

Synthesis and Characterization of Rod-Bent Shape Compounds Containing Bis-Oxadiazole

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Abstract

In this work, two new mesomorphic bent-rod shape compounds containing bis-oxadiazole rings are described. The relationship between the compound structure and the mesomorphic behavior as 3,3'-benzene-1,4-diylbis [5-(4-nitrophenyl)-1,2,4-oxadiazole] and 3,3'-benzene-1,4-diylbis [5-(4-chlorophenyl)-1,2,4-oxadiazole] were established using different terminal groups (i.e., NO₂, Cl). The mesomorphism was categorized using POM and DSC, while the compounds structure were characterized using FT-IR and ¹HNMR.

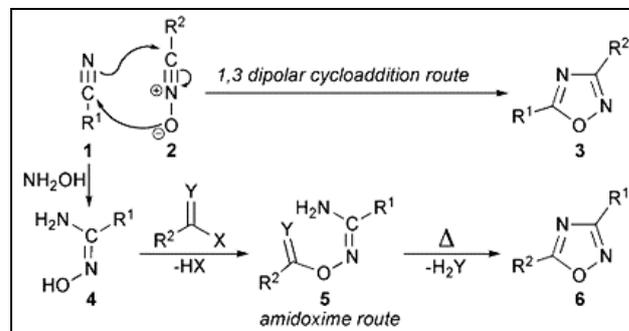
1. Introduction

Liquid crystals (LCs) form a unique state of matter. Between the solid (crystalline) and liquid (isotropic) phases some compounds display a distinctly different, intermediate state^[1]. Specifically, LC phase type is highly affected by the stereo-chemistry factor and structure of the molecules. As well as, some heterocycles are played major rule in modified synthesis mesogen of liquid crystals such as oxazoles, oxadiazoles, etc.^[2]. The lower steric hindrance between hydrogen atoms of hetero cyclic ring, thereby they show the flat nature, instead of twisting, different conformations, due to their polar nature^[3].

Several nematic liquid crystals are prepared with elongated (composition from heterocycles and multiple aromatic rings), rigid cores, or using of linkage groups, which may be rigid, however often add a new factor of flexibility for the core^[4]. The higher rigid linking groups usually involved unsaturated groups that prevent rotation of LC molecule and oftentimes introduce conjugation via one or more domains of the core. Oppositely, flexible linking groups are usually saturated groups that give ability for movement of the core domains by bond rotation of the linkage group, and prohibit conjugation between domains because of their unsaturated nature. Some linking groups, such as ethylene, acetylene, azo, and imine groups can favor nematic LC phase by elongating the core length. Others linking groups, like esters, increased the molecule polarizability, which also favors nematic LC phase in spite of higher molecular breadth and higher flexibility^[5].

The mesomorphic properties of the 1,2,4-oxadiazole derivatives strongly depend on the substitution at both C3 and C5 positions in the ring^[6]. The substitution on 1,2,4-oxadiazoles can be done by substituents with terminal weak polar groups, such as phenyl, cyclohexyl, biphenyl, phenylcyclohexyl (Alkyl, Alkoxy, F, Br) or by substituents with terminal strong polar NO₂-group^[7].

Several methods have been used to synthesize 1,2,4-oxadiazoles, but there are two most popular routes among the known synthetic routes to obtain 1,2,4 oxadiazoles. The two common strategies can be summarized in the following Scheme 1^[8]:



Scheme 1. Synthesized compound (6).

Many variations can be applied successfully on the amidoxime pathway. For example, amidoximes can be synthesized by the reaction of nitrile with hydroxylamine hydrochloride under heating conditions^[9].

In our study, we have developed amidoximes route for the synthesis liquid crystal compounds of 3,5 disubstituted bis-oxadiazole rings from the acyl chloride and N¹, N⁴-dihydroxybenzene-1,4-dicarboximidamide under milder conditions with good reaction yields.

