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# Liquid Crystalline Properties of 3-[4-(4′-Alkoxybenzoyloxybenzylidene) amino]-1,2,4-triazines: Synthesis and Characterization

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*A new series of 3-[4-(4′-alkoxybenzoyloxybenzylidene)amino]-1,2,4-triazines,* $C_3H_2N_3N{=}CHC_6H_4OCOC_6H_4OC_mH_{2m+1}$ *where* $m = 6, 7, 8, 9, 10, 11, 12, 14$, *and 16 have been synthesized. These compounds have been characterized by elemental analyses, FT-IR, UV-visible,* $^1H$, *and* $^{13}C$ *NMR spectroscopy. Mesomorphic properties of these compounds were studied by differential scanning calorimetry and polarizing microscopy. The mesomorphic nature of these compounds is dependent on the alkoxy chain length. The compounds* ($m = 6, 7$) *do not exhibit mesomorphism while the compounds* ($m = 8, 9, 11, 12, 14$) *show a monotropic nematic mesophase in cooling cycle. The 3-[4-(4′-decyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine displays an enantiotropic nematic mesophase and the hexadecyloxy compound exhibits the smectic A mesophase.*

**Keywords** Differential scanning calorimetry; enantiotropic nematic mesophase; monotropic nematic mesophase; polarizing microscopy; smectic A mesophase

## 1. Introduction

1,3,5-Triazine and its derivatives are an interesting class of compounds which show various biological properties such as antimicrobial and antiviral [1,2], and antiseptic [3–5] properties. There have been considerable reports on the synthesis and characterization of compounds containing 1,3,5-triazine unit [6] owing to their liquid crystalline and non linear optical properties as well as their applications in other fields [7–19]. The triazine system has been used as a core of liquid crystalline materials [14,15] and for the development of organic light emitting diodes OLEDS [20–23].

Lee and Yamamoto [24] reported a series of 2,4,6-triphenyl-1,3,5-triazine derivatives having long alkoxy side chains. These compounds behave as liquid crystalline materials and show quantum yields higher than 50% in photoluminescence. Salisu [25] reported that 2,4,6-tris-[4-(4-acetylphenyl azo)phenoxyalkoxyethyleneamino]-1,

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3,5-triazines showing enantiotropic liquid crystal property exhibited smectic mesophase in both heating and cooling cycles.

Maly et al. [26] reported a new series of supramolecular columnar liquid crystalline materials based on self-association of diaminotriazines. These compounds appear to form disc-like hydrogen-bonded rosettes that are able to form columnar mesophases by stacking of an extended aromatic core.

Goldman and Nordsieck [27] reported columnar liquid crystalline phase of 2,4,6-triarylamino-1,3,5-triazines substituted with six long peripheral alkoxy chains. Cowling et al. [28] reported synthesis and properties of new liquid crystals containing 1,2,4-triazine unit which serves as intermediates for the synthesis of new mesomorphic pyridines. Frolova and coworkers [29] reported new mesogenic discotic triazine based esters which yield a low temperature monotropic columnar mesophase.

The literature survey reveals that relatively less work has been reported on the synthesis, characterization, and mesomorphic properties of ester based asymmetric triazines compared to symmetrical ones. The reports on 1,2,4-triazine containing liquid crystals are, however, relatively rare, which might be due to the direct result of their high reactivity and, therefore, low stability. The high reactivity makes them interesting as building blocks for further modification. In view of the above observations the synthesis, characterization, and the mesomorphic properties of a new series of ester-based 3-[4-(4′-alkoxybenzoyloxybenzylideneamino]-1,2,4-triazines are reported in this article.

## 2. Experimental

### *Materials*

3-Amino-1,2,4-triazine, 1-bromoalkanes, 4-hydroxybenzoic acid, 4-hydroxy benzaldehyde (all Aldrich), thionyl chloride, and pyridine (Qualigens) were used as received. All other solvents and reagents were purchased commercially and used after further purification.

### *Measurements*

Elemental analyses were performed on CE-440 Exeter Analytical CHN analyzer. IR spectra (4000–100 cm$^{-1}$) were recorded on Varian 3100 FT-IR Excalibur spectrophotometer. $^1$H and $^{13}$C NMR spectra were obtained by using a JEOL FT NMR AL 300 MHz spectrometer using tetramethylsilane as internal standard. Electronic spectra were recorded on UV-1700 Pharma Spec Shimadzu UV-Visible spectrophotometer. DSC thermograms were recorded by Mettler Toledo TC 15 TA differential scanning calorimeter at the rate of 10.0 K min$^{-1}$ under nitrogen atmosphere using spec pure grade indium as standard by taking samples in close lid aluminum pans. The transition temperatures from DSC have been determined with accuracy of ±0.1 K. The mesophase type was assigned by visual comparison with known phase standards using HT-30.01 NTT 268 LOMO polarizing optical microscope fitted with a hot stage with temperature accuracy of 0.1 K.

