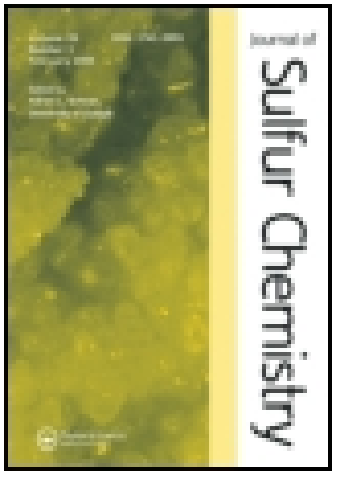

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Synthesis of some new 5-substituted-3-phenyl-4-thioxo-2-thiazolidinones and their fused thiopyrano[2,3-d]thiazole derivatives

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Synthesis of some new 5-substituted-3-phenyl-4-thioxo-2-thiazolidinones and their fused thiopyrano[2,3-*d*]thiazole derivatives

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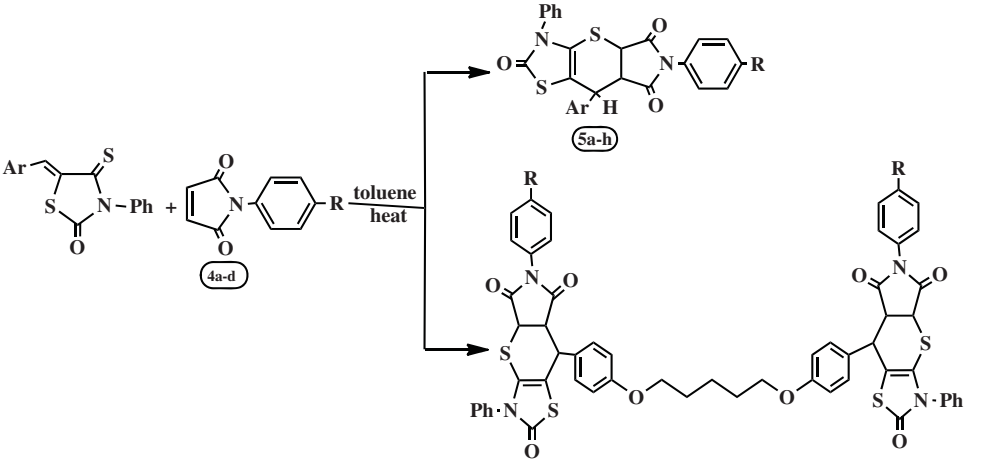
The new 5-arylmethylene-3-phenyl-4-thioxo-2-thiazolidinone derivatives have been synthesized by condensation of *ω*-(4-formylphenoxy)acetophenone derivatives with 3-phenyl-4-thioxo-2-thiazolidinone, in good yields. The cycloaddition of the newly synthesized compounds to *N*-arylmaleimides, ethyl acrylate and *ω*-nitrostyrene has been studied. Under thermal reaction conditions [4 + 2] cycloaddition proceeds with complete site- and regioselectivity to yield the new fused thiopyrano[2,3-d]thiazole derivatives.



Keywords: *ω*-(4-formylphenoxy)acetophenones; 3-phenyl-4-thioxo-2-thiazolidinone; [4 + 2] cycloaddition reaction; 5-[(4-benzoylmethoxy)phenylmethylene]-3-phenyl-4-thioxo-2-thiazolidinones; thiopyrano[2,3-*d*]-thiazoles

1. Introduction

As a part of the general interest in heterocyclic synthesis that have been explored for developing pharmaceutically important compounds, thiazolidinones have been studied extensively due to their ready accessibility, diverse chemical reactivity and broad spectrum of biological

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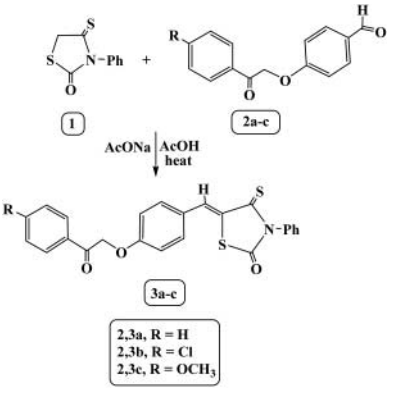
activity.[1–10] Recently, it was established, that the modified 5-substituted thiazolidinone derivatives exhibited diverse pharmacological activities.[11–13] In addition, thiopyrano[2,3-*d*]thiazole derivatives are considered as novel anticancer lead compounds.[14–17] Also, heterocyclic systems having both thiazolidine and thiopyrano moieties have important applications in the field of medicinal chemistry.[18–20] Our objective is that 3-phenyl-4-thioxo-2-thiazolidinones are synthetic precursors of thiopyrano[2,3-*d*]thiazole compounds, which could imitate some pharmacologically important molecular fragments of thiazolidinones. In continuation of our previous studies on 4-thioxo-2-thiazolidines,[21–27] we report here the synthesis of some new thiopyrano[2,3-*d*]thiazole derivatives, starting from *ω*-(4-formylphenoxy)acetophenone derivatives and 3-phenyl-4-thioxo-2-thiazolidunone.