2. Instrumental

All the chemicals that, used are liquid and solid, gained from Fluka, Merck and BDH companies. The FTIR spectra recorded via using disc of the potassium bromide (KBr) on FT-IR instrument. Model 8300 Shimadzu Spectrophotometer, Japan, Fourier-Transform Infrared in the frequency range of 4000 to 400 cm⁻¹ Spectrophotometer of Perkins-Elmer. ¹HNMR spectra recorded on Brüker, ACF 300 spectrometer at 300 MHz, the solvent is DMSO-d₆ with the internal standard tri methyl silane (TMS). A LINSEIS DSC PT-1000 differential scanning calorimeter was used to test the transition temperatures and enthalpies, which were calibrated with indium (156.6 °C, 28.45 J/g) and a heating rate of 10.0 °C/min in air. In this research.

Synthesis of 3, 3'-benzene-1, 4-diylbis [5-(4-substituted phenyl)-1, 2, 4-oxadiazole] [5]

Para nitro benzoic acid or chloro benzoic acid used to synthesize 1,2,4-oxadiazole derivatives through the amidoximes condensation cyclo-addition with para substituted carboxylic acid chlorides under base medium of pyridine/DMF.

Synthesis of benzene-1,4-dicarbaldehyde dioxime [2]

6.95 g of hydroxyl amine hydrochloride (0.1 mole) was dissolved in 60 mL of NaOH (6.66 % w/v) solution. 6.706 g of terephthaldehyde (0.05 mole) then added and the reaction take place under reflux heating conditions for 3 hrs. After that the ice bath used to cool the reaction, and solid precipitated product was filtered then followed by washing with distilled water until the washing solution pH reached to 7, then cleaned solid precipitated was dried at overnight. The resulting white solid crystal, yield 78 %, M.P. decomposition.

Synthesis of terephthalonitrile [3]

A mixture contented 5.412 g of benzene-1, 4-dicarbaldehyde dioxime prepared (0.033 mole) and sufficiently amount of acetic anhydride (15 mL) was heated under reflux for 3 hrs.; then 75 mL of distilled water was added drop by drop at ice bath (0-5) °C and stirrer condition for 2 hrs. The prepared precipitate was collected after filtration and drying at room temperature. The resulting white solid, yield 72%, M.P. decomposition.

Synthesis of N¹, N⁴-dihydroxybenzene-1,4-dicarboximidamide [4]

Firstly, a mixture contented solution of hydroxylamine hydrochloride (12.371 g, 0.178 mole) dissolved in 20 mL of sodium hydroxide (1.78 M) and solution of prepared terephthalonitrile (20.22 g, 0.158 mole) dissolved in 70 mL of ethanol, was heated under reflux for 4 hrs. Secondly, the reaction mixture was cooled in an (0-5) °C bath with stirrer for 3 hrs. to generate the white precipitate which then filtered and dried in room temperature conditions. Finally, the precipitate crystals were collected after the recrystallization from a mixture ethanol/water (1:1). The resulting white solid crystal, yield 68%, M.P 202-210 °C.

Synthesis of chloro and nitro benzoyl chloride derivatives [4a,b] [4]

The acid chlorides were synthesized used refluxing a mixture of (0.01 mole) 4-chloro or nitro benzoic acid and excess (5 mL) of thionyl chloride followed by 2 drops of DMF. After the refluxing of the mixture for 2 hrs.; the excess amount of thionyl chloride was evaporated under reduced pressure. The product was cleaned by distilled water and kept dry under N₂ atmosphere.

Synthesis of 3, 3'-benzene-1, 4-diylbis [5-(4-substituted phenyl)-1, 2, 4-oxadiazole] [5 a,b] [5]