### *Synthesis of Compounds*

*Preparation of 4-octyloxybenzoic Acid* ***2***. To a solution containing 4-hydroxybenzoic acid **(1)** (2.76 g, 20 mmol), in dry ethanol (50 ml) and KOH (3.36 g, 60 mmol) in dry ethanol (20 ml), 1-bromooctane (3.47 ml, 20 mmol) was added in drops with continuous stirring. The reaction mixture was refluxed for ~14 h under dry atmosphere and allowed to cool to room temperature. The solid alkoxy potassium salt was separated and treated with dilute HCl until the pH of the reaction mixture became ~2. The white solid product was filtered off, washed with water and recrystallized successively from glacial acetic acid and toluene. Yield: 74%. IR (KBr, $cm^{-1}$): 3420 (OH), 2926, 2851 (aliphatic C–H), 1688 (C=O), 1606, 1513 (Ph), 1317, 1296, 1254 (OPh). 1 H NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 11.90 (s, 1 H, –OH), 8.06–8.03 (d, 2 H, ArH), 6.94–6.91 (d, 2 H, ArH), 4.04–4.00 (t, 2 H, $-OCH_2$), 1.85–1.29 (m, 12 H, $-[CH_2]_n$), 0.89–0.86 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 171.9, 163.6, 132.3, 121.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 68.2 ($-OCH_2$), 31.7, 29.3, 29.2, 29.0, 25.9, 22.6, 14.0 ($CH_3$).

*Preparation of 4-(4′-Octyloxybenzoyloxy)benzaldehyde **3**.* 4-Octyloxybenzoic acid (1.25 g, 5 mmol) dissolved in dry chloroform (50 ml) was heated under reflux with thionyl chloride (0.57 ml, 8 mmol) for 8 h. The solvent was removed under reduced pressure to give a yellow oil. It was further treated with a solution of (0.61 g, 5 mmol) of 4-hydroxy benzaldehyde in dry chloroform (50 ml) in presence of 2–3 drops of pyridine. The mixture was then refluxed for 9 h. A light yellow solution was obtained. It was washed with water (55 ml), dried over anhydrous $MgSO_4$, and then concentrated to form white crystals of 4-(4′-octyloxybenzoyloxy) benzaldehyde. Yield: 60%, IR (KBr, $cm^{-1}$): 2923, 2853 (aliphatic C–H), 1733 (ester, C=O), 1698 (aldehyde C=O), 1605, 1511 (Ph), 1308, 1260 (OPh). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.02 (s, 1 H, CHO), 8.15–6.88 (m, 8 H, ArH), 4.07–3.97 (m, 2H, $-OCH_2$), 1.81–1.27 (m, 12 H, $-[CH_2]_n$), 0.90–0.86 (t, 3 H, $-CH_3$).

All the other members of the series were prepared following the above procedure.

*Synthesis of 3-[4-(4′-Octyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine **4c**.* A mixture of 3-amino-1,2,4-triazine (0.48 g, 5 mmol) and 4-(4′-octyloxy benzoyloxy) benzaldehyde (1.77 g, 5 mmol) in 50 ml of methanol containing 3–4 drops of glacial acetic acid was heated under reflux for 7 h. A yellow solution thus obtained was evaporated under reduced pressure to yield reddish brown crystals. This product was washed with water and recrystallized from chloroform.

All the other homologous members of the series were prepared in a similar manner. Their IR, analytical, and NMR data are summarized as follows.

*3-[4-(4′-Hexyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{23}H_{24}N_4O_3$ (**4a**).* Yield 67%. IR (KBr, $cm^{-1}$): 2927, 2857 (aliphatic C–H), 1732 (ester C=O), 1699 (CH=N), 1602 (Ph), 1306 (OPh), 1263 (triazine ring C=N conjugated), 1062 (triazine ring C–N non-conjugated), 846 (triazine ring out of plane C–H aromatic bend). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, –CH=N), 8.14–8.01 (q, 2 H, heterocyclic Ar*H*), 7.97–6.90 (m, 8 H, Ar*H*), 4.00–3.99 (t, 2 H, $-OCH_2$), 1.85–1.25 (m, 8 H, $-[CH_2]_n$), 0.91 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 191.0, 171.2, 164.2, 163.8 (–CH=N), 163.4, 155.8, 150.3, 141.1, 133.8, 132.4, 132.1, 131.2, 127.8, 122.5, 121.6, 120.7, 114.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 68.3 ($OCH_2$), 68.2, 31.5, 29.6, 29.0, 25.6, 22.5, 14.0 ($CH_3$). UV-visible ($CHCl_3$): $\lambda_{max} = 272$ nm. Elemental analyses: calculated (for $C_{23}H_{24}N_4O_3$), C, 68.30; H, 5.98; N, 13.85%, found, C, 68.21; H, 5.88; N, 13.67%.