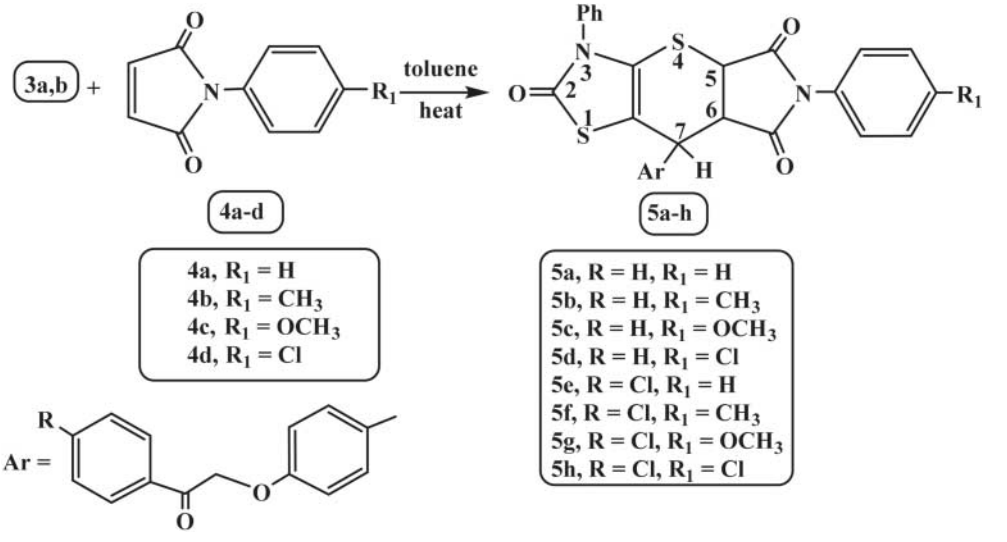
2. Results and discussion

Knoevenagel condensation of 3-phenyl-4-thioxo-2-thiazolidinone 1 with *ω*-(4-formylphenoxy) acetophenone derivatives **2a–2c** in glacial acetic acid afforded colored products **3a–3c** (Scheme 1). The structures of the isolated products **3a–3c** were established by elemental analysis and spectral data. For example, the IR spectrum of **3a** showed absorption bands at ν_{max} 1713, 1681 cm^{-1} due to CO groups, in addition to other absorption bands correlated to the assigned structure. ^{1}H NMR spectrum revealed a singlet signal at $\delta = 5.76$ ppm due to methylene protons and a singlet signal at $\delta = 8.32$ ppm due to vinylic proton besides the other expected signals for aromatic protons. In addition, an evidence to support the structural assignment was gained from the ^{13}C NMR spectrum of the same compound which showed two characteristic signals at $\delta = 71.3$ and 194.1 attributed to methylene and carbonyl carbon atoms. In addition, two characteristic signals at $\delta = 171.4$ and 193.8 assigned to the carbonyl and the thiocarbonyl carbon atoms of thiazolidine ring, respectively, besides the other expected signals.

Also, our study is extended to explore the utility of compounds **3a–3c** in the Diels–Alder reaction with different dienophiles. Thus, heating equimolar amounts of colored compounds **3a,b** with *N*-arylmaleimides **4a–4d** in toluene gave adducts **5a–5h** (Scheme 2). The IR spectrum of the isolated product **5b** taken as a typical example of the prepared series, showed absorption bands at ν_{max} 1765, 1716 and 1658 cm^{-1} corresponding to CO groups. Furthermore, the ^{1}H NMR spectrum of this adduct showed two doublets at $\delta = 4.0$ ppm with J values = 8.7 and 5.7 Hz attributed to H-6, in addition to two doublets at $\delta = 4.50$ and 5.21 ppm with J values = 5.7 and 8.7 Hz, respectively, assigned to H-5 and H-7, besides the other expected signals. The new adducts **5a–5h** showed only one isomer in the ^{1}H NMR spectra (see exp.) and the



Scheme 1. Synthesis of compounds **3a–3c**.

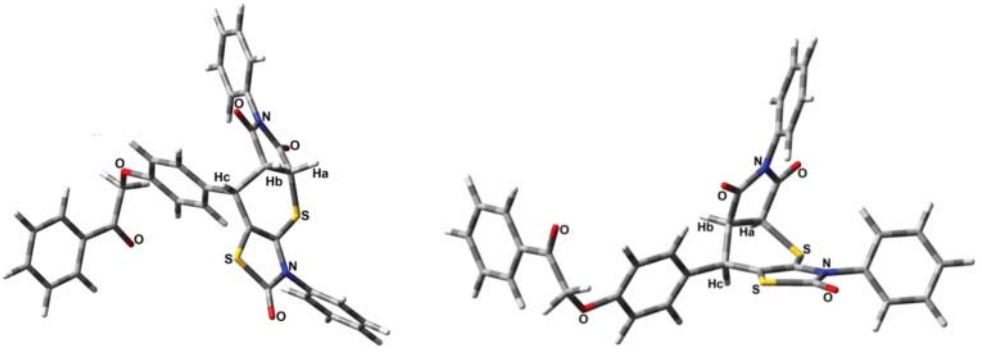


Scheme 2. Synthesis of compounds **5a–5h**.

isolated adduct **5a** studied by density functional theory (DFT). Thus, the geometrical structure of compound **5a** has been fully optimized at the B3LYP/6-31G(d) level of DFT theory. The optimized geometries of the lowest energy *endo* and *exo* adducts are depicted in Figure 1. The corresponding total and relative energies in vacuum and in acetic acid are given. It is obvious that the exo-cycloadduct is more stable than the endo-cycloadduct by about 0.89 and 0.78 kcal/mol in vacuum and in acetic acid, respectively.

Based on the above collective data, the structure **5** was assigned for the isolated products.

