ISSN 1022-8594
JUJS

Vol. 41, No.1, pp.31-42

Synthesis and Characterization of Some 4-Aryl Substituted Thiosemicarbazides, N-Alkyloxybenzaldehydes Containing Long Alkyl Chains and their Corresponding Thiosemicarbazones

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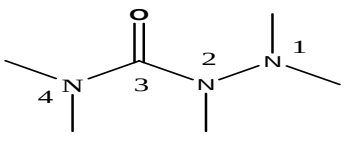
Abstract

The synthesis and spectroscopic characterization of 4-aryl substituted thiosemicarbazide, 3,4-bis(alkyloxy)benzaldehydes containing long alkyl chains and their corresponding thiosemicarbazones generated from the condensation reaction between 4-aryl substituted thiosemicarbazide and 3,4-bis (alkyloxy) benzaldehydes in presence of conc. hydrochloric acid have been studied. Six 3,4-bis (alkoxy) benzal-[4-(*p*-tolyl)] thiosemicarbazones have been synthesized by the usual method as described in the literature. All the synthesized compounds have been characterized on the basis of their physical properties, spectroscopic analysis viz: ^{1}H-NMR and IR spectra. The thermal behavior of the synthesized thiosemicarbazones has been examined under polarizing microscope fitted with a hot and cold stage to observe the liquid crystalline properties of these synthesized compounds.

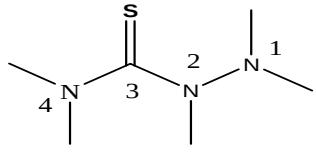
Keywords: Synthesis, Thiosemicarbazides, Thiosemicarbazones, Condensation, Spectral data.

Introduction

Thiosemicarbazide (origin: thio- + semicarbazide) is an analogue of semicarbazide that contains a sulfur atom in place of oxygen atom. Thiosemicarbazides are odorless, white, sand-like powder; soluble in water, ethanol, alcohols and hot methanol.



Semicarbazide



Thiosemicarbazide

Thiosemicarbazides are commonly represented by the the structure (I), where in the numbering system for nomenclature is also shown.

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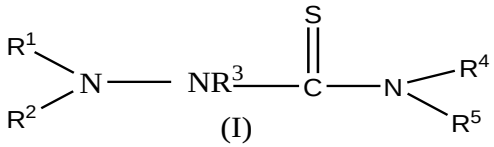
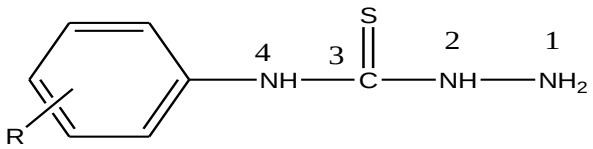
Knowledge of chemistry of thiosemicarbazides is more recent and to a great extent based on the systematic investigations of Jensen and co-workers[1].



(I)

R^n= H, alkyl, aryl, etc.

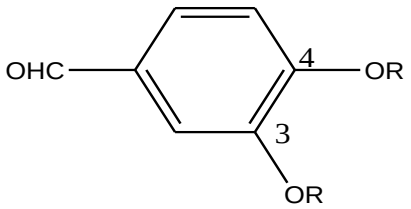
4-Aryl substituted thiosemicarbazide (II) may be prepared from aromatic amine by treatment with NH_4OH, CS_2, sodium chloroacetate and finally with hydrazine hydrate [2].



(II)

Thiosemicarbazides are the valuable building blocks for the synthesis of five-membered heterocycles [3].Biologically active thiosemicarbazides derivatives include 1,3,4-thiadiazoles as antibacterial agents [4], and 1,3,4-thiadiazolines as antitubercular [5] and anticonvulsiveagents [6].

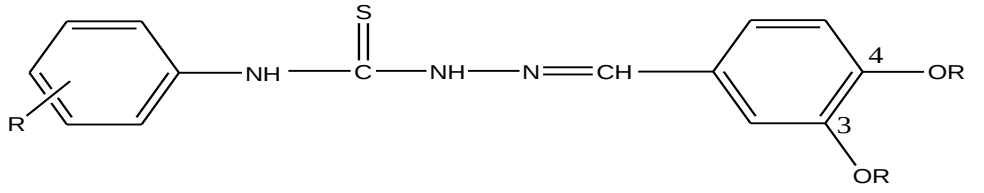
Alkyloxybenzaldehydes (III) are obtained by the treatment of hydroxybenzaldehydes with anhydrous K_2CO_3, and corresponding n-alkyl bromide in presence of dry acetone[7-8].



