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Solvent-Free Green Synthesis of Pyridazine Derivatives by Hydrothermal Method and Characterization of their Mesogenic Properties

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ABSTRACT

Hydrothermal synthesis of a homologous series of symmetrical pyridazine derivatives from 4-alkoxy benzaldehyde azines and maleic anhydride is described. The liquid crystalline properties of the synthesized compounds were investigated by Polarizing Optical Microscope (POM) and Differential Scanning Calorimetry (DSC). It is observed that most members of the series exhibited only Nematic phase (N); while others are non-mesogenic.

Keywords: Phase Transfer Catalysis, Azine, Maleic anhydride, [4+2] cycloaddition reaction, Hydrothermal / Solvothermal method, Nematic phase (N).

INTRODUCTION

Pyridazines have no household use, but are mostly found in research and industry as a building block for most of the complex organic compounds and in natural product synthesis. They are found in medicinally useful compounds such as Minaprine (antidepressant) [1], Gabazine [2] and Hydralazine [3] (control high blood pressure); and in a number of herbicides such as Cadralazine, Credazine, Pyridafol and Pyridate [4]. They also serve as ligands in the synthesis of several novel coordination complexes [5]. Several derivatives of 3-amino pyridazines act as selective GABA-A receptor antagonists and acetylcholinesterase inhibitors [6].

Pyridazines have also been incorporated into iptycene frameworks[7], compounds researched for conjugated polymer sensors [8], high mechanical performance polymers [9], gas absorption/storage [10], host-guest chemistry [11] and also in compounds researched for molecular-recognition properties [12]. Molecular organic electronic materials have advantages such as lower cost of production, ability to function on flexible substrates, high processibility etc., over inorganic semiconducting materials. Pyridazines also have the properties of conducting electricity. Pyrrolopyridazine [13] which is a derivative of pyridazine has fluorescent properties and is used in sensors, lasers and vulcanization of rubber. There are also pyridazine based liquid crystals [14, 15, 16]. Amongst the most technically important liquid crystals are the thermotropic nematic liquid crystals which are used as operating fluids in liquid crystal displays; and are usually composed of rigid, rod-like or disc-like molecules. Hence, the development of

liquid crystals having broad thermal range of nematic phase, high clearing points and appropriate melting points are significant.

Recently, there has been growing research interest associated with the solvent –free synthesis of molecular materials via solvothermal/hydrothermal method. Solvothermal/hydrothermal method involves hetero geneous chemical reaction, which occur at solid-liquid or solid-liquid-gaseous interfaces under conditions of high temperature and pressure. Solvothermal method is used for the synthesis of aryl esters from aromatic acids [17]. Thioesters and thioamides are synthesized from the corresponding amides and esters by solvothermal method using thiourea as a thionating agent [18]. Recently, thiadiazoles were synthesized from azines and sulphur by hydrothermal method [19].

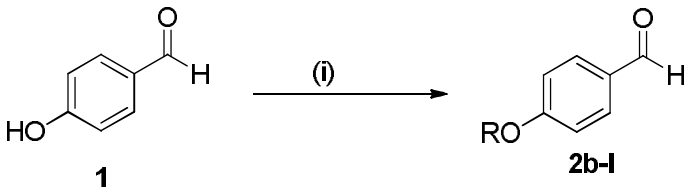
The usual synthesis of pyridazine derivatives is by reaction of hydrazine hydrate with 1, 4-dicarbonyl compounds, reaction of aryl glyoxals with β-keto esters or alkyl-2-cyanoacetates in the presence of hydrazine hydrate [20, 21] and by reaction of ketohydrazones containing α-methylene group with olefinic compounds using Chloramine T (CAT) and triethyl amine [22]. Azines exhibit interesting liquid crystalline [23], biological [24], optical [25] and conductive properties [26]. They are extensively used as substrates in the synthesis of substituted hydrazones and heterocyclic compounds [27]. However, their role as component/s in cycloaddition reaction/s is limited. In this paper, we are reporting the hydrothermal synthesis of a homologous series of symmetrical pyridazines from 4-alkoxy benzaldehyde azines and maleic anhydride by [4+2] cycloaddition reaction.