*3-[4-(4′-Heptyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{24}H_{26}N_4O_3$ (**4b**).* Yield 62%. IR (KBr, $cm^{-1}$): 2928, 2855 (aliphatic C−H), 1733 (ester C=O), 1696 (CH=N), 1604 (Ph), 1306 (OPh), 1260 (triazine ring C=N conjugated), 1064 (triazine ring C–N non-conjugated), 844 (triazine ring out of plane C−H aromatic bend). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, CH=N), 8.14–8.01 (q, 2 H, heterocyclic Ar*H*), 7.98–6.88 (m, 8 H, Ar*H*), 4.07–3.97 (t, 2 H, $OCH_2$), 1.82–1.31 (m, 10 H, $-[CH_2]_n$), 0.88 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 166.8, 162.9, 131.5, 122.2, 114.0, 77.4, 77.0, 76.5 ($CDCl_3$), 68.1, 31.7, 29.0, 25.9, 22.5, 14.0 ($CH_3$). UV-visible ($CHC1_3$): $\lambda_{max} = 269$ nm. Elemental analyses: calculated (for $C_{24}H_{26}N_4O_3$), C, 68.88; H, 6.26; N, 13.38%, found, C, 68.79; H, 5.96; N, 13.31%.

*3-[4-(4′-Odyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{25}H_{28}N_4O_3$ (**4c**).* Yield 64%. IR (KBr, $cm^{-1}$): 2926, 2854 (aliphatic C−H), 1735 (ester C=O), 1685 (CH=N), 1605 (Ph), 1306 (OPh), 1258 (triazine ring C=N conjugated), 1063 (triazine ring C−N non-conjugated), 845 (triazine out of plane C−H aromatic bend). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1H, CH=N), 8.14–8.02 (q, 2 H, heterocyclic Ar*H*), 7.97–6.90 (m, 8 H, Ar*H*), 4.04–4.00 (t, 2 H, $-OCH_2$), 1.80–1.29 (m, 12 H, $-[CH_2]_n$), 0.89 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 191.0, 171.5, 164.2, 163.8 (−CH=N), 163.6, 155.9, 133.8, 132.4, 132.3, 131.2, 122.6, 121.3, 120.7, 114.4, 114.1, 77.4, 77.0, 76.5, 68.4 ($-OCH_2$), 68.2, 31.7, 29.6, 29.3, 29.2, 29.0, 25.9, 22.6, 14.0 ($CH_3$). UV-visible ($CHC1_3$): $\lambda_{max} = 274$ nm. Elemental analyses: calculated (for $C_{25}H_{28}N_4O_3$), C, 69.42; H, 6.52; N, 12.95%, found, C, 69.25; H, 6.39; N, 12.78%.

*3-[4-(4′-Nonyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{26}H_{30}N_4O_3$ (**4d**).* Yield 60%. IR (KBr, $cm^{-1}$): 2925, 2853 (aliphatic C−H), 1733 (ester C=O), 1684 (CH=N), 1605 (Ph), 1307 (OPh), 1255 (triazine ring C=N conjugated), 1059 (triazine ring C−N non-conjugated), 844 (triazine out of plane C−H aromatic bend). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, −CH=N), 8.14–8.02 (q, 2 H, heterocyclic Ar*H*), 7.99–6.87 (m, 8 H, Ar*H*), 4.04–3.97 (t, 2 H, $-OCH_2$), 1.81–1.28 (m, 14 H, $-[CH_2]_n$), 0.88 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 190.9, 171.5, 166.4, 163.6 (−CH=N), 162.8, 132.4, 132.2, 131.4, 131.2, 122.6, 122.5, 121.3, 114.4, 114.1, 113.9, 77.4, 77.0, 76.5 ($CDCl_3$), 68.3 ($-OCH_2$), 68.2, 68.1, 60.5, 31.8, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 25.9, 22.6, 14.0 ($CH_3$). UV-visible ($CHC1_3$): $\lambda_{max} = 285$, 259 nm. Elemental analyses: calculated (for $C_{26}H_{30}N_4O_3$), C, 69.93; H, 6.77; N, 12.54%, found, C, 69.44; H, 5.23; N, 12.48%.

*3-[4-(4′-Decyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{27}H_{32}N_4O_3$ (**4e**).* Yield 65%. IR (KBr, $cm^{-1}$): 2925, 2854 (aliphatic C−H), 1732 (ester C = 0), 1681 (CH=N), 1605 (Ph), 1307 (OPh), 1256 (triazine ring C=N conjugated), 1060 (triazine ring C−N non-conjugated), 844 (triazine out of plane C−H aromatic bend). $^1H$ NMR ($CDCl_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, −CH=N), 8.14–8.04 (q, 2 H, heterocyclic Ar*H*), 7.99–6.91 (m, 8 H, −Ar*H*), 4.04–3.99 (t, 2 H, $-OCH_2$), 1.80–1.27 (m, 16 H, $-[CH_2]_n$), 0.88–0.86 (t, 3 H, $-CH_3$). $^{13}C$ NMR $\delta_C$ ($CDCl_3$): 163.6, 132.3, 121.3, 114.1, 77.4, 77.0, 76.5 ($CDCl_3$), 68.2, 31.8, 29.7, 29.5, 29.3, 29.0, 25.9, 22.6, 14.1 ($CH_3$). UV-visible ($CHCl_3$): $\lambda_{max} = 328$, 266 nm. Elemental analyses: calculated (for $C_{27}H_{32}N_4O_3$), C, 70.41; H, 7.00; N, 12.16%, found, C, 70.28; H, 6.83; N, 11.90%.