(III)

Where R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$ etc.

Substituted thiosemicarbazides undergo condensation reactions with different alkyloxybenzaldehydes producing thiosemicarbazones (IV).



(IV)

Where R = C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$ etc.

In this study, we prepared new 3,4-bis(alkyloxy)benzaldehydes containing long alkyl chains; and synthesized substituted thiosemicarbazones from 4-aryl substituted thiosemicarbazide and 3,4-bis(alkyloxy)benzaldehydes in ethanol with trace amount of conc. hydrochloric acid.

Experimental

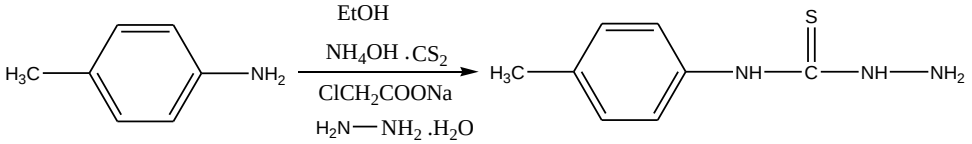
Materials and methods

All the starting materials and solvents were purchased from ACROS organics and E. Merck and used without further purification. Melting points were recorded by thin disc 'FISCHER-JOHNS' electro-thermal melting point apparatus and are uncorrected. Care was taken to ensure that the heating was at a steady state. The purity of the synthesized compouds was determined by TLC using pre-coated silica gel aluminium sheet (silica gel 60, GF_{254} , 0.25 mm) from E- Merck. IR spectra were recorded on a Nicolet iS10 spectrometer as KBr-disc at ambient temperature at WMSRC in Jahangirnagar University. ^{1}H NMR spectra were recorded in WMSRC on a BRUKER- 400 MHz spectrometer using $CDCl_3$ and DMSO-d_6 solvents at 300K. ^{13}C NMR spetra were also recorded on a BRUKER- 400 MHz spectrometer at WMSRC in Jahangirnagar University, Bangladesh.

Methods of preparation and physical data of synthesized compounds 1**A**, 2(**A**-**F**) and 3(**A**-**F**)

General procedure for the preparation of 4-(p-tolyl) thiosemicarbazide (1**A**)

p-Toluidine (2.14 gm, 20 mmol) in ethanol (20 cm^3) was treated with ammonium hydroxide (25%, 4 cm^3) followed by carbon disulfide (3 cm^3). The resultant mixture was stirred for one hour and was allowed to stand at room temperature for two hours. At this stage, sodium chloroacetate (2.33 gm, 20 mmol) was added to the reaction mixture with stirring. Finally, hydrazine hydrate (80%, 4 cm^3) was slowly added to this solution. After the addition of hydrazine hydrate was complete, permanent precipitation took place. The whole mass was filtered off and the filtrate was kept overnight to give white crystalline solid [9].By washing the crystalline solid with methanol the pure compound (1**A**) was obtained.



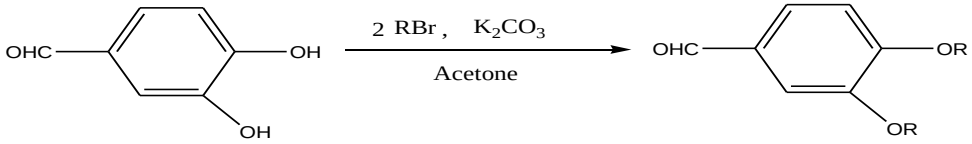
p-Toluidine (1**A**)