MATERIALS AND METHODS

All reagents and solvents were used without further purification from the suppliers. 4-hydroxy benzaldehyde and anisaldehyde were bought from Loba Chemie. Hydrazine dihydro chloride was brought from Loba Chemie. N-Propyl bromide, n-butyl bromide, n-pentyl bromide, n-hexyl bromide, n-heptyl bromide and n-octyl bromide were bought from Loba Chemie. 1-bromodecane, 1-bromododecane, 1-bromotetradecane and 1-bromohexadecane were bought from Alfa Aesar. Maleic anhydride was bought from Loba Chemie. Ethylacetate and n-hexane was bought from Rankem. Melting points were determined by a digital melting point apparatus in melting point capillaries and are uncorrected. The purity of the compounds were checked by TLC on silica gel G plates using ethyl acetate and n-hexane solvent system and the spots were identified by iodine chamber and U.V lamp was used as visualizing agent. IR spectra were recorded by using KBr pellets on a FTIR Spectrophotometer (Shimadzu 8400S, 4000-400 cm^{-1}).

Experimental Procedures

Synthesis of 4-alkoxybenzaldehyde: (Phase Transfer Catalysis).Typical procedure for the synthesis of 4-ethoxy benzaldehyde (2b): 4-hydroxybenzaldehyde (2.0g, 0.0164mol) was taken in a 100mL round bottomed flask containing about 25mL tetrahydrofuran (THF). Then ethyl bromide (2.64mL, 1.78g, 0.0164mol), tetra n-butyl ammonium bromide (0.52g, 0.00164mol) and powdered potassium hydroxide (1.37g, 0.0164mol) were added and stirred at room temperature for 10 -12 h. The mixture was then filtered, extracted into ethyl acetate (25mL), washed repeatedly with 10% sodium hydroxide solution (2*10mL) to remove traces of unreacted 4-hydroxybenzaldehyde, then with water, brine and finally dried over anhydrous sodium sulphate. The solvent was evaporated under reduced pressure to give 1.34g of 4-ethoxy benzaldehyde as a solid in about 54.69% yield. It was further purified by recrystalization using ethanol as the solvent.

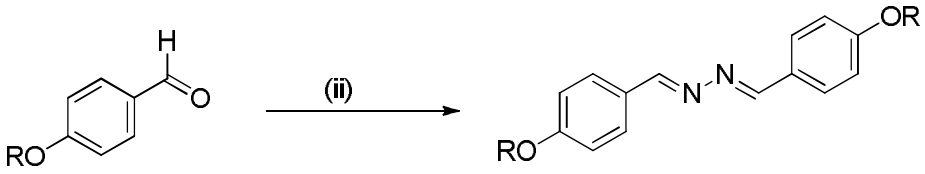


1 **2b-l**

(i) RBr, TBAB, THF, 10-12h, rt
R=C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15} C_8H_{17},$C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

Scheme 1

Synthesis of 4-alkoxybenzaldehyde azines: Typical procedure for the synthesis of 4-methoxybenzaldehyde azine (3a):



2a-l **3a-l**

(ii)$N_2H_4.2HCl$, aq. NH_3,

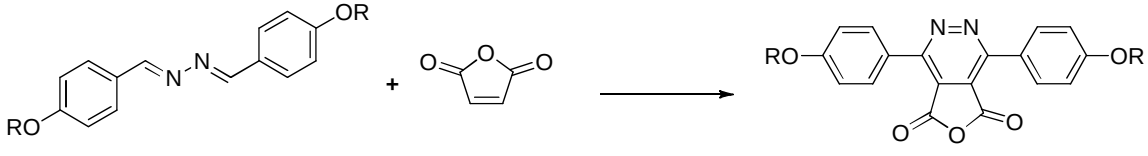
R= CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15} C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

Scheme 2

A mixture of 2.54g (0.0241mol) of hydrazine dihydro chloride, 15mL of distilled water and 3.4mL of concentrated aqueous ammonia was stirred for 10 min, then 2.7mL (2.41g,0.018mol) of 4-methoxy benzaldehyde was added dropwise and stirred for 2 h. The precipitated solid was collected by suction filtration and washed with 15mL distilled water to get the crude product of 4-methoxy benzylideneazine. The crude product was recrystalized from methanol to get 2.36g of 4-methoxy benzylidene azine as a yellow solid in about 46.23% yield.

Typical procedure for the Hydrothermal Synthesis of Pyridazine Derivative

Synthesis of 1, 4-bis(4-methoxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5a): 4-methoxybenzaldehyde azine (1.235g, 0.0046 mol) and maleic anhydride (0.451g, 0.0046mol) were taken in a Teflon liner. The Teflon liner was closed tightly and lowered inside a steel autoclave. The steel autoclave was kept inside a pre-heated oven at 170^0C and heated for about 18-38 h. Then, the autoclave was taken out of the oven and allowed to attain room temperature. The Teflon liner inside the steel autoclave was opened and the residue was extracted into 50mL ethyl acetate, washed twice with distilled water (2*15mL), brine (10mL), finally dried over anhydrous sodium sulphate and evaporated using a rotavapour to a dark reddish brown liquid. The crude dark reddish brown liquid was further purified by column chromatography using ethylacetate and petroleum ether and further was recrystalized from methanol to get the pure product (5a).