*3-[4-(4′-Undecyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{28}H_{34}N_4O_3$ (**4f**).* Yield 59%. IR (KBr, $cm^{-1}$): 2924, 2853 (aliphatic C−H), 1733 (ester C = 0), 1680 (CH=N), 1605 (Ph), 1307 (OPh), 1255 (triazine ring C=N conjugated), 1060 (triazine ring C—N non-conjugated), 845 (triazine out of plane C—H aromatic bend). $^1$H NMR (CDCl$_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, –CH=N), 8.14–8.01 (q, 2 H, heterocyclic Ar*H*), 7.99–6.87 (m, 8 H, Ar*H*), 4.04–3.97 (t, 2 H, –OCH$_2$), 1.81–1.26 (m, 18 H, –[CH$_2$]$_n$), 0.88–0.85 (t, 3 H, –CH$_3$). UV-visible (CHC1$_3$): $\lambda_{max} = 267$ nm. Elemental analyses: calculated (for $C_{28}H_{34}N_4O_3$), C, 70.86; H, 7.22; N, 11.80%, found, C, 70.81; H, 7.04; N, 11.64%.

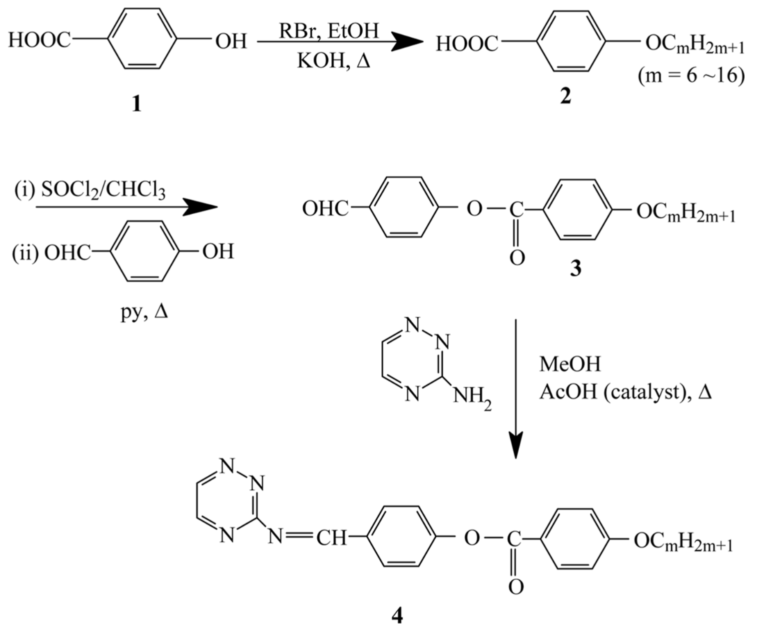
*3-[4-(4′-Dodecyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{29}H_{36}N_4O_3$ (**4g**).* Yield 68%. IR (KBr, cm$^{-1}$): 2921, 2853 (aliphatic C—H), 1733 (ester C=O), 1651 (CH=N), 1604 (Ph), 1306 (OPh), 1263 (triazine ring C=N conjugated), 1056 (triazine ring C—N non-conjugated), 855 (triazine out of plane C—H aromatic bend). $^1$H NMR (CDCl$_3$, TMS) $\delta_H$ (ppm): 10.02 (s, 1 H, –CH=N), 8.14–8.05 (q, 2 H, heterocyclic Ar*H*), 7.97–6.94 (m, 8 H, Ar*H*), 4.07–4.03 (t, 2 H, –OCH$_2$), 1.82–1.26 (m, 20 H, –[CH$_2$]$_n$), 0.90–0.86 (t, 3 H, –CH$_3$). UV-visible (CHCl$_3$): $\lambda_{max} = 337$, 272 nm. Elemental analyses: calculated (for $C_{29}H_{36}N_4O_3$), C, 71.28; H, 7.42; N, 11.46%, found, C, 71.34; H, 7.32; N, 11.34%.

*3-[4-(4′-Tetradecyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{31}H_{40}N_4O_3$ (**4h**).* Yield 70%. IR (KBr, cm$^{-1}$): 2920, 2851 (aliphatic C—H), 1732 (ester C=O), 1680 (CH=N), 1606 (Ph), 1307 (OPh), 1257 (triazine ring C=N conjugated), 1062 (triazine C—N non-conjugated), 846 (triazine out of plane C—H aromatic bend). $^1$H NMR (CDCl$_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, –CH=N), 8.15–8.00 (q, 2 H, heterocyclic Ar*H*), 7.98–6.88 (m, 8 H, Ar*H*), 4.04–3.97 (t, 2 H, –OCH$_2$), 1.81–1.26 (m, 24 H, –[CH$_2$]$_n$), 0.90–0.85 (t, 3 H, –CH$_3$). Elemental analyses: calculated (for $C_{31}H_{40}N_4O_3$), C, 72.06; H, 7.80; N, 10.84%, found, C, 71.84; H, 7.42; N, 10.62%.