*4-(p-tolyl) thiosemicarbazide (1**A**):* This compound was obtained as white crystalline solids, yield 53%, m.p. 135-136^oC, soluble in dimethyl sulfoxide (DMSO) and sparingly soluble in ethanol and hot methanol. IR (KBr, ν_{max} , cm^{-1}): 3298 and 3194 (m, ν_{NH} for NH_2); 3250 (s, ν_{NH} for NH); 3040 (w, ν_{CH} aromatic); 2963 and 2913 (w, ν_{CH}aliphatic); 1619 (sh, $\nu_{C=C}$ aromatic); 1589 and 1533 (m, δ_{NH}); 1312 (w, $\nu_{C=S}$); 1201 (s, ν_{C-N}); 1064 (s, δ_{CH} in plane); 986 (m, δ_{CH} out-of-plane); 807 (s, para substituted benzene ring). ^{1}H-NMR (DMSO-d_6, 400 MHz, δ, ppm): 9.58 (s, 1H, NH); 9.00 (s, 1H, NH); 7.48 (d, J=7.8 Hz, 2H, aromatic); 7.11 (d, J= 8 Hz, 2H, aromatic); 4.73 (br, 2H, NH_2); 2.23 (s, 3H, CH_3).

*General procedure for the preparation of 3,4-bis(alkyloxy)benzaldehyde*2(**A**-**F***)*

3,4-Dihydroxybenzaldehyde (1.40 gm, 10 mmol) was treated with anhydrous K_2CO_3 (2.74 gm, 20 mmol) and hexyl bromide (20 mmol) in acetone (35-50 cm^3). The reaction mixture was refluxed on water bath for 10-12 hours. The whole mass was filtered off and the solvent was removed from the filtrate by using rotary vacuum evaporator to give a crude product. This crude product was dissolved in dichloromethane and was successively washed with water and 5% NaOH solution to remove the unreacted 3,4-

dihydroxybenzaldehyde[7-8]. Then a small amount of anhydrous Na_2SO_4 was added to this solution and filtered off. The filtrate was concentrated by rotary evaporator under reduced pressure to give pure compound 2(**A**-**F**).



3,4-Dihydroxybenzaldehyde 3,4-bis(alkyloxy)benzaldehyde

2(**A**-**F**)

R = C_6H_{13} (**A**), $C_{10}H_{21}$ (**B**), $C_{12}H_{25}$ (**C**), $C_{14}H_{29}$ (**D**), $C_{16}H_{33}$ (**E**), $C_{18}H_{37}$(**F**).

3,4-bis(hexyloxy)benzaldehyde(2**A**): This compound was obtained as dark oily suspension, yield 76%, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3050 (w, ν_{CH} aromatic); 2955 and 2873 (w, ν_{CH} aliphatic, CH_3); 2922 and 2851 (s, ν_{CH} aliphatic, CH_2); 1687 (sh, $\nu_{C=O}$ aldehyde); 1596 (s, $\nu_{C=C}$ aromatic); 1277 (s, ν_{C-O}); 1394 and 1021 (m, δ_{CH}in- and oop of aliphatic C-H); 808 and 730 (s, para- and meta- substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.85 (s, 1H, CHO); 7.45 (dd, J= 8, 2.8 Hz, 1H, aromatic); 7.41 (d, J= 2.8 Hz, 1H, aromatic); 6.98 (d, J= 8.4 Hz, 1H, aromatic); 4.09 (m, 4H, OCH_2); 1.94 (m, 4H, CH_2); 1.73 (m, 4H, CH_2); 1.52 (m, 8H, CH_2); 0.93 (t, 6H, CH_3).

3,4-bis(decyloxy)benzaldehyde(2**B**): This compound was obtained as pale yellow crystalline solid, yield 81%,m.p. 65^o-66^{o}C, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3050 (w, ν_{CH} aromatic); 2940 and 2864 (w, ν_{CH} aliphatic, CH_3); 2922 and 2848 (s, ν_{CH} aliphatic, CH_2); 1630 (sh, $\nu_{C=O}$ aldehyde); 1597 (s, $\nu_{C=C}$ aromatic); 1249 (s, ν_{C-O}); 1386 and 1167 (m, δ_{CH}in- and oop of aliphatic C-H); 838 and 668 (s, para- and meta- substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.85 (s, 1H, CHO); 7.45 (dd, J= 8, 2.8 Hz, 1H, aromatic); 7.41 (d, J= 2.8 Hz, 1H, aromatic); 6.98 (d, J= 8 Hz, 1H, aromatic); 4.09 (m, 4H, OCH_2); 1.90 (m, 4H, CH_2); 1.58 (m, 4H, CH_2); 1.38 (m, 24H, CH_2); 0.92 (t, 6H, CH_3).