3a-l **4** **5a-l**

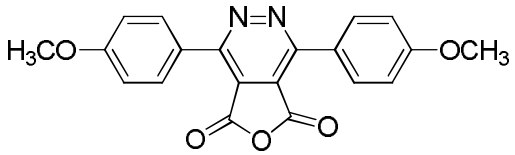
R=CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15} C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$

Scheme 3

RESULTS AND DISCUSSION

Spectral data

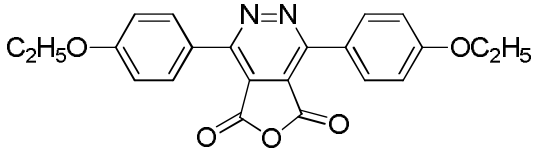
5a: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.49 (m, 4H, ArH), δ 6.98 (m, 4H, ArH), δ 3.80 (s, 6H, OCH_3). **^{13}C NMR (100MHz, $CDCl_3$):**164.92, 161.59, 156.71, 132.57, 129.76, 126.51, 115.54, 56.29. **Molecular formula:** $C_{20}H_{14}N_2O_5$.**Mass Spectra: Calculated=** 362.34 **Found=** 364.69[M+2]. **IR Analysis:** 3079cm^{-1}, 3065 cm^{-1} , 3040 cm^{-1} , 1875cm^{-1}, 1799cm^{-1}, 1582 cm^{-1},1447 cm^{-1} , 1305cm^{-1},1293 cm^{-1} ,1054 cm^{-1},1010 cm^{-1}, 987cm^{-1}, 937 cm^{-1}. **Elemental analysis: Calculated: C**=66.30, **H**=3.89, **O**=22.08, **N**=7.73, **Found: C**= 65.89, **H**= 3.78, **O**=21.78, **N**= 7.45. **Melting point=** 122-124^{0}C. **Yield=** 0.254g (14.03%, pale brown solid).



5a

1,4-bis(4-methoxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5a)

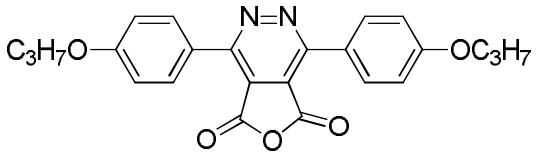
5b: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.51 (m, 4H, ArH), δ 7.07 (m, 4H, ArH), δ 4.11 (q, 4H), δ 1.46(t, 6H). **^{13}C NMR (100MHz, $CDCl_3$):**164.12, 160.99, 156.31, 131.97, 129.76, 125.81, 115.44, 65.03, 15.06. **Molecular formula:** $C_{22}H_{18}N_2O_5$.**Mass Spectra: Calculated=** 390.12, **Found=** 391.29[M+1]. **IR Analysis:** 3072cm^{-1}, 3063 cm^{-1} , 3046 cm^{-1} , 1881cm^{-1}, 1801cm^{-1}, 1580 cm^{-1} , 1449 cm^{-1},1300cm^{-1},1297 cm^{-1} ,1053 cm^{-1},1001 cm^{-1}, 986cm^{-1}, 934 cm^{-1}. **Elemental analysis: Calculated: C**= 67.69, **H**= 4.65, **O**=20.49, **N**=7.18 **Found: C**= 67.29, **H**= 4.38, **O**=20.08, **N**= 7.05 **Melting point=** 122-124^{0}C. **Yield=** 0.196g (14.45%, pale brown solid).



5b

1,4-bis(4-ethoxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5b)