Similarly, cycloaddition of **3a,b** with acrylonitrile **6a** and ethyl acrylate **6b** in refluxing toluene gave the corresponding thiopyrano[2,3-*d*]thiazole derivatives **7a–7d** (Scheme 3). The structures of **7a–7d** were assigned on the basis of the obtained elemental analysis and spectral data (see exp.). The formation of compounds **7a–7d** can be explained in terms of [4 + 2] cycloaddition to conjugated thiocarbonyl moiety.



exo isomer: E = -2592.08780 a.u

(vacuum) = -2592.10538 a.u. (acetic acid)

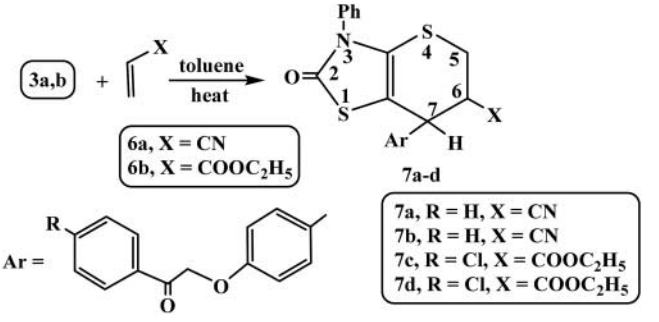
ΔE = 0.0 kcal/mol

endo isomer: E = -2592. 08639 a.u.

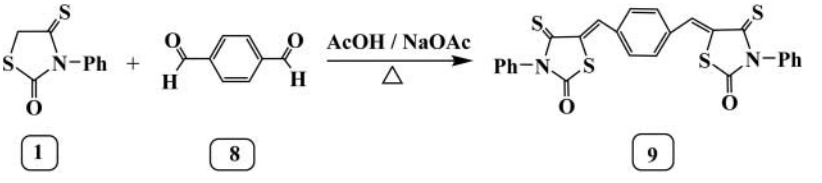
(vacuum) = -2592.10413 a.u. (acetic acid)

ΔE = 0.89 (0.78) kcal/mol

Figure 1. Optimized geometries of the lowest energy endo and exo adducts of 5a.



Scheme 3. Synthesis of compounds **7a–7d**.



Scheme 4. Synthesis of compound **9**.

Also, 3-phenyl-4-thioxo-2-thiazolidineone **1** undergoes condensation with terephthaldehyde **8** in glacial acetic acid and in the presence of sodium acetate in 2:1 molar ratio to afford compound **9** in good yield (Scheme 4).

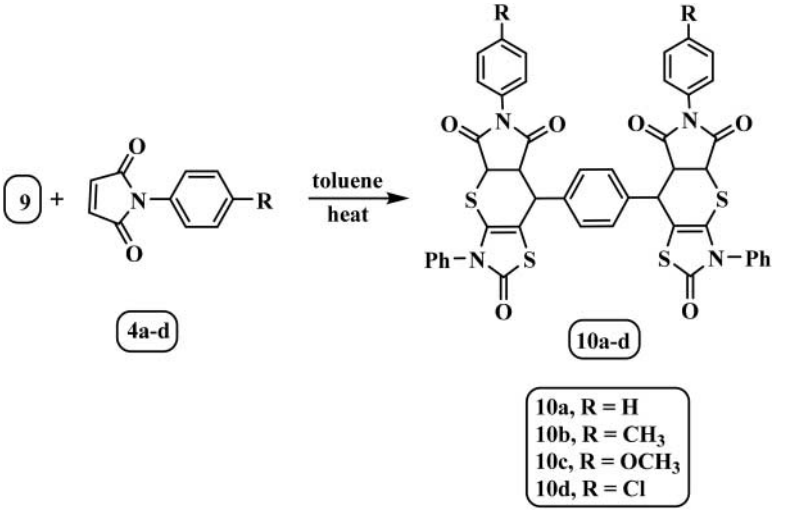
The structure of the isolated product **9** was established by the elemental analysis and spectral data. IR spectrum of **9** showed absorption band ν_{max} 1680 cm^{-1} due to the carbonyl group. It's ^{1}H NMR spectrum revealed a singlet signal at $\delta = 8.34$ ppm due to vinylic protons. The mass spectrum showed correct molecular ion peak at $m/z = 516$ (M^+). The [4 + 2] cycloaddition reaction of compound **9** with some dienophiles was also investigated. Thus, refluxing of **9** with *N*-arylmaleimides **4a–4d** in 1:2 molar ratio in acetic acid gave adducts **10a–10d** (Scheme 5). The structure of the adducts was confirmed on the basis of their elemental analysis and spectral data (see exp.)

Similarly, the reaction of **9** with acrylonitrile **6a** and ethylacrylate **6b** under the same reaction conditions gave colorless cycloadducts **11a,b** (Scheme 6). The structure of the adducts was confirmed on the basis of their elemental analysis and spectral data (see exp.).

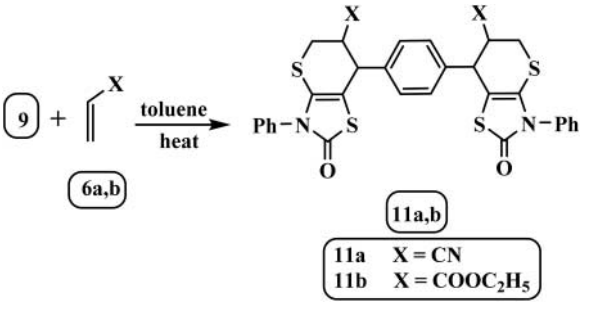
Condensation of 1 with 4,4′-(pentane-1,5-diylbisoxy)dibenzaldehyde **12** in glacial acetic acid in the presence of sodium acetate in 1:1 or 1:2 molar ratio gave a mixture of mono- and bis-3-phenyl-4-thioxo-2-thiazolidinone derivative **13** and **14**, respectively, which were separated by crystallization from ethanol (Scheme 7).

Some reactions were performed on mono- and bis-3-phenyl-4-thioxo-2-thiazolidinones. Thus, compound **14** undergoes [4 + 2] cycloaddition reaction in refluxing toluene in 1:2 molar ratio with some dienophiles such as *N*-arylmaleimides **4a–4d**, acrylonitrile **6a** and ethylacrylate **6b** afforded the bis-adducts **15** and **16**, respectively (Scheme 8). The structure of the isolated bis-adducts was confirmed based on their elemental analysis and spectral data (see exp.).