3,4-bis(dodecyloxy)benzaldehyde(2**C**): This compound was obtained as deep yellow crystalline solid, yield 91%, m.p. 70^o-72^{o}C, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3030 (w, ν_{CH} aromatic); 2956 and 2873 (w, ν_{CH}

aliphatic, CH_3); 2917 and 1850 (s, ν_{CH} aliphatic, CH_2); 1687 (sh, $\nu_{C=O}$ aldehyde); 1597 (s, $\nu_{C=C}$ aromatic); 1279 (s, ν_{C-O}); 1393 and 1134 (m, δ_{CH}in- and oop of aliphatic C-H); 808 and 730 (s, para- and meta-substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.85 (s, 1H, CHO); 7.45 (dd, J= 8, 2.0 Hz, 1H, aromatic);

7.41 (d, J= 2.0 Hz, 1H, aromatic); 6.98 (d, J= 8.2 Hz, 1H, aromatic); 4.09 (m, 4H, OCH_2); 1.90 (m, 4H, CH_2); 1.60 (m, 4H, CH_2); 1.38 (m, 32H, CH_2); 0.92 (t, 6H, CH_3).

3,4-bis(tetradecyloxy)benzaldehyde(2**D**): This compound was obtained as pale yellow crystalline solid, yield 98%, m.p. 75^o-76^{o}C, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3030 (w, ν_{CH} aromatic); 2956 and 2873 (w, ν_{CH} aliphatic, CH_3); 2917 and 1850 (s, ν_{CH} aliphatic, CH_2); 1687 (sh, $\nu_{C=O}$ aldehyde); 1597 (s, $\nu_{C=C}$ aromatic); 1279 (s, ν_{C-O}); 1393 and 1134 (m, δ_{CH}in- and oop of aliphatic C-H); 808 and 730 (s, para- and meta-substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.85 (s, 1H, CHO); 7.45 (dd, J= 8.4, 2.0 Hz, 1H, aromatic); 7.41 (d, J= 2.0 Hz, 1H, aromatic); 6.98 (d, J= 8.2 Hz, 1H, aromatic); 4.08 (m, 4H, OCH_2); 1.92 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.38 (m, 40H, CH_2); 0.92 (t, 6H, CH_3).

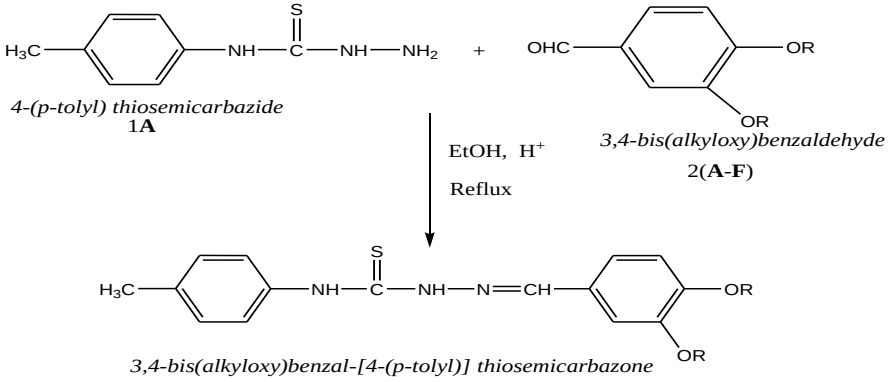
3,4-bis(hexadecyloxy)benzaldehyde(2**E**): This compound was obtained as pale yellow crystalline solid, yield 68%, m.p. 78^o-79^{o}C, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3030 (w, ν_{CH} aromatic); 2956, 2919 and 2850 (w, ν_{CH} aliphatic, C-H); 1627 (sh, $\nu_{C=O}$ aldehyde); 1599 (s, $\nu_{C=C}$ aromatic); 1275 (s, ν_{C-O}); 1234 and 1065 (m, δ_{CH}in- and oop of aliphatic C-H); 807 and 730 (s, para- and meta- substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.85 (s, 1H, CHO); 7.45 (dd, J= 8, 2.0 Hz, 1H, aromatic); 7.41 (d, J= 2.0 Hz, 1H, aromatic); 6.98 (d, J= 8 Hz, 1H, aromatic); 4.10 (m, 4H, OCH_2); 1.91 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.38 (m, 48H, CH_2); 0.92 (t, 6H, CH_3).