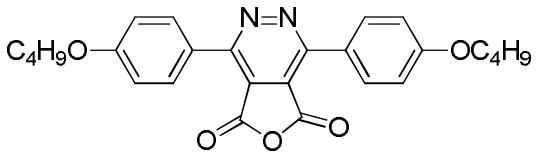
5c: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.50 (m, 4H, ArH), δ 7.07 (m, 4H, ArH), δ 3.98 (t, 4H) δ 1.83(m, 4H), δ 1.14 (t,6H). **^{13}C NMR (100MHz, $CDCl_3$):**163.12, 161.09, 157.11, 130.99, 128.46, 125.51, 114.54, 68.89, 23.07, 11.55. **Molecular formula:** $C_{24}H_{22}N_2O_5$..**Mass Spectra: Calculated=** 418.41, **Found=** 419.04 [M+1]. **IR Analysis:** 3071cm^{-1}, 3061 cm^{-1} , 3049 cm^{-1} , 1881cm^{-1}, 1729cm^{-1}, 1582 cm^{-1} , 1443 cm^{-1}, 1315cm^{-1}, 1299 cm^{-1} ,1051 cm^{-1} , 1015 cm^{-1} , 981cm^{-1} ,936cm^{-1}. **Elemental analysis: Calculated: C**=68.89, **H**= 5.30, **O**=19.12, **N**=6.69 **Found: C**= 67.89, **H**= 5.18, **O**= 18.68, **N**= 6.55 **Melting point=** 128-130^{0}C. **Yield=** 0.419g (20.39%, pale brown solid).



5c

1, 4-bis(4-propoxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5c)

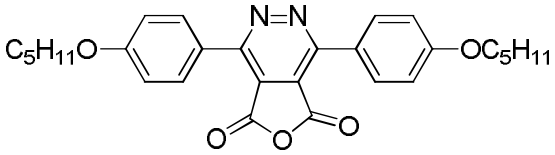
5d: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.48 (m, 4H, ArH), δ 7.05 (m, 4H, ArH), δ4.02(t,4H), δ1.79 (m, 4H), δ1.45(m, 4H), δ0.98 (t, 6H) **^{13}C NMR (100MHz, $CDCl_3$):**162.19, 161.41, 152.51,131.03, 128.71,125.05, 113.91, 68.59, 32.26, 19.07, 15.06**. Molecular formula:** $C_{26}H_{26}N_2O_5$. **Mass Spectra: Calculated=** 446.21, **Found=** 446.77[M^+]. **IR Analysis:** 3069cm^{-1}, 3059 cm^{-1} , 3041 cm^{-1} , 1870cm^{-1}, 1789cm^{-1}, 1582 cm^{-1} , 1440 cm^{-1}, 1301cm^{-1}, 1293 cm^{-1}, 1049 cm^{-1} , 1011 cm^{-1}, 980cm^{-1}, 940 cm^{-1}. **Elemental Analysis: Calculated: C**=69.94, **H=** 5.87, **O=** 17.92, **N**=6.27 **Found: C**=68.56**, H=** 5.57**, O=** 17.14**, N=** 5.97**, Melting point=** 131-132^{0}C. **Yield=** 0.399g (29.04%, pale brown solid).



5d

1,4-bis(4-butoxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5d)

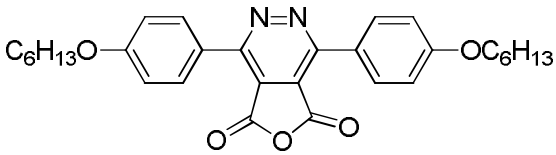
5e: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.49 (m, 4H, ArH), δ 7.09 (m, 4H, ArH), δ3.82 (t, 4H), δ1.79 (m, 4H), δ1.44(m, 8H), δ0.95 (m, 6H). **^{13}C NMR (100MHz, $CDCl_3$):** 163.91, 162.19, 157.01, 131.99, 128.97, 125.50, 116.02, 67.99, 29.45, 28.55, 23.05, 14.25. **Molecular formula:** $C_{28}H_{30}N_2O_5$.**Mass Spectra: Calculated=** 474.21, **Found=**475.73[M+1]. **IR Analysis=** 3081cm^{-1}, 3067 cm^{-1} , 3040 cm^{-1} , 1871cm^{-1}, 1792cm^{-1}, 1582 cm^{-1} , 1447 cm^{-1} , 1305cm^{-1},1293 cm^{-1} ,1049 cm^{-1} , 1017 cm^{-1} , 987cm^{-1}, 937 cm^{-1}. **Elemental Analysis: Calculated: C**= 70.87, **H=** 6.37, **N=** 5.90 **O=** 16.86 **Found: C**= 69.86**, H=** 6.31**, N=** 5.74**, O=** 15.74**. Melting Point=** 127-129^{0}C.**Yield=** 0.296g (15.33%, pale brown solid).