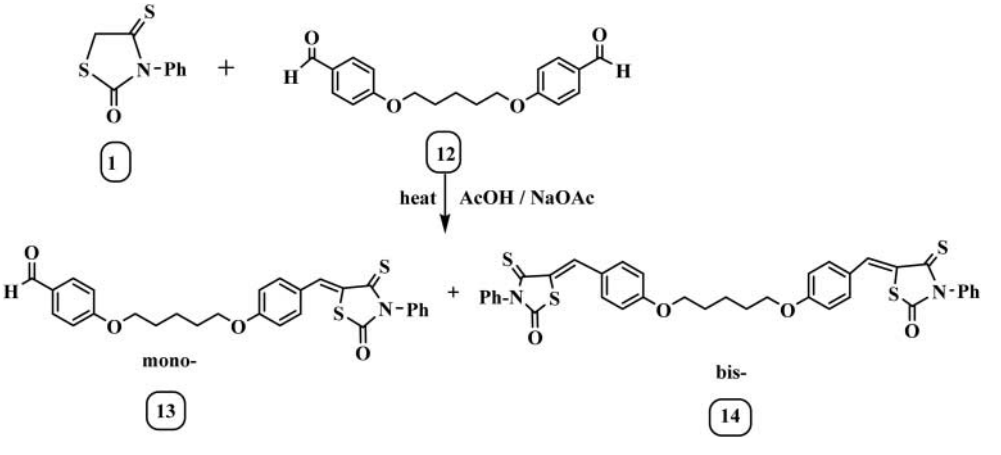
All the new adducts **7**, **10**, **11**, **15** and **16** showed only one isomer in the ^{1}H NMR spectra (see exp.) and this seems logic, since the endo-cycloadduct is obtained as a kinetically controlled product at room temperature, but under thermal conditions it is transformed into the exo-cycloadduct which is a thermally stable controlled product.



Scheme 5. Synthesis of compounds **10a–10d**.

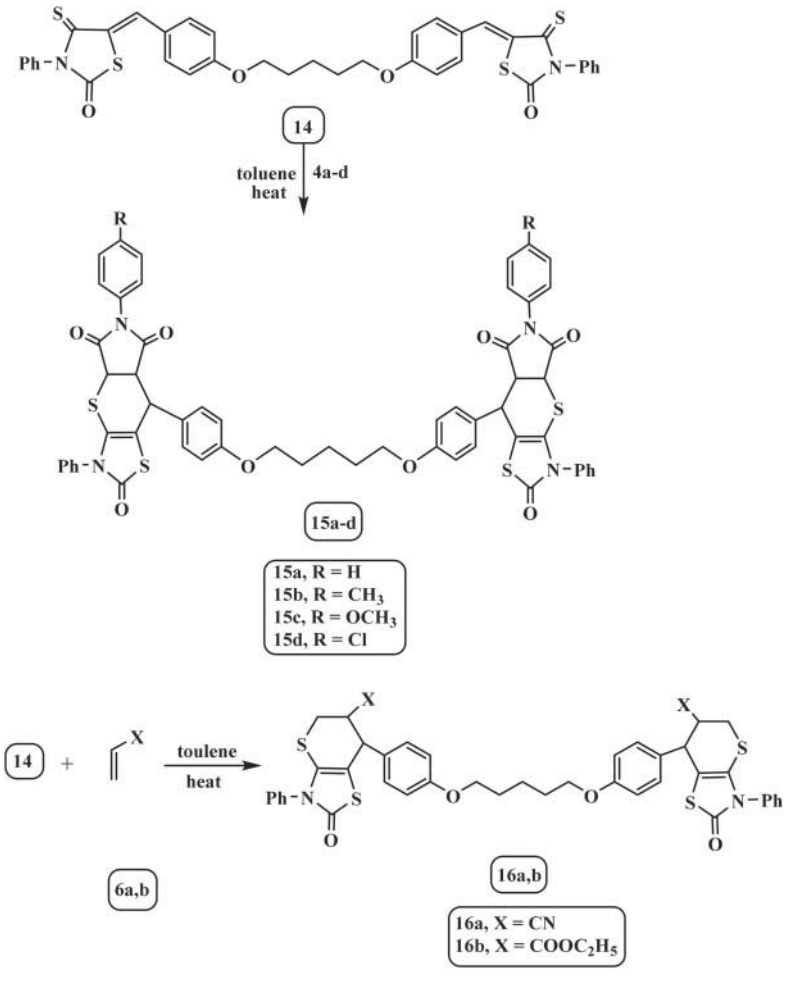


Scheme 6. Synthesis of compounds **11a**,**b**.

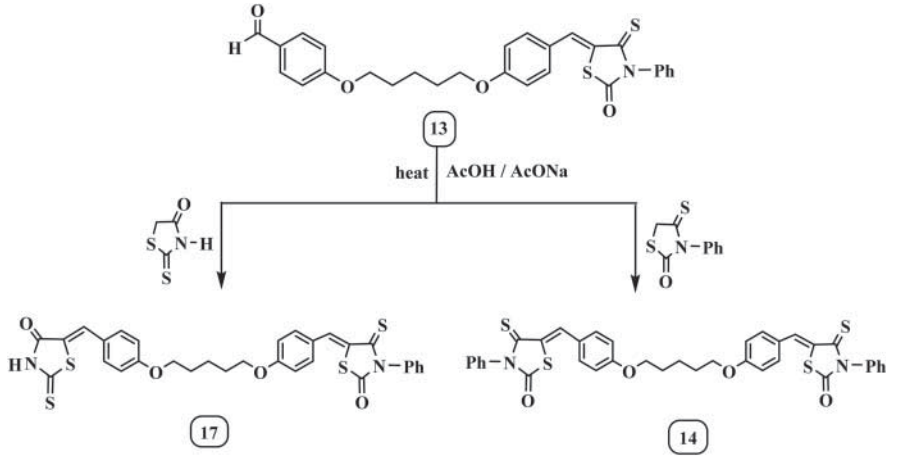


Scheme 7. Synthesis of compounds **13** and **14**.