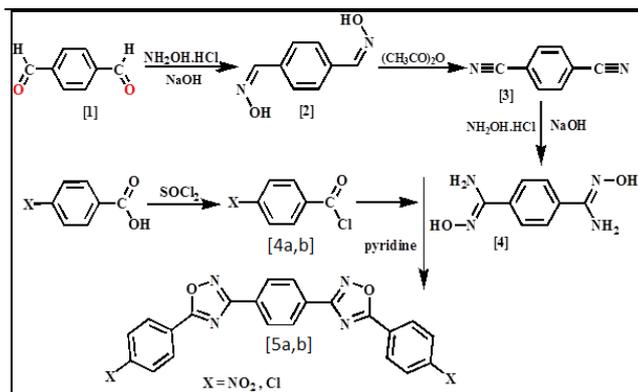
0.873 g of N¹, N⁴-dihydroxybenzene-1, 4-dicarboximidamide (0.045 mole) was added to 15 mL pyridine, then drop wise addition of p-substituted (nitro or chloro) benzoyl chloride (0.094 mole) was followed, and the mixture aging under stirrer for 24hrs. After The reaction contents were poured into distilled water (100 mL). The recrystallization process of crude products were done from ethanol. Table 1 shows melting points and yield product of the synthesized compounds.

Table 1. Physical properties of compounds [5a,b] [5].

Compound name	Symbols	M.P.(°C)	Color	Yield (%)
3,3'-benzene-1,4-diylbis[5-(4-nitrophenyl)-1,2,4-oxadiazole]	a	72-80	brown	78%
3,3'-benzene-1,4-diylbis[5-(4-chlorophenyl)-1,2,4-oxadiazole]	b	124-132	yellow	72%

The synthetic route was illustrated in Scheme 1. Para nitro benzoic acid or chloro benzoic acid benzoic acid used to synthesize 1,2,4-oxadiazole derivatives through the amidoximes condensation cyclo-addition with para

substituted carboxylic acid chlorides under base medium of pyridine/DMF.



Scheme 2. Synthetic route of 3,3'-benzene-1,4-diylbis [5-(4-substituted phenyl)-1,2,4-oxadiazole] derivatives.

Under basic condition, two groups hydroxyl amine hydrochloride condensation with terephthalaldehyde [1] to produce Benzene-1,4-dicarbaldehyde dioxime [2], which then dehydrating by acetic anhydride to synthesis of terephthalonitrile [3]. N', N''-4-dihydroxy-benzene-1,4-dicarboximidamide intermediates formed after added hydroxyl amine hydrochloride in present potassium hydroxide dissolving in a mixture ethanol/water. At last, the 1,2,4-oxadiazole derivatives [5 a,b] was formed via reacting amidoximes with the freshly prepared para-substituted benzoyl chloride [4a,b] in the conditions of reflux and dry pyridine. The structures of prepared liquid crystals were estimated by FT-IR, ¹HNMR spectra.

3. Results and Discussion

[2]: (FTIR); Broad band at 3162 cm^{-1} that could be assigned to $\nu(\text{H}-\text{O})$ stretching, bands at 1652 , 1588 and 850 cm^{-1} due to $\nu(\text{N}=\text{CH})$, $\nu(\text{C}=\text{C})$ and out of plane bending for *p*-disubstituted benzene ring, respectively.

[3]: (FTIR); Sharp band at 3039 cm^{-1} and that could be attributed to $\nu(\text{C}-\text{H Aromatic})$ stretching of phenyl group, strong sharp band at 2226 cm^{-1} due to $\nu(\text{C}\equiv\text{N})$. Bands at 1612 and 839 cm^{-1} could be attributed to $\nu(\text{C}=\text{C})$, and out of plane bending for *p*-disubstituted benzene ring.

[4]: (FTIR); Sharp bands at 3455 , 3415 , 3354 and 3185 cm^{-1} that could be attributed to $\nu(\text{N}-\text{H})$ stretching of NH_2 and $\text{C}-\text{H Aromatic}$, the OH bands at 1645.5 , 1591.1 , 1520 , 1123.8 and 842 cm^{-1} due to $\nu(\text{CH}=\text{N})$, $\nu(\text{C}=\text{C})$, $\nu(\text{C}-\text{O})$ and out of plane bending for *p*-disubstituted benzene ring, respectively

[5]_{a-b}: (FTIR); Weak bands at $(3067.6-3092)\text{ cm}^{-1}$ that could be attributed to $\nu(\text{Ar}-\text{H})$ stretching of phenyl group, characteristic two bands observed at 1519.1 and 544.3 due to $\nu(\text{C}-\text{NO}_2)$ and $\nu(\text{C}-\text{Cl})$. Bands at $(1690.9-1635.1)$, $(1602-1600.1)$ and $(850.1-834)\text{ cm}^{-1}$ due to $\text{CH}=\text{N}$, $\text{C}=\text{C}$, and out of plane bending for *p*-disubstituted benzene ring, respectively.