5e

1, 4-bis(4-pentyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5e)

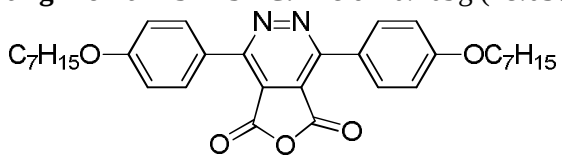
5f: ^{1}H NMR (400MHz, $CDCl_3$): δ 7.51 (m, 4H, ArH), δ 7.04 (m, 4H, ArH), δ4.00(t, 4H), δ1.77(m, 4H), δ1.46(m, 4H), δ1.29(m, 8H), δ0.88(m, 6H).**^{13}C NMR (100MHz, $CDCl_3$):**162.99, 160.95, 156.00, 131.58, 128.17, 127.53, 113.34, 69.10, 32.03, 29.55, 25.77, 22.79, 13.78. **Molecular formula:** $C_{30}H_{34}N_2O_5$. **Mass Spectra: Calculated=** 502.24, **Found=** 503.78 [M+1]. **IR Analysis=**3072cm^{-1}, 3069 cm^{-1} , 3042 cm^{-1} , 1875cm^{-1}, 1789cm^{-1}, 1582 cm^{-1} , 1442 cm^{-1} , 1301cm^{-1},1293 cm^{-1} ,1054 cm^{-1},1010 cm^{-1}, 981cm^{-1} , 939 cm^{-1}. **Elemental Analysis: Calculated: C**=71.69 **H**=6.82, **O=** 15.92 **N**=5.57**, Found: C=** 70.86**, H=** 6.56**, O=** 15.34, **N=** 5.34**.Melting Point=** 135-137^{0}C.**Yield=** 0.185g (17.51%, pale brown solid).



5f

1,4-bis(4-hexyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5f)

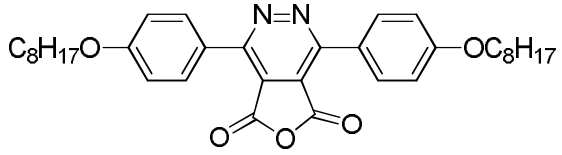
5g: ^{1}H NMR (400MHz, CDCl$_3$): δ 7.47 (m, 4H, ArH), δ 7.06 (m, 4H, ArH), δ 4.02 (t, 4H), δ 1.73 (m, 4H), δ 1.29 (m, 16H), δ 0.85 (m, 6H). **^{13}C NMR (100MHz, CDCl$_3$):**162.99, 162.05, 156.66, 132.51, 128.77, 123.51, 116.15, 67.99, 31.56, 29.91, 29.56, 26.07, 23.05, 14.55. **Molecular formula:** $C_{32}H_{38}N_2O_5$. **Mass Spectra: Calculated=** 530.278**, Found=** 532.892 [M+2]**. IR Analysis=**3071cm^{-1}, 3064 cm^{-1} , 3040 cm^{-1} , 1879cm^{-1}, 1791cm^{-1}, 1586 cm^{-1} , 1449 cm^{-1} , 1301cm^{-1},1293 cm^{-1},1059 cm^{-1},1013 cm^{-1}, 987cm^{-1}, 931 cm^{-1}. **Elemental Analysis: Calculated: C=** 72.43 **H=** 7.22 **O=** 15.08 **N=** 5.28, **Found: C=** 72.17**, H=** 6.98**, O=** 14.94, **N=** 5.06**. Melting Point=** 132-134^{0}C**. Yield=** 0.209g (18.05%, pale brown solid).



5g

1,4-bis(4-heptyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5g)

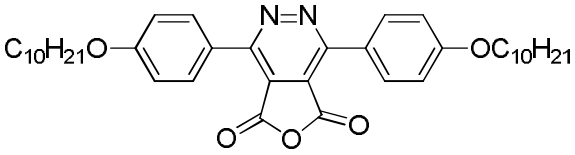
5h: ^{1}H NMR (400MHz, CDCl$_3$): δ7.48 (m, 4H, ArH), δ7.07 (m,4H, ArH), δ4.01 (t, 4H), 1.82 (m,4H),1.39 (m, 4H), 1.29 (m, 16H), 0.89 (m, 6H). **^{13}C NMR (100MHz, CDCl$_3$):**162.99, 161.51, 155.99, 132.05, 129.17,126.25, 114.55, 68.37,31.99, 29.64, 29.44, 26.04, 25.76, 22.71, 14.12. **Molecular formula:** $C_{34}H_{42}N_2O_5$. **Mass Spectra: Calculated=** 558.30**, Found=** 559.29 [M+1]**. Elemental Analysis: Calculated: C=** 73.09 **H=** 7.58 **O=** 14.32 **N=** 5.01, **Found: C=** 72.67**, H=** 6.98**, N=** 4.76**, O=** 13.94**. IR Analysis=**3078cm^{-1}, 3063 cm^{-1} , 3038 cm^{-1} , 1868cm^{-1}, 1789cm^{-1}, 1587 cm^{-1} , 1447 cm^{-1} , 1305cm^{-1},1293 cm^{-1} ,1051 cm^{-1} , 1009 cm^{-1} , 989cm^{-1}, 941 cm^{-1}. **Melting Point=** 137-139^{0}C**. Yield=** 0.180g (14.47%, pale brown solid).