*3-[4-(4′-Hexadecyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine, $C_{33}H_{44}N_4O_3$ (**4i**).* Yield 74%. IR (KBr, cm$^{-1}$): 2918, 2851 (aliphatic C—H), 1736 (ester C=O), 1691 (CH=N), 1606 (Ph), 1306 (OPh), 1264 (triazine ring C=N conjugated), 1067 (triazine ring C—N non-conjugated), 845 (triazine out of plane C—H aromatic bend). $^1$H NMR (CDCl$_3$, TMS) $\delta_H$ (ppm): 10.01 (s, 1 H, –CH=N), 8.14–8.01 (q, 2 H, heterocyclic Ar*H*), 7.97–6.90 (m, 8 H, Ar*H*), 4.06–4.00 (t, 2 H, –OCH$_2$), 1.84–1.26 (m, 28 H, –[CH$_2$]$_n$), 0.90–0.85 (t, 3 H, –CH$_3$). $^{13}$C NMR $\delta_C$ (CDCl$_3$): 190.9, 163.8, 163.6, 133.8, 132.4, 132.3, 131.2, 122.5, 120.7, 114.4, 114.1, 77.4, 77.0, 76.5 (CDCl$_3$), 68.3, 68.2, (–OCH$_2$), 31.9, 29.6, 29.5, 29.3, 29.0, 25.9, 22.6, 14.1 (CH$_3$). UV-visible (CHCl$_3$): $\lambda_{max} = 339$, 270 nm. Elemental analyses: calculated (for $C_{33}H_{44}N_4O_3$), C, 72.76; H, 8.14; N, 10.28%, found, C, 72.38; H, 8.11; N, 10.12%.

## 3. Results and Discussion

The compounds 3-[4-(4′-alkoxybenzoyloxybenzylidene)amino]-1,2,4-triazines **4a–i** have been prepared as shown in Scheme 1. The elemental data are in agreement with the formulae of the compounds. The IR and NMR spectral data are fully consistent with the structure. In the IR spectrum of 3-amino-1,2,4-triazine the bands observed are designated as 3312 $v_{as}$(N—H), 3113 $v_s$(N—H), 1650 (NH$_2$ bend), 1341 and 1266 (C=N conjugated aromatic ring), 1044 (C—N non-conjugated aromatic ring) and 860 cm$^{-1}$ (C—H out of plane bend of aromatic ring) respectively. The IR spectrum of 4-(4′-octyloxybenzoyloxy)benzaldehyde **3** shows absorption bands which are designated as 2923 and 2853 (aliphatic C—H), 1733 (C=O ester), 1698



**Scheme 1.** Synthetic route for 3-[4-(4′-alkoxybenzoyloxybenzylidene)amino]-1,2,4-triazines.

(C=O aldehyde), 1605, 1511 (Ph), 1308, and 1260 cm$^{-1}$ for (OPh), respectively. The IR spectrum of 3-[4-(4′-octyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine **4c** shows absorption bands assigned as 2926, 2854 (aliphatic C–H), 1735 (ester C=O), 1685 (CH=N), 1605 (Ph), 1306 (OPh), 1258 (triazine ring C=N conjugated), 1063 (triazine ring C–N non-conjugated), 845 cm$^{-1}$ (triazine out of plane aromatic C–H bend), respectively. The disappearance of the $NH_2$ bending mode of triazine $\beta(NH_2)$ at 1650 cm$^{-1}$, and v(C=O) band (1698 cm$^{-1}$) of 4-(4′-octyloxybenzoyloxy)-benzaldehyde along with the appearance of a new band in the compound 3-[4-(4′-octyloxybenzoloxybenzylidene)amino]-1,2,4-triazine centered at 1685 cm$^{-1}$ due to $\nu$(C=N) indicates condensation of amine with aldehyde forming the Schiff base. The proton NMR spectrum of 3-amino-1,2,4-triazine depicts peaks which are assigned as $\delta$ 8.54 (s, 1 H, triazine ring), 8.20 (s, 1 H, triazine ring) and 7.17 (s, 2H, $NH_2$), respectively. The proton NMR spectrum of 4-(4′-octyloxybenzoyloxy)-benzaldehyde exhibits peaks at $\delta$ 10.02 (s, 1 H, –CHO), 8.15–6.88 (m, 8 H, ArH), 4.07–3.97 (m, 2 H, $-OCH_2$), 1.81–1.27 (m, 12 H, $-[CH_2]_n$), 0.90–0.86 (t, 3 H, $-CH_3$). The proton NMR spectrum of 3-[4-(4′-octyloxybenzoyloxybenzylidene)-amino]-1,2,4-triazine **4c** shows peaks at $\delta$ 10.01 (s, 1 H, CH=N), 8.14–8.02 (q, 2 H, heterocyclic Ar*H*), 7.97–6.90 (m, 8 H, Ar*H*), 4.04–4.00 (t, 2 H, $-OCH_2$), 1.80–1.29 (m, 12 H, $-[CH_2]_n$), and 0.89 (t, 3 H, $-CH_3$), respectively. The disappearance of the NMR signals concerning $NH_2$ ($\delta$ 7.17) of 3-amino-1,2,4-triazine and CHO ($\delta$ 10.02) of 4-(4′-octyloxybenzoyloxy)benzaldehyde along with the appearance of a new signal in the compound **4c** at $\delta$ 10.01 confirms the formation of Schiff base. The signals of two aromatic rings across the ester linkage in compound **4c** overlap and are observed at $\delta$ 7.97–6.90 whereas that of heterocyclic aromatic triazine ring is observed at $\delta$ 8.14–8.02 ppm. The length of alkyl chain has no significant effect on the position of the signals due to –CH=N, heterocyclic aromatic triazine ring, phenyl ring, $-OCH_2$, $-[CH_2]_n$ and $-CH_3$ protons. The UV-visible spectrum of 3-[4-(4′-octyloxybenzoyloxybenzylideneamino)]-1,2,4-triazine **4c** shows bands at 274 nm ($n \rightarrow \pi^*$ transition, R band) in which an unshaired electron pair on a heteroatom is excited to $\pi^*$ antibonding orbital. This involves least amount of energy than all the transitions, and therefore, this transition gives rise to an absorption band at longer wavelength.