¹HNMR; [5]_a, ($\text{d}_6\text{-DMSO}$, ppm), A three pairs of doublets at $\delta 7.10-8.25$ ppm could be attributed to the twelve protons of the phenyl rings.

¹HNMR; [5]_b, ($\text{d}_6\text{-DMSO}$, ppm), A three pairs of doublets at $\delta 7.58-8.05$ ppm could be attributed to the twelve protons of the phenyl rings.

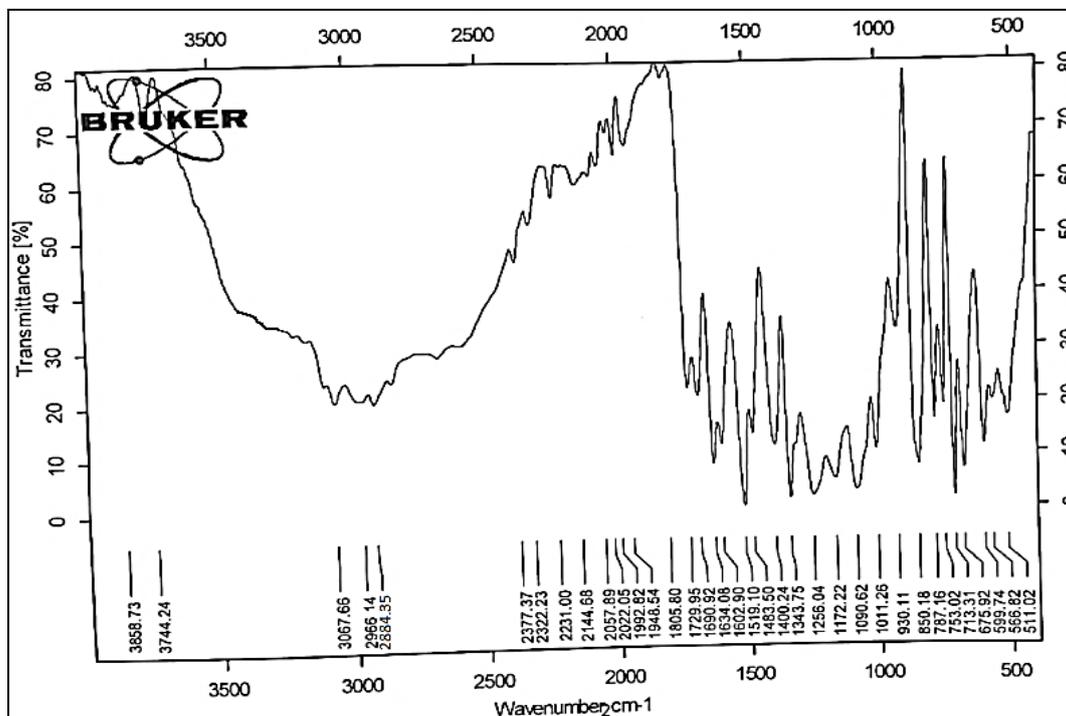


Figure 1. FTIR spectra of 3,3'-benzene-1,4-diylbis [5-(4-nitrophenyl)-1,2,4-oxadiazole] [5] a.

