1	67.12	-1.56
3c	Cr–Iso	98.32	52.91
	Iso–N	94.53	-9.06
	N–Cr	77.39	-43.92
4c	Cr–Iso	128.70	62.48
	Iso-Cr2	79.26	-25.61
	Cr2-Cr1	58.81	-33.17
5c	Cr–Iso	133.72	81.23
	Iso-Cr2	92.61	-58.68
	Cr2-Cr1	61.95	-42.65

with C1', C2' and C14', respectively. The **2c–5c** are different from **2a–5a** and **2b–5b** because they possess additional aromatic ring (C9–C10–C12–C13–C14–C15) adjacent to seven-membered ring. The presence of this additional ring can be substantiated by the correlation rule via the one-bond $^{13}C-^{1}H$ connectivity between H12, H13, H14 and H15 with respective C12, C13, C14 and C15.

The aromatic quaternary carbons for all compounds were established via the connectivities between the carbon and its neighboring proton by HMBC correlation spectra (Table 9). The spectra of each series (**a**, **b** and **c**) have similar correlation depending on the position of heterocyclic ring. However, the aliphatic protons for all title compounds exhibit no correlation with any aromatic and heterocyclic ring carbons. However, the HMBC spectra of compound **4c** (Fig. 4), for example, has shown that the H2 (or H6) was correlated with the carbons C1 and C3 (or C5) with ²J, C4 with ³J, C9, C12 and C18 (or C20) with ^{intra}J, respectively. The H3 (or H5) is also correlated with carbons C4, C2 (or C6) with ²J and C1 with ³I on the basis of this analysis. The long range connectivities through intramolecular interaction (^{intra}]) among C9, C12, C17 (or C21) and H3 (or H5) proton can be established even though these atoms are far away from H3 (or H5). In the same way, the H17 (or H21) located at the phenyl ring adjacent to nitrogen atom in heterocyclic ring is correlated with C16, C18 (or C20) with ²J, C19 with ³J and C7 with ⁴J while the ^{intra}J long range connectivities for both C3 (or C 5) and C15 with H17 (or H21) have been observed. A similar phenomenon can also be observed wherein the H18 (or H20) is correlated with C17 (or C21), C19 with ²J, C16 with ³J, and C2 (or C6) with ^{intra}J. The long rang connectivities for each H12, H13, H14 and H15 with C8 and C11 are also detectable. The emergence of the cross peaks associated with the correlations of C2', C3', and C13' with respective H1', H2' and H14' has confirmed the presence of carbon nuclei from the aliphatic chain.







3.3. Mesomorphic behaviour

The textures observed under the polarized light are compared with those photomicrographs reported in the literatures [27,28]. The sequence of phase and related transition temperatures upon heating and cooling runs for all final compounds are listed in Table 10. The DSC thermograms of **3a**, **3b**, **2c** and **3c** during the heating and cooling scans are depicted in Fig. 5. Fig. 5a reveals that **3a** is a non-mesogenic compound as only one transition temperature associated with the crystal-isotropic (Cr–Iso) was observed at 74.9 °C upon heating. The same phenomenon was observed when this compound was cooled down wherein the Iso–Cr transition occurred at 45.6 °C. Similarly, the compounds **2a**, **4a**, **5a**, **2b**, **4b** and **5b** possess the same characteristics as shown by **3a** (Table 10).

However, the thermogram for compound **3b** (Fig. 5b) shows more than one peak. The peak which appears at 32.5 °C with enthalpy value (ΔH) of 3.99 kJ mol⁻¹ during the heating run is characteristic to Cr₁–Cr₂. Subsequently, the isotropization occurred at 123.9 °C (ΔH = 20.62 kJ mol⁻¹). Similar phenomenon is observed when the same compound is cooled down wherein the Iso-Cr₁ and Cr₂-Cr₁ transitions are observed at 109.6 °C and 52.4 °C, respectively.

As for compound **2c**, it is very clear that upon heating the isotropization has taken place at 105.6 °C (Fig. 5c). However, upon cooling two peaks are observed at 74.8 °C and 67.1 °C, respectively. The peak at 67.12 °C can be ascribed to Cr_2-Cr_1 within crystal phase as the phenomenon reported for unsymmetric pyrazoles [29]. The compounds **4c** and **5c** exhibit the same behaviour as that observed in **2c**.

Only one compound **3c** (Fig. 5d), in which R=H and the heterocyclic ring fused with benzene ring, shows the liquid crystalline behaviour upon the cooling run. A relatively large temperature range of mesomorphic region (17.1 °C) in compound **3c** is observed within this series which suggests that this compound possesses remarkable phase stability [30,31]. The optical photomicrograph of **3c** is shown in Fig. 6 in which the compound exhibits nematic phase at 77.4 °C.

Further investigation upon the mesomorphic properties of these compounds is underway and will be reported elsewhere.



Fig. 6. Optical photomicrograph of compound 3c displaying nematic schlieren texture.

4. Conclusion

Some new heterocyclic compounds with oxazepine and oxazepane cores have been synthesized and characterized. The compound with RC_6H_4 -group (where R=Br, H, NO₂ and NH₂) attached to the endocyclic –N in the respective 1,3-oxazepine-4,7-dione, 1,3-oxazepane-4,7-dione and 1,3-oxazepine-1,5-dione cores have been investigated ranging from the elucidation of molecular structures to the studies on their thermal and optical behaviours. Except compound with C_5H_4 - as substituent in the third series of 1,3-oxazepine-1,5-diones exhibits the nematic phase, all the other compounds with oxazepine and oxazepane cores reported in this paper are non-mesogenic.

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