3,4-bis(octadecyloxy)benzaldehyde(2**F**): This compound was obtained as pale yellow crystalline solid, yield 66%, m.p. 82^o-83^{o}C, soluble in $CHCl_3$. IR (KBr, ν_{max} , cm^{-1}): 3030 (w, ν_{CH} aromatic); 2955, 2921 and 2851 (w, ν_{CH} aliphatic, C-H); 1682 (sh, $\nu_{C=O}$ aldehyde); 1603 (s, $\nu_{C=C}$ aromatic); 1281 (s, ν_{C-O}); 1244 and 1110 (m, δ_{CH}in- and oop of aliphatic C-H); 807 and 721 (s, para- and meta- substituted benzene ring). ^{1}H-NMR ($CDCl_3$, 400 MHz, δ,

ppm): 9.86 (s, 1H, CHO); 7.46 (dd, J= 7.8, 2.8 Hz, 1H, aromatic); 7.41 (d, J= 2.8 Hz, 1H, aromatic); 6.98 (d, J= 8 Hz, 1H, aromatic); 4.17 (m, 4H, OCH_2); 1.91 (m, 4H, CH_2); 1.49 (m, 4H, CH_2); 1.38 (m, 56H, CH_2); 0.92 (t, 6H, CH_3).

General procedure for preparation of 3,4-bis(alkyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone 3(**A**-**F**)

To a boiling solution of 3,4- bis(alkyloxy)benzaldehydes 2(**A**-**F**) (10 mmol) in ethanol (35-40 cm^3), a few drops of conc. hydrochloric acid (pH: 3-4) were added. After half an hour 4-(*p*-tolyl) thiosemicarbazide(1**A**) (1.80 gm, 10 mmol) in ethanol was added dropwise with stirring. The reaction mixture was refluxed for 8 hours and cooled for the product to precipitate which was collected and recrystallized from ethanol [10].



4-(p-tolyl) thiosemicarbazide
1**A**

3,4-bis(alkyloxy)benzaldehyde
2(**A**-**F**)

3,4-bis(alkyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone
3(**A**-**F**)

R = C_6H_{13} (**A**), $C_{10}H_{21}$ (**B**), $C_{12}H_{25}$ (**C**), $C_{14}H_{29}$ (**D**), $C_{16}H_{33}$ (**E**), $C_{18}H_{37}$ (**F**).

3,4-bis(hexyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**A**): This compound was obtained as pale yellow crystalline solid, yield 72%, m.p. 92°-93°C, soluble in $CHCl_3$. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.69 (s, 1H, NH); 9.06 (s, 1H, NH); 7.83 (s, 1H, CH=N); 7.51 (d, J= 6 Hz, 2H, aromatic); 7.25-7.16 (m, 4H, aromatic); 6.91 (d, J= 4 Hz, 1H, aromatic); 4.08 (t, 4H, OCH_2); 2.44 (s, 3H, d); 1.89 (m, 4H, CH_2); 1.53 (m, 4H, CH_2); 1.37 (m, 8H, CH_2); 0.95 (t, 6H, CH_3).

3,4-bis(decyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**B**): This compound was obtained as yellowish-white mass, yield 75%, m.p. 98°-

99°C, soluble in $CHCl_3$. ^{1}H-NMR($CDCl_3$, 400 MHz, δ, ppm): 9.60 (s, 1H, NH); 9.10 (s, 1H, NH); 7.82 (s, 1H, HC=N); 7.51 (d, J= 4.8 Hz, 2H, aromatic); 7.25-7.16 (m, 4H, aromatic); 6.91 (d, J= 8.4 Hz, 1H, aromatic); 4.07 (t, 4H, OCH_2); 2.44 (s, 3H, d); 1.89 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.38 (m, 24H, CH_2); 0.92 (t, 6H, CH_3).