## 4. Optical Properties

The liquid crystalline character of 3-[4-(4′-alkoxybenzoyloxybenzylidine) amino]-1-,2,4-triazine **4a–i** was investigated by polarizing optical microscope (POM) using a hot stage. The phase transition temperatures and enthalpies were obtained by carrying out DSC thermal analysis. The phase transition temperatures along with the enthalpy values for the compounds are summarized in Table 1. The symbol K, N, SmA, and I are used to denote crystalline, nematic, smectic A, and isotropic phases, respectively. The compound 3-[4-(4′-decyloxybenzoyloxybenzylidene)amino]-1,2,4-triazine **4e** exhibits endothermic peaks at 64.3°C ($\Delta H = 0.35\,kJmol^{-1}$), 82.5°C ($\Delta H = 22.24\,kJmol^{-1}$), and 91.7°C ($\Delta H = 11.44\,kJmol^{-1}$); the first two peaks are indicative of a crystal-to-crystal transition, while the third indicates a crystal-to-mesophase transition, and the one observed at 141.6°C defines a mesophase-to-isotropic phase transition. The exothermic peaks are observed at 103.8°C ($\Delta H = 0.64\,kJmol^{-1}$), 86.8°C ($\Delta H = 12.07\,kJmol^{-1}$), 70.9°C ($\Delta H = 8.07\,kJmol^{-1}$), and 60.5°C ($\Delta H = 0.57\,kJmol^{-1}$), which are attributed to isotropic-to-mesophase and mesophase-to-crystal phase transitions followed by subsequent crystal phase. This compound (**4e**) under polarizing optical microscope reveals an enantiotropic nematic phase both in heating and cooling cycles at 91.7°C and 103.8°C, respectively. The optical micrograph at 91.7°C is characteristic of a nematic phase with black brushes 2–4 in numbers are seen emanating from the central nuclei formed by disclination lines (line defects) giving rise to a schlieren texture. In cooling cycle nematic droplets appear at 103.8°C which displays the black stripes 2–4 fold with a schlieren texture. The droplets increase in size and collapse with each other to form a film showing prominent black stripes. The joining of radiating arms of one nucleus (molecule) with the other nucleus is clearly seen within the droplets in this phase of the compound. The compound **4g** exhibits endothermic peaks at 46.7°C ($\Delta H = 49.17\,kJmol^{-1}$) and 65.2°C ($\Delta H = 0.42\,kJmol^{-1}$) due to crystal-to-crystal phase transitions followed by an isotropic phase transition at 191.8°C. The exothermic peaks are observed at 150.1°C ($\Delta H = 0.22\,kJmol^{-1}$) and 109.1°C ($\Delta H = 0.56\,kJmol^{-1}$), characteristics of isotropic to mesophase and mesophase-to-crystal phase transitions, respectively. The optical micrograph reveals monotropic nematic behavior of this compound which is observed only in cooling cycle at 150.1°C.