5h

1,4-bis(4-octyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione(5h)

5i: ^{1}H NMR (400MHz, CDCl$_3$): δ 7.51 (m, 4H, ArH), δ 7.07 (m,4H, ArH), 4.02(t, 4H),1.75 (m,4H), 1.38(m,4H), 1.24 (m,24H) ,0.89(m, 6H). **^{13}C NMR (100MHz, CDCl$_3$):**164.03, 160.58, 157.07, 132.15, 128.71,126.52, 115.52, 68.15, 31.75, 29.88, 29.61, 29.39, 29.14, 25.99, 24.13, 22.65, 14.05. **Molecular Formula:** $C_{38}H_{50}N_2O_5$. **Mass Spectra: Calculated=** 614.81, **Found=** 615.09 [M+1]. **IR Analysis=** 3075cm^{-1}, 3069 cm^{-1} , 3046 cm^{-1} , 1875cm^{-1}, 1802cm^{-1}, 1582 cm^{-1} , 1440 cm^{-1} , 1315cm^{-1},1293 cm^{-1} ,1050 cm^{-1} , 1010 cm^{-1} , 987cm^{-1}, 939 cm^{-1}. **Elemental Analysis: Calculated: C=**74.23, **H=**8.20, **O=** 13.01, **N=**4.56**. Found: C=** 73.93, **H=** 8.05, **O=** 12.87, **N=** 4.44. **Melting Point=** 136-138^{0}C. **Yield=** 0.334g (28.67%, pale brown solid).

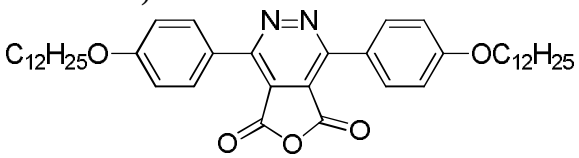


5i

1,4-bis(4-decyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione(5i)

5j: ^{1}H NMR (400MHz, CDCl$_3$): δ 7.50 (m, 4H, ArH), δ 7.05 (m, 4H, ArH), 3.98 (t, 4H),1.72(m, 4H), 1.38(m, 4H),1.22 (m,32H), 0.88(m,6H).**^{13}C NMR (100MHz, CDCl$_3$):**164.19, 161.05, 156.37, 132.54,

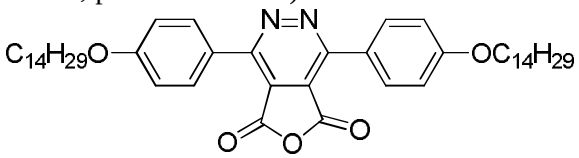
129.07, 126.45, 115.09, 67.66, 31.08, 29.64, 29.51, 29.45, 29.33, 29.21, 29.04, 28.87, 26.54, 22.49, 13.78. **Molecular formula:** $C_{42}H_{58}N_2O_5$.**Mass Spectra: Calculated=** 670.92, **Found=** 671.13 [M+1].**IR Analysis:** 3081cm^{-1}, 3070 cm^{-1} , 3038 cm^{-1} , 1870cm^{-1}, 1794cm^{-1}, 1587 cm^{-1} , 1447 cm^{-1} , 1309cm^{-1},1299 cm^{-1} ,1054 cm^{-1} , 1011 cm^{-1} , 987cm^{-1}, 944 cm^{-1}.**Melting point=** 139-141^{0}C. **Elemental Analysis: Calculated: C**=75.19, **H=** 8.71, **O**=11.92, **N**=4.18**, Found: C=** 74.67**, H=** 7.95**, O=** 11.23**, N=** 3.89**. Yield=**0.309g (20.58%, pale brown solid).