3,4-bis(dodecyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**C**): This compound was obtained as pale yellow crystalline solid, yield 90%, m.p. 102°-103°C, soluble in $CHCl_3$. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.55 (s, 1H, NH); 9.07 (s, 1H, NH); 7.81 (s, 1H, HC=N); 7.53 (d, J= 8.4 Hz, 2H, aromatic); 7.26-7.15 (m, 4H, aromatic); 6.91 (d, J= 8 Hz, 1H, aromatic); 4.07 (t, 4H, OCH_2); 2.40 (s, 3H, d); 1.89 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.38 (m, 32H, CH_2); 0.92 (t, 6H, CH_3). ^{13}C-NMR ($CDCl_3$, δ, ppm): 175.88, 151.43, 149.46, 143.49, 136.24, 135.36, 129.44, 125.79, 125.13, 122.39, 112.92, 111.29, 69.53, 31.93, 29.71, 29.67, 29.64, 29.45, 29.37, 29.16, 26.07, 26.01, 22.67, 21.08, 14.11.

3,4-bis(tetradecyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**D**): This compound was obtained as yellowish-white crystalline solid, yield 82%, m.p. 102°-103°C, soluble in $CHCl_3$. ^{1}H- NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.52 (s, 1H, NH); 9.05 (s, 1H, NH); 7.80 (s, 1H, HC=N); 7.51 (d, J= 7.6 Hz, 2H, aromatic); 7.26-7.16 (m, 4H, aromatic); 6.91 (d, J= 8.4 Hz, 1H, aromatic); 4.07 (t, 4H, OCH_2); 2.39 (s, 3H, d); 1.87 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.38 (m, 40H, CH_2); 0.92 (t, 6H, CH_3).

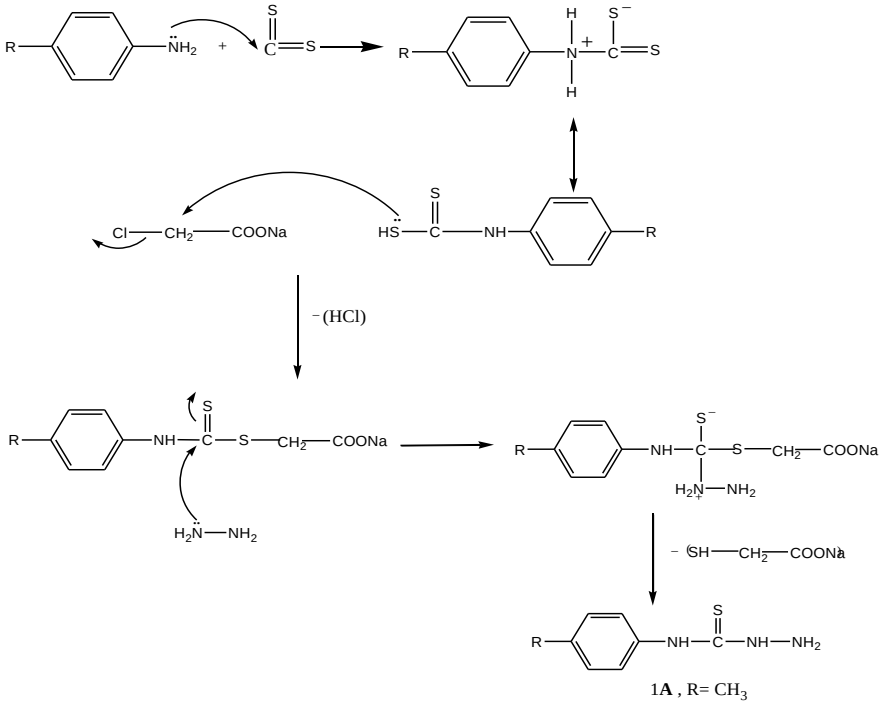
3,4-bis(hexadecyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**E**): This compound was obtained as yellowish-white crystalline solid, yield 70%, m.p. 103°-104°C, soluble in $CHCl_3$. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.49 (s, 1H, NH); 9.05 (s, 1H, NH); 7.80 (s, 1H, CH=N); 7.51 (d, J= 7.2 Hz, 2H, aromatic); 7.25-7.16 (m, 4H, aromatic); 6.91 (d, J= 8.4 Hz, 1H, aromatic); 4.08 (t, 4H, OCH_2); 2.38 (s, 3H, d); 1.88 (m, 4H, CH_2); 1.51 (m, 4H, CH_2); 1.37 (m, 48H, CH_2); 0.92 (t, 6H, CH_3).