Moreover, mono 5-arylmethylene-3-phenyl-4-thioxo-2-thiazolidinone derivative **13** condensed with some active methylene compounds such as 2-thioxo-4-thiazolidinone and 3-phenyl-4-thioxo-2-thiazolidinone to give compounds **17** and **14**, respectively (Scheme 9). The



Scheme 8. Synthesis of compounds **15a–15d** and **16a,b**.



Scheme 9. Synthesis of compounds **17** and **14**.

structure of products **17** and **14** was established on their elemental analysis and spectral data (see exp.).

3. Conclusion

The method reported here describes the synthesis of 5-(4-(2-(aryl)-2-oxoethoxy)benzylidene)-3-phenyl-4-thioxothiazolidin-2-ones **3a–3c** and reaction of latter compounds with *N*-arylmaleimides **4a–4d** in glacial acetic acid underwent 4 + 2-cycloaddition reaction to give 1:1 cycloadducts **5a–5h**. Also, the method describes the reaction of bis-3-phenyl-4-thioxo-4-thioxo-2-thiazoldinones with some different dienophiles in refluxing toluene to give the bis-cycloadducts.

4. Experimental

All melting points were determined on an Electrothermal (9100) apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Perkin Elmer 1430 spectrophotometer. ^{1}H NMR spectra were recorded in deuterated dimethylsulfoxide at 300 MHz on a Varian Gemini NMR spectrometer using tetramethylsilane as the internal reference and results are expressed as δ values. ^{13}C NMR spectra were recorded in dimethylsulfoxide (DMSO-d_6) at 75.46 MHz on a Varian Mercury VXR-300 NMR spectrometer using tetramethylsilane as the internal reference and results are expressed as δ values. Mass spectra were taken on a Shimadzu GCMS-QP 1000 Ex mass spectrometer at 70 eV. Elemental analyses were carried out at the Microanalysis Center of Cairo University. The starting compounds **2a–2c**, and **12** were prepared according to lit.[26,29]

4.1. *Preparation of 3-phenyl-4-thioxo-2-thiazolidinone 1*

A mixture of 3-phenyl-2,4-thiazolidinedione (0.25 mol) and 20 g of phosphorus pentasulfide was refluxed for 3 h in 200 ml dry dioxane. The mixture was filtered off and the dioxane was distilled under reduced pressure to give pale yellow crystals of m.p. 110°C of compound **1**.[28]

4.2. *Preparation 5-(4-(2-(aryl)-2-oxoethoxy)benzylidene)-3-phenyl-4-thioxothiazolidin-2-one 3a–3c*

4.2.1. *General procedure*

To a solution of 1 (0.01 mol) in glacial acetic acid (25 ml) and fused sodium acetate (1.64 g, 0.02 mol), the appropriate aldehyde **2a–2c** (0.01 mol) was added. The reaction mixture was refluxed for 30 min on a water bath, cooled and then poured into cold water. The solid so formed was filtered off and recrystallized from an ethanol and dioxane mixture to give compounds **3a–3c**.

4.2.1.1. *5-[4-(2-Oxo-2-phenylethoxy)benzylidene]-3-phenyl-4-thioxo-2-thiazolidinone (**3a**).* Orange crystals (88%); m.p. 213°C; ν_{max}/cm^{-1} (KBr) 1713, 1681 (CO); ^{1}H NMR (DMSO-d_6) δ = 5.76 (s, 2H, CH_2), 7.18-8.05 (m, 14H, Ar), 8.32 (s, 1H, CH). ^{13}C NMR (DMSO-d_6) δ = 71.3, 115.0, 126.7, 127.8, 128.3, 128.6, 128.8, 129.0, 131.0, 132.7, 133.9, 134.2, 135.3, 146.8, 160.3, 171.4, 193.8 and 194.1. Anal. Calcd $C_{24}H_{17}NO_3S_2$ (431.52): C, 66.80; H, 3.97; N, 3.25; S, 14.86. Found: C, 66.96; H, 3.77; N, 3.48; S, 14.67.

4.2.1.2. *5-[4-(2-(4-Chlorophenyl)-2-oxoethoxy)benzylidene]-3-phenyl-4-thioxo-2-thiazolidinone (**3b**).* Orange crystals (72%); m.p. 242°C; ν_{max}/cm^{-1} (KBr) 1713, 1681 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 5.73$ (s, 2H, CH_2), 7.11–8.10 (m, 13H, Ar), 8.31 (s, 1H, CH). Anal. Calcd $C_{24}H_{16}ClNO_3S_2$ (465.97): C, 61.86; H, 3.46; Cl, 7.61; N, 3.01; S, 13.76. Found: C, 61.67; H, 3.64; Cl, 7.79; N, 3.28; S, 13.58.

4.2.1.3. *5-[4-(2-(4-Methoxyphenyl)-2-oxoethoxy)benzylidene]-3-phenyl-4-thioxo-2-thiazolidinone (**3c**).* Orange crystals (80%); m.p. 255°C; ν_{max}/cm^{-1} (KBr) 1725, 1692 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 3.97$ (s, 3H, OCH_3), 5.70 (s, 2H, CH_2), 7.17–8.24 (m, 13H, Ar), 8.31 (s, 1H, CH). *m/z* = 462 ($M^+ + 1$, 4.7%), 399 (4.5%), 313 (10.3%), 284 (7.1%), 212 (100%), 165 (7.1%), 121 (31.8%), 91 (17.5%), 77 (98.9%). Anal. Calcd $C_{25}H_{19}NO_4S_2$: C, 65.06; H, 4.15; N, 3.03; S, 13.89. Found: C, 65.25; H, 4.34; N, 3.26; S, 13.71.