The compound **4c** exhibits endothermic peaks at 71.1°C ($\Delta H = 18.66\,kJmol^{-1}$), 104.6°C ($\Delta H = 0.40\,kJmol^{-1}$), 145.4°C ($\Delta H = 0.06\,kJmol^{-1}$), which are due to successive polymorphic phase involving crystal to crystal transitions and a peak observed at 186.7°C is attributed to isotropic phase, transition. The exothermic peaks for this compound are observed at 150.7°C ($\Delta H = 0.12\,kJmol^{-1}$), 109.7°C ($\Delta H = 0.25\,kJmol^{-1}$), 103.0°C ($\Delta H = 2.47\,kJmol^{-1}$), and 65.0°C ($\Delta H = 3.64\,kJmol^{-1}$), which are attributed to the transition from isotropic-to-mesophase and mesophase-to-crystal phase followed by the subsequent crystal phases. The optical micrograph reveals the monotropic nematic phase for this compound with

**Table 1.** Thermal transition temperatures, associated enthalpy (ΔH), and entropy (ΔS), changes of 3-[4-(4′-alkoxybenzoyloxybenzylidene) amino]-1,2,4-triazines

| Compound | Transitions | T/°C | $\Delta H/\mathrm{kJmol^{-1}}$ | $\Delta S/\mathrm{JK^{-1}mol^{-1}}$ |
|---|---|---|---|---|
| 4a | $K^1$–$K^2$ | 46.0 | 14.13 | 44.29 |
| | $K^2$–$K^3$ | 60.7 | 1.27 | 3.80 |
| | $K^3$–$K^4$ | 73.0 | 0.54 | 1.56 |
| | $K^4$–I | 168.6 | 12.73 | 28.82 |
| | I–$K^4$ | 150.0 | 0.11 | 0.26 |
| | $K^4$–K | 108.8 | 0.18 | 0.47 |
| 4b | $K^1$–I | 83.1 | 22.28 | 62.56 |
| | I–$K^1$ | 65.9 | 5.71 | 16.84 |
| | $K^1$–K | 57.1 | 14.90 | 45.13 |
| 4c | $K^1$–$K^2$ | 71.1 | 18.66 | 54.22 |
| | $K^2$–$K^3$ | 104.6 | 0.40 | 1.05 |
| | $K^3$–$K^4$ | 145.4 | 0.06 | 0.14 |
| | $K^4$–I | 186.7 | 0.15 | 0.32 |
| | I–N | 150.7 | 0.12 | 0.28 |
| | N–$K^4$ | 109.7 | 0.25 | 0.65 |
| | $K^4$–$K^3$ | 103.0 | 2.47 | 6.56 |
| | $K^3$–K | 65.0 | 3.64 | 10.76 |
| 4d | $K^1$–$K^2$ | 64.2 | 0.12 | 0.35 |
| | $K^2$–I | 77.8 | 9.93 | 28.30 |
| | I–N | 46.8 | 1.24 | 3.87 |
| | N–K | 38.2 | 12.81 | 41.16 |
| 4e | $K^1$–$K^2$ | 64.3 | 0.35 | 1.03 |
| | $K^2$–$K^3$ | 82.5 | 22.24 | 62.55 |
| | $K^3$–N | 91.7 | 11.44 | 31.36 |
| | N–I | 141.6 | 0.14 | 0.33 |
| | I–N | 103.8 | 0.64 | 1.69 |
| | N–$K^3$ | 86.8 | 12.07 | 33.54 |
| | $K^3$–$K^2$ | 70.9 | 8.07 | 23.46 |
| | $K^2$–$K^1$ | 60.5 | 0.57 | 1.70 |
| 4f | $K^1$–$K^2$ | 64.2 | 0.30 | 0.88 |
| | $K^2$–I | 70.5 | 2.78 | 8.09 |
| | I–N | 66.1 | 1.09 | 3.21 |
| | N–K | 60.2 | 1.23 | 3.69 |
| 4g | $K^1$–$K^2$ | 46.7 | 49.17 | 153.80 |
| | $K^2$–$K^3$ | 65.2 | 0.42 | 1.24 |
| | $K^3$–I | 191.8 | 0.19 | 0.40 |
| | I–N | 150.1 | 0.22 | 0.52 |
| | N–K | 109.1 | 0.56 | 1.46 |
| 4h | $K^1$–$K^2$ | 64.4 | 0.14 | 0.41 |
| | $K^2$–I | 120.0 | 16.93 | 43.07 |
| | I–N | 109.5 | 0.09 | 0.23 |
| | N–K | 43.6 | 20.52 | 64.81 |
| 4i | $K^1$–$K^2$ | 70.8 | 34.37 | 99.97 |
| | $K^2$–$K^3$ | 89.1 | 22.60 | 62.41 |

(*Continued*)

Table 1. Continued

| Compound | Transitions | T/°C | ΔH/kJmol$^{-1}$ | ΔS/JK$^{-1}$mol$^{-1}$ |
|---|---|---|---|---|
| | K$^3$–K$^4$ | 104.7 | 0.11 | 0.29 |
| | K$^4$–K$^5$ | 112.1 | 2.69 | 6.98 |
| | K$^5$–I | 192.0 | 0.08 | 0.17 |
| | I–SmA | 113.9 | 3.36 | 8.68 |
| | SmA–K$^5$ | 106.3 | 0.80 | 2.10 |
| | K$^5$–K | 58.9 | 13.72 | 41.33 |

the appearance of schlieren texture with black brushes or black stripes emanating from the central nuclei formed as a result of disclination or line defects in the compound.