3,4-bis(octadecyloxy)benzal-[4-(p-tolyl)] thiosemicarbazone (3**F**): This compound was obtained as yellowish-white crystalline solid, yield 83%, m.p. 104°-105°C, soluble in $CHCl_3$. ^{1}H-NMR ($CDCl_3$, 400 MHz, δ, ppm): 9.35 (s, 1H, NH); 9.06 (s, 1H, NH); 7.78 (s, 1H, CH=N); 7.52 (d, J= 8 Hz, 2H, aromatic); 7.32-7.16 (m, 4H, aromatic); 6.91 (d, J= 4.4 Hz, 1H,

aromatic); 4.07 (t, 4H, OCH_2); 2.39 (s, 3H, d); 1.89 (m, 4H, CH_2); 1.50 (m, 4H, CH_2); 1.37 (m, 56H, CH_2); 0.91 (t, 6H, CH_3).

Results and discussion

The compound 4-(*p*-tolyl) thiosemicarbazide (1**A**) was prepared in around 50% yield by the reaction of *p*-toluidine with ammonium hydroxide, carbon disulfide, sodium chloroacetate and finally with hydrazine hydrate. The proposed mechanism of this reaction was described by Fusco and Justoni and was shown in scheme 1.



Scheme 1: The mechanism of formation of compound (1**A**).

The FT-IR spectrum of the compound (1**A**) showed absorption bands at 3298 and 3194 cm^{-1} (m, -NH str.), 3040 cm^{-1} (aromatic, -CH str.), 2963 and 2913 cm^{-1} (aliphatic, -CH str.), absorption bands in the region 1312-1302 cm^{-1} (-C=S str.) and 1278- 1201 cm^{-1} (-C-N str.). The bands at 807 cm^{-1} corresponds to the para-substituted benzene ring. ^{1}H-NMR spectrum of this compound (1**A**) showed signals at δ (9.58 and 9.0 ppm) due to NH protons

and a broad signal at δ 4.73 ppm due to the NH_2 protons. The symmetric peaks at δ (7.48 and 7.11 ppm) could be assigned the protons of para-substituted benzene ring. These spectral data confirm the structure of compound (1**A**).

3,4-bis(alkyloxy)benzaldehydes 2(**A**-**F**) were prepared in good yields by the reaction of 3,4-dihydroxybenzaldehyde with corresponding n-alkyl bromides in dry acetone in the presence of anhydrous K_2CO_3. The FI-IR spectra of compounds 2(**A**-**F**) showedabsorption bands at 3030 cm^{-1} (aromatic, -CH str.), 2956, 2873 cm^{-1} (methyl, -CH str.) and 2917, 2850 cm^{-1} (methylene, -CH str.). The sharp band at 1687 cm^{-1} for C=O absorption and 1597 cm^{-1} for C=C (aromatic) absorption.The absorption frequencies at 808 and 730 cm^{-1} could be attributed to para- and meta-substituted benzene ring.^{1}H-NMR spectra of these compounds showed a singlet at δ 9.85 ppm for aldehydic proton, signals at δ 7.45 (dd, J= 8, 2.0 Hz), 7.41 (d, J=2.0 Hz) and 6.98 ppm (d, J=8.2 Hz) could be observed for aromatic protons, a multiplet δ 4.09 ppm for OCH_2 protons and other multiplets for methylene protons, signals δ 0.92 ppm for methyl protons.

Table 1: The FT-IR spectral data of all compounds 3(**A**-**F**).

Comp. No.	Ar-CH cm^{-1} stretching	R-CH cm^{-1} stretching	C=O cm^{-1} stretching	C=N cm^{-1} stretching	C=S cm^{-1} stretching	C-N cm^{-1} stretching	para- and meta-substitution
3**A**	3048	2952,2857	1596	1559	1320	1269	810,724
3**B**	3039	2952,2850	1597	1558	1322	1253	811,722
3**C**	3030	2951,2849	1596	1556	1324	1267	809, 721
3**D**	3030	2951,2848	1596	1563	1321	1233	810,722
3**E**	3044	2951,2849	1598	1554	1343	1265	807,726
3**F**	3029	2951,2848	1601	1558	1330	1231	810,721