4.3. *Preparation of compounds 5a–5h and 7a–7d*

4.3.1. *General procedure*

A solution of equimolecular amounts (0.01 mol) of each of **3a,b** and the appropriate dienophile in toluene (30 ml) was refluxed for 1 h. The solid so formed was filtered off and recrystallized from an ethanol and dioxane mixture. The physical constants together with spectral data of compounds **5a–5h** and **7a–7d** are shown below.

4.3.1.1. *8-[4-(2-Oxo-2-phenylethoxy)phenyl]-3,6-diphenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]-thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5a**).* White crystals (59%); m.p. 162°C; ν_{max}/cm^{-1} (KBr) 1776, 1711, 1660 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 4.0$ (dd, 1H, $J = 8.7, 5.7$ Hz, H-6), 4.58 (d, 1H, $J = 5.7$ Hz, H-5), 5.17 (d, 1H, $J = 8.7$ Hz, H-7), 5.61 (s, 2H, CH_2), 6.66–8.05 (m, 19H, Ar). *m/z* = 605 ($M^+ + 1$, 3.4%), 542 (3.7%), 474 (2.9%), 400 (3.3%), 312 (11.5%), 222 (3.8%), 173 (6.4%), 131 (5.1%), 105 (100%), 77 (74.9%). Anal. Calcd $C_{34}H_{24}N_2O_5S_2$: C, 67.53; H, 4.00; N, 4.63; S, 10.60. Found: C, 67.35; H, 4.18; N, 4.86; S, 10.44.

4.3.1.2. *8-[4-(2-Oxo-2-phenylethoxy)phenyl]-6-(4-methyl-phenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5b**).* Whitish yellow crystals (58%); m.p. 145°C; ν_{max}/cm^{-1} (KBr) 1765, 1716, 1658 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 2.31$(s, 3H, CH_3), 4.01 (dd, 1H, $J = 8.7, 5.7$ Hz, H-6), 4.50 (d, 1H, $J = 5.7$ Hz, H-5), 5.21 (d, 1H, $J = 8.7$ Hz, H-7), 5.58 (s, 2H, CH_2), 6.51–7.88 (m, 18H, Ar). Anal. Calcd $C_{35}H_{26}N_2O_5S_2$ (618.72): C, 67.94; H, 4.24; N, 4.53; S, 10.36. Found: C, 67.75; H, 4.44; N, 4.79; S, 10.17.

4.3.1.3. *6-(4-Methoxyphenyl)-8-[4-(2-oxo-2-phenylethoxy)phenyl]-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5c**).* Pale brown crystals (61%); m.p. 167°C; ν_{max}/cm^{-1} (KBr) 1779, 1710, 1665 (CO);^{1}H NMR (DMSO-d_6) $\delta = 3.74$ (s, 3H, OCH_3), 4.04 (dd, 1H, $J = 8.7, 5.7$ Hz, H-6), 4.55 (d, 1H, $J = 5.7$ Hz, H-5), 5.23 (d, 1H, $J = 8.7$ Hz, H-7), 5.63 (s, 2H, CH_2), 6.54–8.04 (m, 18H, Ar). Anal. Calcd $C_{35}H_{26}N_2O_6S_2$ (634.72): C, 66.23; H, 4.13; N, 4.41; S, 10.10. Found: C, 66.04; H, 4.32; N, 4.66; S, 10.30.

4.3.1.4. *6-(4-Chlorophenyl)-8-[4-(2-oxo-2-phenylethoxy)phenyl]-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5d**).* White crystals (64%); m.p. 175°C; ν_{max}/cm^{-1} (KBr) 1781, 1711, 1668 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 4.04$ (dd, 1H, $J = 8.1, 5.7$ Hz, H-6), 4.59 (d, 1H, $J = 5.7$ Hz, H-5), 5.34 (d, 1H, $J = 8.1$ Hz, H-7),

5.63 (s, 2H, CH_2), 6.70–8.08 (m, 18H, Ar). *m/z* = 639 ($M^+ + 1$, 5.9%), 584 (6.9%), 541 (6.8%), 483 (4.7%), 387 (4.4%), 338 (6.0%), 257 (5.9%), 207 (22.5%), 151 (8.3%), 105 (100%), 77 (75.4%). Anal. Calcd $C_{34}H_{23}ClN_2O_5S_2$: C, 63.89; H, 3.63; Cl, 5.55; N, 4.38; S, 10.03. Found: C, 64.08; H, 3.45; Cl, 5.76; N, 4.66; S, 10.20.

4.3.1.5. *8-[4-(2-(4-Chlorophenyl)-2-oxoethoxy)phenyl]-3,6-diphenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5e**).* Whitish yellow crystals (54%); m.p. 159°C; ν_{max}/cm^{-1} (KBr) 1780, 1713, 1661 (CO); ^1H NMR (DMSO-d_6) δ = 4.03 (dd, 1H, *J* = 8.4, 6.3 Hz, H-6), 4.59 (d, 1H, *J* = 6.3 Hz, H-5), 5.35 (d, 1H, *J* = 8.4 Hz, H-7), 5.61 (s, 2H, CH_2), 6.65–8.11 (m, 18H, Ar). Anal. Calcd $C_{34}H_{23}ClN_2O_5S_2$ (639.14): C, 63.89; H, 3.63; Cl, 5.55; N, 4.38; S, 10.03. Found: C, 63.71; H, 3.46; Cl, 5.74; N, 4.55; S, 10.21.