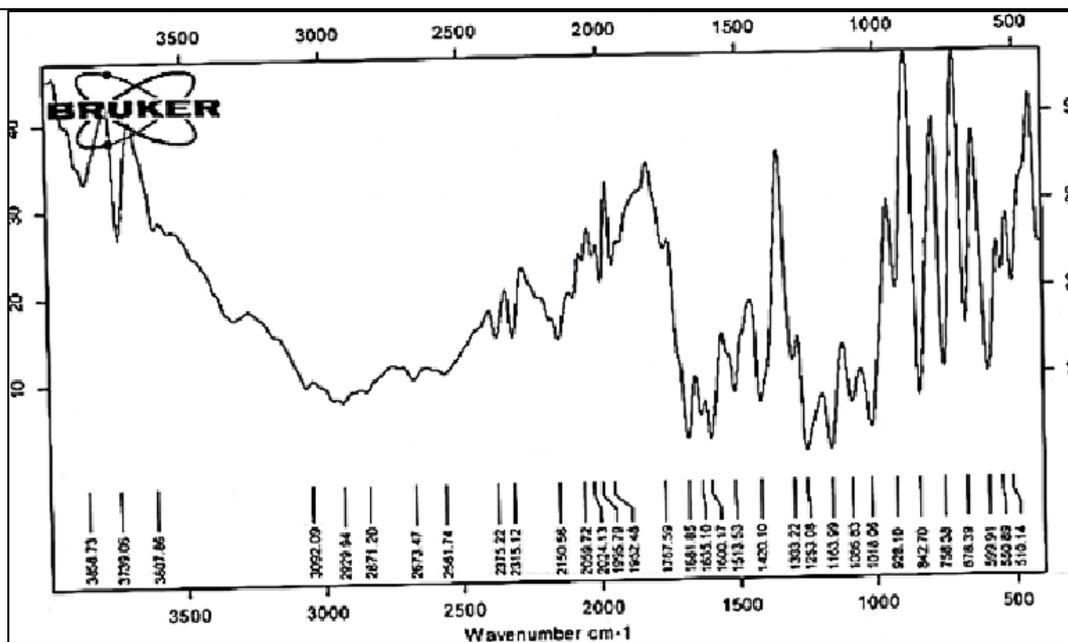


Figure 2. FTIR spectra of 3,3'-benzene-1,4-diylbis [5-(4-chlorophenyl)-1,2,4-oxadiazole] [5] b.

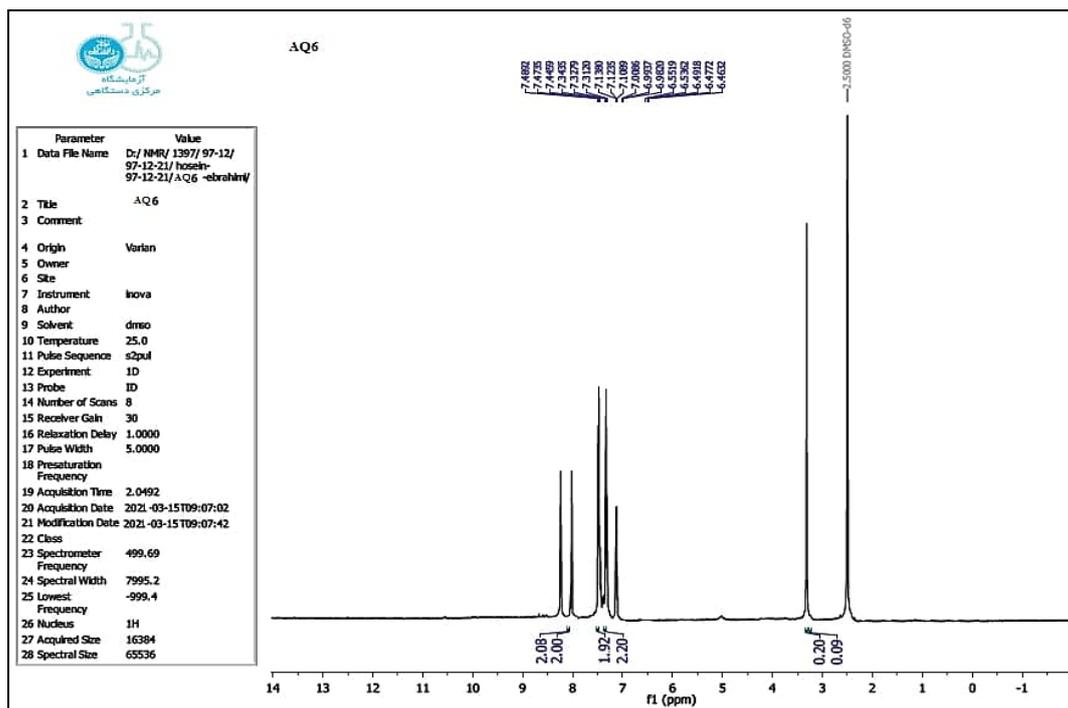


Figure 3. ¹H NMR spectra of 3,3'-benzene-1,4-diylbis [5-(4-nitrophenyl)-1,2,4-oxadiazole] [5] a.