3,4-bis(alkyloxy)benzal-[4-(*p*-tolyl)] thiosemicarbazones 3(**A**-**F**) were synthesized by the condensation reaction of compounds 2(**A**-**F**) with 4-(*p*-tolyl) thiosemicarbazide (1**A**) in ethanol in presence of conc. hydrochloric acid. The characteristic FI-IR absorption bands of compounds 3(**A**-**F**) showed the disappearance of two absorption bands due to NH_2 group which was observed for compound (1**A**). The C-H stretching absorption bands near (2951 and 2849 cm^{-1}), 1596 cm^{-1} (aromatic, C=C str.), C=N

stretching bands near 1554 cm^{-1} and C=S stretching bands near 1320 cm^{-1}. The FT-IR spectral data of all compounds 3(**A**-**F**) are listed in table 1.

^{1}H-NMR spectra of compounds 3(**A**-**F**) showed signals at δ (9.55 and 9.05 ppm) due to NH protons, singlet at δ 7.81 ppm for CH=N proton. Dubletsat δ 7.53 and 6.91 ppm for Ar-H , other aromatic protons at 7.26-7.15 ppm gave a multiplet. A triplet at δ 4.07 ppm could be assigned to OCH_2 protons, multiplets for methylene protons, signals δ 0.92 ppm for methyl protons.

Microscopic view and thermal behavior

The thermal behavior of the synthesized thiosemicarbazones was examined under polarizing microscope fitted with a cold and hot stage. When heated under polarizing microscope all the compounds were found to melt to isotropic liquid without forming any liquid crystal phase. Typical pattern of crystals growth from isotropic melt could be observed when cooling from the isotropic liquid under polarizing microscope which led us to conclude that these compounds 3(**A**-**F**) were non liquid crystalline. The liquid crystalline properties of these compounds depend on the number of alkoxy chains, the length of the alkoxy chains as well as the position of the alkoxy chains in the aromatic ring. It seems that the addition of flexible side chains at the benzal-benzene moiety could not stabilize the liquid crystal phase as the dialkoxy substituents in the aromatic portion broaden the molecule to a large extent.

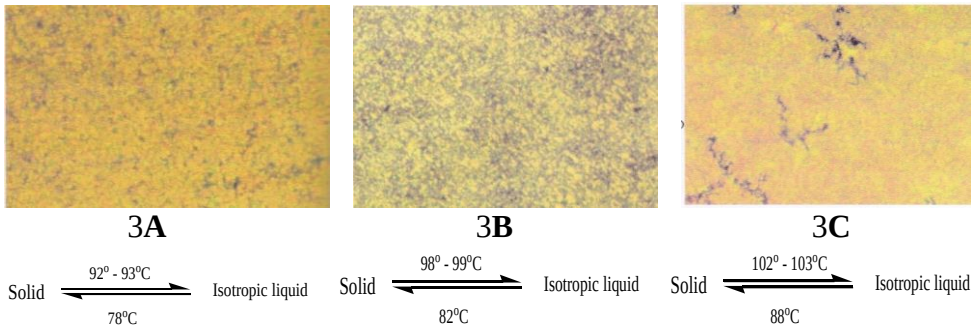


Figure 1: Microscopic view and thermal behaviorof compounds 3**A**, 3**B** and 3**C**.

Conclusion

The compounds 3,4-bis(alkyloxy)benzal-[4-(*p*-tolyl)] thiosemicarbazones were prepared from 4-(*p*-tolyl) thiosemicarbazide and 3,4-bis (alkyloxy)

benzaldehydes. The synthetic route started from the nucleophilic addition reaction between aromatic amine and CS_2 in presence of sodium chloroacetate followed by the addition of hydrazine hydrate to obtain thiosemicarbazide. 3,4-bis(alkyloxy)benzaldehydes were prepared from 3,4-dihydroxybenzaldehyde with corresponding n-alkyl bromides in dry acetone in the presence of anhydrous K_2CO_3. All synthesized compounds were characterized with the help of different spectroscopic techniques. The thermal behavior of the synthesized thiosemicarbazones was examined under polarizing microscope to observe the liquid crystalline properties.

Acknowledgments

We gratefully acknowledge the cooperation extended byWazed Miah Science Research Centre (WMSRC) at Jahangirnagar University, Dhaka, Bangladesh for recording ^{1}H NMR and IR spectra which made this study possible.

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