4.3.1.6. *8-[4-(2-(4-Chlorophenyl)-2-oxoethoxy)phenyl]-3-phenyl-6-(4-methyl-phenyl)-3,4a, 7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5f**).* Pale yellow crystals (58%); m.p. 163°C; ν_{max}/cm^{-1} (KBr) 1776, 1713, 1667 (CO); ^1H NMR (DMSO-d_6) δ = 2.36 (s, 3H, CH_3), 4.05 (dd, 1H, *J* = 9, 6 Hz, H-6), 4.63 (d, 1H, *J* = 6 Hz, H-5), 5.23 (d, 1H, *J* = 9 Hz, H-7), 5.67 (s, 2H, CH_2), 6.67-8.15 (m, 17H, Ar). Anal. Calcd $C_{35}H_{25}ClN_2O_5S_2$ (653.16): C, 64.36; H, 3.86; Cl, 5.43; N, 4.29; S, 9.82. Found: C, 64.16; H, 3.69; Cl, 5.60; N, 4.55; S, 9.99.

4.3.1.7. *8-[4-(2-(4-Chlorophenyl)-2-oxoethoxy)phenyl]-6-(4-methoxyphenyl)-3-phenyl-3,4a, 7a,8-tetraydropyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5g**).* Pale yellow crystals (60%); m.p. 181°C; ν_{max}/cm^{-1} (KBr) 1778, 1713, 1668 (CO); ^1H NMR (DMSO-d_6) δ = 3.86 (s, 3H, OCH_3), 4.18 (dd, 1H, *J* = 9, 5.4 Hz, H-6), 4.66 (d, 1H, *J* = 5.4 Hz, H-5), 5.27 (d, 1H, *J* = 9 Hz, H-7), 5.65 (s, 2H, CH_2), 6.70–8.17 (m, 17H, Ar). Anal. Calcd $C_{35}H_{25}ClN_2O_6S_2$ (669.16): C, 62.82; H, 3.77; Cl, 5.30; N, 4.19; S, 9.58. Found: C, 63.0; H, 3.60; Cl, 5.48; N, 4.45; S, 9.38.

4.3.1.8. *6-(4-Chlorophenyl)-8-[4-(2-(4-chlorophenyl)-2-oxoethoxy)phenyl]-3-phenyl-3,4a,7a, 8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione (**5h**).* Pale yellow crystals (64%); m.p. 200°C; ν_{max}/cm^{-1} (KBr) 1783, 1712, 1660 (CO); ^1H NMR (DMSO-d_6) δ = 4.23 (dd, 1H, *J* = 9, 6 Hz, H-6), 4.67 (d, 1H, *J* = 6 Hz, H-5), 4.84 (d, 1H, *J* = 9 Hz, H-7), 5.64 (s, 2H, CH_2), 6.69–8.18 (m, 17H, Ar). Anal. Calcd $C_{34}H_{22}Cl_2N_2O_5S_2$ (673.58): C, 60.63; H, 3.29; Cl, 10.53; N, 4.16; S, 9.52. Found: C, 60.44; H, 3.46; Cl, 10.35; N, 4.38; S, 9.70.

4.3.1.9. *2-Oxo-7-[4-(2-oxo-2-phenylethoxy)phenyl]-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano-[2,3-d]thiazole-6-carbonitrile (**7a**).* Whitish yellow crystals (56%); m.p. 215°C; ν_{max}/cm^{-1} (KBr) 2219 (CN), 1713, 1654 (CO); ^1H NMR (DMSO-d_6) δ = 3.59–3.62 (m, 2H, H-5), 4.03 (t, 1H, *J* = 5.7 Hz, H-6), 4.49 (d, 1H, *J* = 7.2 Hz, H-7), 5.66 (s, 2H, CH_2), 7.09–8.13 (m, 14H, Ar). Anal. Calcd $C_{27}H_{20}N_2O_3S_2$ (484.59): C, 66.92; H, 4.16; N, 5.78; S, 13.23. Found: C, 66.74; H, 4.33; N, 5.52; S, 13.04.

4.3.1.10. *7-(4-(2-(4-Chlorophenyl)-2-oxoethoxy)phenyl)-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano[2,3-d]thiazole-6-carbonitrile (**7b**).* Pale brown crystals (60%); m.p. 179°C; ν_{max}/cm^{-1} (KBr) 2218 (CN), 1711, 1660 (CO); ^1H NMR (DMSO-d_6) δ = 3.59–3.62 (m, 2H, H-5), 4.03 (t, 1H, *J* = 5.1 Hz, H-6), 4.49 (d, 1H, *J* = 7.2 Hz, H-7), 5.66 (s, 2H, CH_2), 7.09–8.13 (m, 13H, Ar). Anal. Calcd $C_{27}H_{19}ClN_2O_3S_2$ (519.03): C, 62.48; H, 3.69; Cl, 6.83; N, 5.40; S, 12.35. Found: C, 62.67; H, 3.87; Cl, 6.66; N, 5.65; S, 12.19.

4.3.1.11. *Ethyl 2-oxo-7-[4-(2-oxo-2-phenylethoxy)phenyl]-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano[2,3-d]thiazole-6-carboxylate (**7c**).* Pale brown crystals (55%); m.p. 140°C; ν_{max}/cm^{-1} (KBr) 1720, 1713, 1658 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.13$ (t, 3H, $J = 7.2$ Hz, CH_3), 3.58–3.60 (m, 2H, H-5), 4.04 (t, 1H, $J = 6.3$ Hz, H-6), 3.72 (q, 2H, $J = 6$ Hz, CH_2), 4.50 (d, 1H, $J = 6.9$ Hz, H-7), 5.69 (s, 2H, CH_2), 7.06–8.16 (m, 14H, Ar). Anal. Calcd $C_{29}H_{25}NO_5S_2$ (531.64): C, 65.52; H, 4.74; N, 2.63; S, 12.06. Found: C, 65.72; H, 4.56; N, 2.87; S, 12.24.