5j

1, 4-bis(4-dodecyloxyphenyl) furo[3,4-d]pyridazine-5,7-dione (5j)

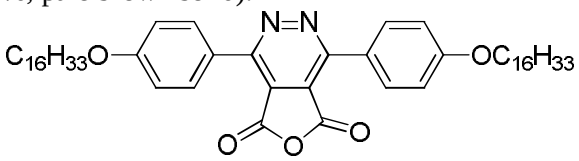
5k: ^{1}H NMR (400MHz, CDCl$_3$): δ 7.55 (m, 4H, ArH), δ 7.10 (m, 4H, ArH), δ4.05(t, 4H), δ 1.69(m,4H), δ1.49(m, 4H), δ1.308(m, 40H), δ 1.09(m, 6H). **^{13}C NMR (100MHz, CDCl$_3$):**164.21, 162.01,155.17 ,131.19 ,130.90, 126.25, 115.59, 67.95, 32.73, 29.95, 29.76, 29.55, 29.41, 29.32, 28.79, 28.63, 28.52, 26.88, 26.07, 22.54, 14.15. **Mol. Formula:** $C_{46}H_{66}N_2O_5$. **Mass Spectra: Calculated:** 726.02**, Found:** 728.78[M+2]. **IR Analysis:** 3073cm^{-1}, 3065 cm^{-1} , 3047 cm^{-1} , 1879cm^{-1}, 1792cm^{-1}, 1579 cm^{-1} , 1450 cm^{-1} , 1305cm^{-1}, 1213 cm^{-1} ,1054 cm^{-1} , 1010 cm^{-1} , 988cm^{-1} ,935 cm^{-1}. **Elemental Analysis: Calculated: C**=75.99, **H**=9.15, **O=** 11.00, **N**=3.85. **Found: C=** 74.67**, H=** 8.75**, O=** 10.73**, N=** 3.68**. Melting point=** 140-142^{0}C. **Yield=** 0.268g (16.77%, pale brown solid).



5k

1, 4-bis(4-tetradecyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5k)

5l: ^{1}H NMR (400MHz, CDCl$_3$): δ 7.49(m,4H, ArH), δ 7.05 (m, 4H, ArH), δ 3.98 (t, 4H), δ 1.73 (m, 4H), δ1.56 (m,52H), δ 1.22 (m, 6H).**^{13}C NMR (100MHz, CDCl$_3$):**164.10, 161.12, 156.57, 131.95, 129.00, 127.05, 114.81, 67.74, 31.96, 29.92, 29.87, 29.64, 29.51, 29.40, 29.32, 29.22, 29.15, 26.88, 26.54, 25.77, 25.49, 22.66, 14.01. **Mol. Formula:** $C_{50}H_{74}N_2O_5$. **Mass Spectra: Calculated:** 782.56, **Found:** 783.69[M+1]. **IR Analysis:** 3074cm^{-1}, 3061 cm^{-1} , 3046 cm^{-1} , 1871cm^{-1}, 1792cm^{-1}, 1586 cm^{-1} , 1443 cm^{-1} , 1305cm^{-1},1293 cm^{-1} ,1058 cm^{-1} , 1014 cm^{-1} , 989cm^{-1}, 939 cm^{-1}. **Elemental Analysis: Calculated: C**= 76.68, **H**=9.52 **O**=10.21, **N**=3.58. **Found: C=** 76.56**, H=** 8.85 **O=** 9.56, **N=** 3.45. **Melting Point:** 141-143^{0}C. **Yield=** 0.308g (26.21%, pale brown solid).



5l

1, 4-bis(4-hexadecyloxyphenyl)furo[3,4-d]pyridazine-5,7-dione (5l)

Liquid crystalline phases of pyridazine liquid crystals: The mesomorphic properties of all the synthesized symmetrical pyridazines was investigated by Polarizing Optical Microscope (POM) fixed with a controllable hot stage, and they were found to be in good agreement with the Differential Scanning

Calorimetry (DSC) transition temperatures with scanning rate at 5^0C min^{-1}. The results are listed in Table 1.

Table 1

Compound No	Phase transition temperature (0^0C) and associated enthalpy changes (J/g) Cr=Crystalline, N=Nematic, I=Isotropic	
	Heating	**Cooling**
5c	Cr51.9(4.12) N73.3(1.45)I	I72.6(-1.6)N34.4(-3.2)Cr
5d	Cr52.9(4.44)N78.4(1.56)I	I77.3(- 1.34)N38.9(-3.7)Cr
5e	Cr68.5(4.9)N83.5(1.03)I	I78.2(-0.9)N44.4(-4.1)Cr
5f	Cr72.1(6.3)N91.8(0.9)I	I89.4(-0.7)N53.2(-4.3)Cr
5g	Cr43.9(19.5)N97.9(2.4)I	I95.3(-1.8)N22.5(-18.3)Cr
5h	Cr52.9(20.4)N132.9(1.6)I	I133.7(-1.1)N22.5(-18.9)Cr
5i	Cr53.5(24.4)N80.5(2.3)I	I79.9(-2.1)N21.4(-22.4)Cr
5j	Cr55.7(10.6)N113.5(1.5)I	I115.3(-2.1)N40.5(-12.3)Cr
5k	Cr49.3(14.9)N119.1(2.7)I	I120.3(-2.4)N36.4(-13.1)Cr
5l	Cr45.2(16.5)N125.9(3.5)I	I123.3(-3.2)N40.0(-11.3)Cr