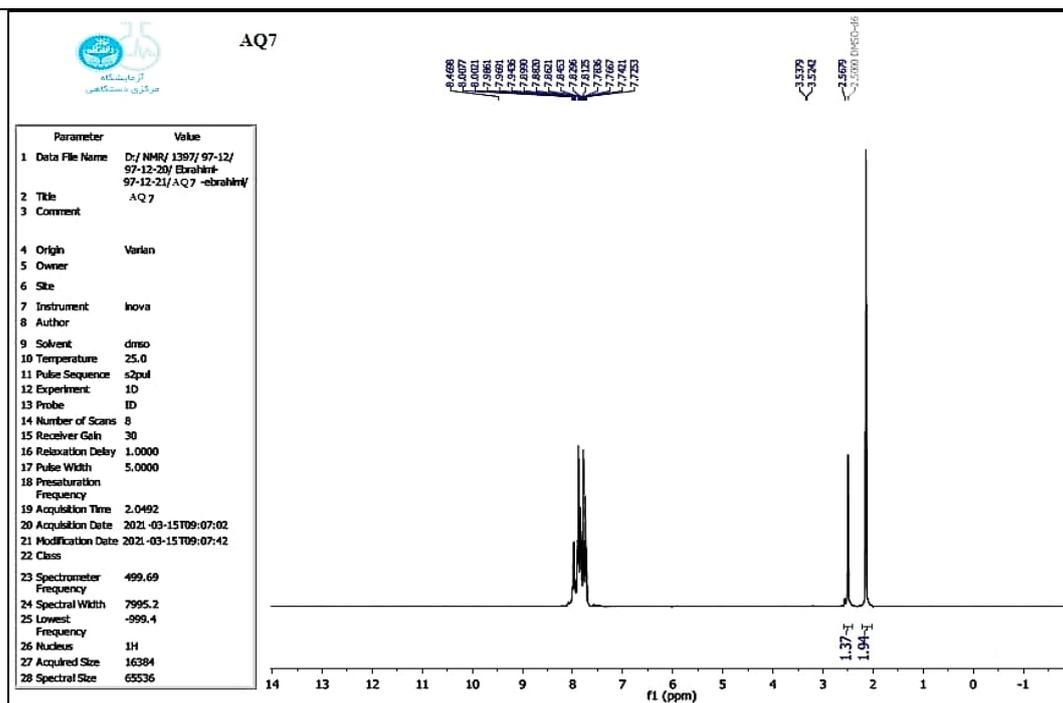


Figure 4. ¹H NMR spectra of 3,3'-benzene-1,4-diylbis [5-(4-chlorophenyl)-1,2,4-oxadiazole] [5] b.

4. Mesomorphic Properties

Phase transitions

The transition temperatures and phase sequences are summarized in Table 2. Phase identification was once primarily based on the optical textures, and the magnitude of isotropization on enthalpies is regular with the undertaking of every mesophase type, the use of the classification structures said by using Sackmann and Demus (1966) and Gray and Goodby (1984)^[10,11]. The differential scanning calorimeter (DSC) thermogram of compounds [5]a-b exhibit three peaks represent the (I) crystal-crystal, (II) crystal-mesophase and (III) crystal-isotropic transition, that means the compounds exhibit mesomorphic properties^[12].

Table 2. Melting points and type of transition for compounds [5]a-b.

Compound No.	Melting point °C	Transition
[5]a	72-80	C → N
	85-94	N → I
[5]b	124-132	C → S
	138-146	S → I

C = Crystal; S = Smectic; N = Nematic; I = isotropic.