The compound **4d** exhibits sharp endothermic peaks at 64.2°C (ΔH = 0.12 kJmol$^{-1}$) and 77.8°C (ΔH = 9.93 kJmol$^{-1}$), which are indicative of crystal-to-crystal and crystal-to-isotropic phase transitions, respectively. The exothermic peaks in DSC thermogram of this compound are observed at 46.8°C (ΔH = 1.24 kJmol$^{-1}$) and 38.2°C (ΔH = 12.81 kJmol$^{-1}$) due to isotropic to mesophase and mesophase-to-crystal phase transition, respectively. The optical micrograph at 46.8°C in cooling cycle displays numerous nematic droplets (bubbles) with radial outline confirming nematic phase. The similar phase transitions and texture patterns are observed for the compounds **4f** and **4h**.

The compound **4i** exhibits endothermic peaks at 70.8°C (ΔH = 34.37 kJmol$^{-1}$), 89.1°C (ΔH = 22.60 kJmol$^{-1}$), 104.7°C (ΔH = 0.11 kJmol$^{-1}$), and 112.1°C (ΔH = 2.69 kJmol$^{-1}$) attributed to subsequent crystal-to-crystal phase transitions (polymorphism) and that observed at 192°C defines a crystal-to-isotropic phase transition. The exothermic peaks for this compound are observed at 113.9°C (ΔH = 3.36 kJmol$^{-1}$), 106.3°C (ΔH = 0.80 kJmol$^{-1}$), and 58.9°C (ΔH = 13.72 kJmol$^{-1}$), which are characteristic of isotropic-to-mesophase and mesophase-to-crystal followed by another crystal phase transition. This compound exhibits polymorphic changes (i.e., crystal–crystal transitions) in heating cycle mainly. The optical microscopy displays monotropic smectic A phase for this compound appearing only in cooling cycle at 113.9°C. The compound **4a** exhibits endothermic peaks at 46.0°C (ΔH = 14.13 kJmol$^{-1}$), 60.7°C (ΔH = 1.27 kJmol$^{-1}$), and 73.0°C (ΔH = 0.54 kJmol$^{-1}$) which correspond to subsequent crystal-to-crystal phase transitions, and the one observed at 168.6°C is assigned to a crystal-to-isotropic liquid transition. The exothermic peaks were observed at 150°C (ΔH = 0.11 kJmol$^{-1}$) and 108.8°C (ΔH = 0.18 kJmol$^{-1}$) which define isotropic-to-crystal phase transition followed by the next crystal phase. The compound **4b** exhibits an endothermic peak at 83.1°C (ΔH = 22.28 kJmol$^{-1}$) which defines a sharp crystal to isotropic phase transition whereas the appearance of an exothermic peak at 65.9°C (ΔH = 5.71 kJmol$^{-1}$) and 57.1°C (ΔH = 14.90 kJmol$^{-1}$) indicates an isotropic to crystal transition followed by the next crystal phase. The optical analysis revealed no texture pattern for this compound both in heating and cooling cycles.

Thus, the interactions between aromatic rings are expected to play an important role in molecular ordering. The alkyl chain length provides the mobility necessary for molecular arrangement into an ordered structure. The lower homologs of the series with m = 6 and 7 exhibit no mesomorphism, the homologs with m = 8, 9, 11, 12, and

14 exhibit monotropic nematic mesophase in cooling cycle whereas the member with m = 10 exhibits enantiotropic nematic mesophases both in heating and cooling cycle. The higher member of the series with m = 16 displays a monotropic smectic A mesophase exclusively. Thus at the shorter alkyl chain length, a monotropic nematic phase is seen but as the alkyl chain length increases the smectic A phase appears. Apparently, the lone pairs of electrons on the nitrogen atoms act to broaden the molecule and also introduce attractive forces which aid smectic formation.

The shape anisotropy in the triazines is responsible for the calamitic mesophase exhibited by the 3-[4-(4′-alkoxybenzoyloxybenzylidene) amino]-1,2,4-triazines. The mesophase behavior is further affected by the chain length. The intermolecular forces are strong for $C_6$ and $C_7$, resulting in the crystalline nature. However, for $C_8$, $C_9$, $C_{11}$, $C_{12}$, and $C_{14}$ the molecular forces are weak yielding thermodynamically less stable monotropic nematic mesophase. While in the $C_{10}$ homologue, the thermodynamically stable enantiotropic nematic mesophase is stabilized; the larger chain length $C_{16}$ results in the further more stable smectic A mesophase.

## 5. Conclusions

A new series of 3-[4-(4′-alkoxybenzoyloxybenzylidene)amino]-1,2,4-triazines have been synthesized having terminal alkoxy chains ($m = 6{\sim}16$). The chemical structures of the final products were investigated by FT-IR, NMR, UV-visible, $^1$H, and $^{13}$C NMR spectra. The mesomorphic properties and optical textures of the products were characterized by DSC and POM. The existence of nematic (schlieren) and smectic A (focal-conic) texture was confirmed by POM. It was found that the mesogenic nature of these compounds is dependent on the alkoxy chain length. The lower homologues with (m = 6, 7) were found to be non-mesogenic, whereas the higher homologues displayed nematic and smectic A pattern.

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