The POM observations revealed that all of the synthesized symmetrical 1,4-bis(4-alkoxyphenyl) furo[3,4-d] pyridazine-5,7-dione (**5c-l**) were enantiotropic liquid crystals. The compounds 5a and 5b with methoxy and ethoxy terminal groups are non-mesogenic.

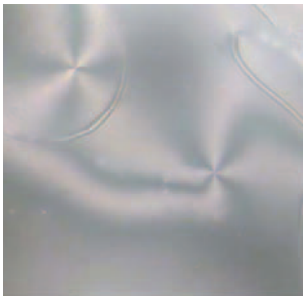


Fig 1

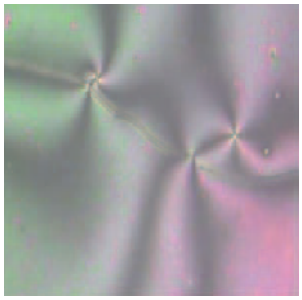


Fig 2

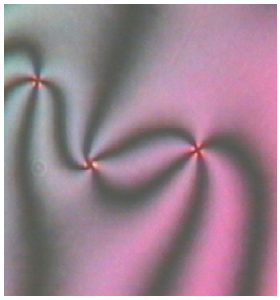
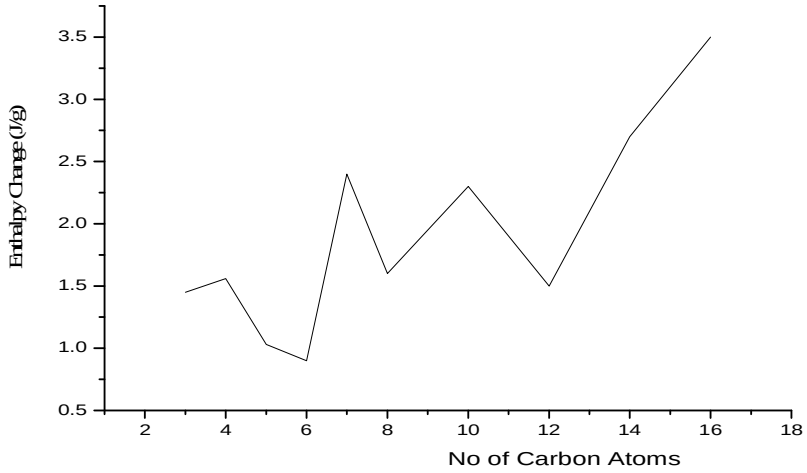


Fig 3

Figures 1 and 2 show the Nematic Phase textures of Compound 5d; while **Fig 3** shows the Nematic Phase texture of Compound 5g.All the images were observed under Polarizing Optical Microscope in 125x magnification.

5c, 5d, 5e, 5f, 5g, 5h,5i, 5j, 5k and 5l showed similar mesogenic properties. They exhibited only Schelieren texture of the nematic phase as shown by figures **1**, **2** and **3**; observed between the crossed polarizers . The nematic phase in these compounds were characterized first by the formation of small droplet textures, and then by the formation of schelieren textures. In conclusion, the target compounds (5c-l) with propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, dodecyl, and tetradecyl and hexadecyl terminal groups exhibited moderate clearing points and broad thermal range of nematic phase. Observed enthalpy changes of Nematic phase- Isotropic phase transitions show odd-even effect, which is routinely reported for many Nematic phase compounds as shown by the graph below.



APPLICATIONS

The hydrothermal method of pyridazine derivatives has advantages such as good product yields, eco-friendly benign reaction conditions and easy isolation of products.

CONCLUSIONS

A solvent-free, clean and efficient method has been developed for the synthesis of 1,4-bis(4-alkoxyphenyl)furo[3,4-d]pyridazine-5,7-diones from azines and maleic anhydride by [4+2] cycloaddition reaction. All the synthesized compounds were characterized by elemental, ^{1}H and ^{13}C NMR, Mass and FTIR analysis. Also, the liquid crystalline properties of all the synthesized compounds were investigated by DSC and POM studies. The observed ΔH value shows odd-even effect in this series.

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