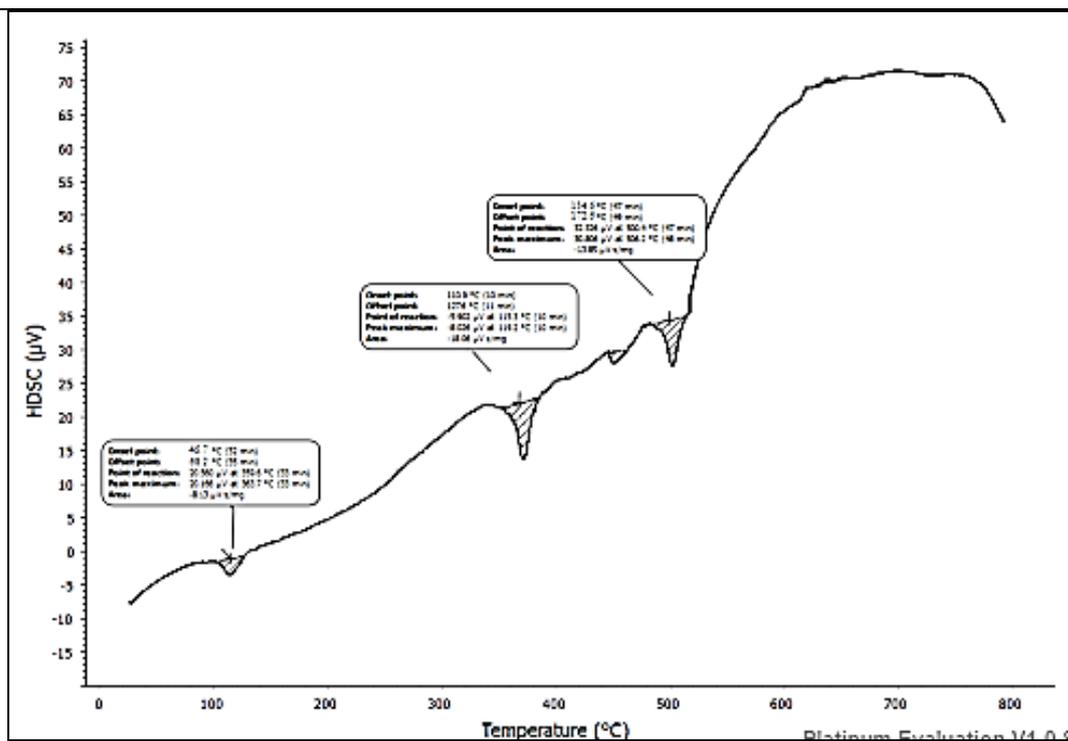


Figure 5. DSC of compound [5a,b] for the second heating and cooling cycles (scan rate 10 °C min⁻¹).

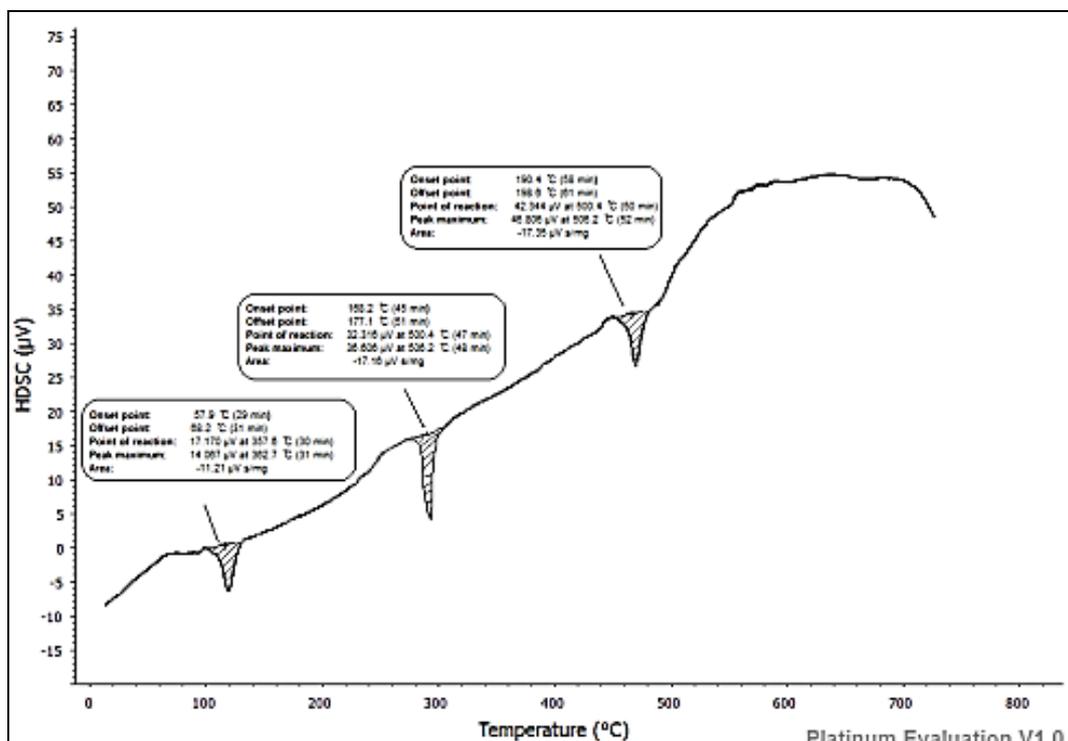


Figure 6. DSC of compound [5]b for the second heating and cooling cycles (scan rate 10 °C min⁻¹).

Phase structure

The synthesized compounds displayed interesting facts thermotropic properties and its melting conduct was once cautiously monitored by using polarizing optical microscope (POM) all through each heating and cooling

scans^[13]. The consequences from the POM remark had been established by way of the DSC measurements. Figures 7-8 shows the nematic texture for compounds [5] a-b.

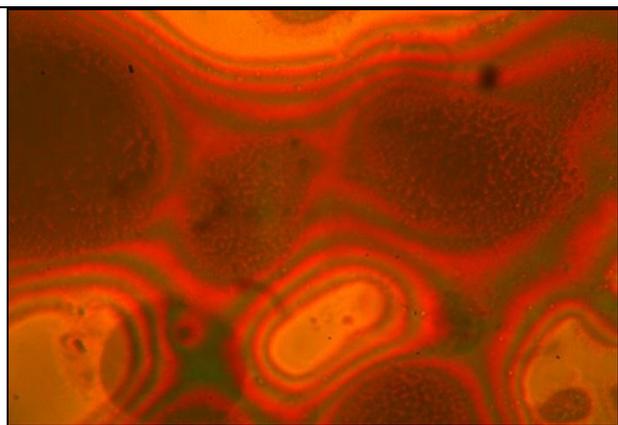


Figure 7. Nematic texture of model compound 3,3'-benzene-1,4-diylbis [5-(4-nitrophenyl)-1,2,4-oxadiazole] [5] b (magnification 10×10).

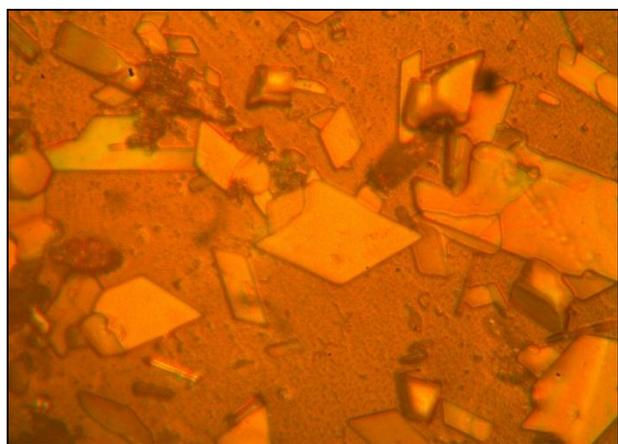


Figure 8. Smectic texture of model compound 3,3'-benzene-1,4-diylbis [5-(4-chlorophenyl)-1,2,4-oxadiazole] [5] b (magnification 10×10).

5. Conclusions

A new derivatives of 3,3'-benzene-1,4-diylbis [5-(4-substituted phenyl)-1,2,4-oxadiazole] [5]a-b have been synthesized and evaluated for their mesomorphic properties using POM and DSC.

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