4.3.1.12. *Ethyl 7-(4-(2-(4-chlorophenyl)-2-oxoethoxy)phenyl)-2-oxo-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano[2,3-d]thiazole-6-carboxylate (**7d**).* Pale brown crystals (58%); m.p. 109°C; ν_{max}/cm^{-1} (KBr) 1720, 1713, 1661 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.13$ (t, 3H, $J = 6.9$ Hz, CH_3), 3.58–3.60 (m, 2H, H-5), 4.04 (t, 1H, $J = 5.1$ Hz, H-6), 3.72 (q, 2H, $J = 6$ Hz, CH_2), 4.50 (d, 1H, $J = 6$ Hz, H-7), 5.69 (s, 2H, CH_2), 7.06–8.16 (m, 13H, Ar). *m/z* = 566 ($M^+ + 1$, 3.5%), 466 (6.1%), 391 (4.5%), 312 (11.2%), 236 (6.1%), 207 (9.2%), 135 (6.7%), 105 (100%), 77 (72.8%). Anal. Calcd $C_{29}H_{24}ClNO_5S_2$: C, 61.53; H, 4.27; Cl, 6.26; N, 2.47; S, 11.33. Found: C, 61.34; H, 4.44; Cl, 6.45; N, 2.23; S, 11.50.

4.4. *Preparation of 5,5′-[1,4-phenylenebis(methanylylidene)]bis(3-phenyl-4-thioxo-2-thiazolidinone) (9)*

To a solution of 1 (0.02 mol) in glacial acetic acid (25 ml) and anhydrous sodium acetate (1.64 g, 0.02 mol) terephthaldehyde 8 (0.01 mol) was added. The reaction mixture was refluxed for 30 min cooled and then poured into cold water. The solid so formed was filtered off and recrystallized from dimethylformamide to give red crystals (83%); m.p. 290°C; ν_{max}/cm^{-1} (KBr) 1680 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 7.44$–7.94 (m, 14H, Ar), 8.34 (s, 2H, 2CH); *m/z* = 516 (M^+, 18%), 325 (46.2%), 296 (20.5%), 162 (30.8%), 122 (20.5%), 116 (17.9%), 110 (5.1%), 104 (30.8%), 89 (51.3%), 77 (43.6%), 66 (20.5%), 60 (100%). Anal. Calcd $C_{26}H_{16}N_2O_2S_4$: C, 60.44; H, 3.12; N, 5.42; S, 24.82. Found: C, 60.62; H, 3.32; N, 5.16; S, 25.01.

4.5. *Preparation of cycloadducts 10a–10d and 11a,b*

4.5.1. *General procedure*

To compound **9** (0.01 mol), suspended in glacial acetic acid (20 ml), were added *N*-arylmaleimides **4a–4d**, acrylonitrile **6a** and ethyl acrylate **6b** (0.02 mol). The mixture was refluxed for 30 min, or till decolorization took place, then it was left overnight at room temperature. The solid so formed was filtered off, and recrystallized from an ethanol and dioxane mixture.

4.5.1.1. *8,8′-(1,4-Phenylene)bis(3,6-diphenyl-3,4a,7a,8-tetrahydro-pyrrolo-[3′,4′:5,6] thiopyrano-[2,3-d]thiazole-2,5,7(6H)-trione) (**10a**).* Pale yellow crystals (65%); m.p. 215°C; ν_{max}/cm^{-1} (KBr) 1702, 1662 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 3.40$ (m, 2H, H-6, H-6′), 4.82 (d, 2H, $J = 6.3$ Hz, H-5, H-5′), 5.16 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 7.21–7.61 (m, 24H, Ar). Anal. Calcd $C_{46}H_{30}N_4O_6S_4$ (863.01): C, 64.02; H, 3.50; N, 6.49; S, 14.86. Found: C, 64.20; H, 3.69; N, 6.76; S, 14.69.

4.5.1.2. *8,8′-(1,4-Phenylene)bis(6-(4-methyl-phenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo-[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione) (**10b**).* Pale yellow crystals (60%); m.p. 222°C; ν_{max}/cm^{-1} (KBr) 1702, 1660 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 2.37$ (s, 6H, $2CH_3$), 3.38 (m, 2H, H-6, H-6′), 4.85 (d, 2H, $J = 6.3$ Hz, H-5, H-5′), 5.11 (d, 2H, $J = 8.7$ Hz, H-7, H-7′),

7.19–7.59 (m, 22H, Ar). Anal. Calcd $C_{48}H_{34}N_4O_6S_4$ (891.06): C, 64.70; H, 3.85; N, 6.29; S, 14.39. Found: C, 64.50; H, 3.68; N, 6.02; S, 14.56.

4.5.1.3. *8,8′-(1,4-Phenylene)bis(6-(4-methoxyphenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo-[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione)* ***(10c)***. Pale yellow crystals (60%); m.p. 214°C; ν_{max}/cm^{-1} (KBr) 1701, 1659 (CO);^{1}H NMR (DMSO-d_6) $\delta = 3.80$ (s, 6H, $2OCH_3$), 4.68 (m, 2H, H-6, H-6′), 5.13 (d, 2H, $J = 6.0$ Hz, H-5, H-5′), 5.15 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 6.51–7.66 (m, 22H, Ar). Anal. Calcd $C_{48}H_{34}N_4O_8S_4$ (923.06): C, 62.46; H, 3.71; N, 6.07; S, 13.89. Found: C, 62.63; H, 3.88; N, 6.30; S, 13.71.

4.5.1.4. *8,8′-(1,4-Phenylene)bis(6-(4-chlorophenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo-[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione)* ***(10d)***. Pale yellow crystals (61%); m.p. 230°C; ν_{max}/cm^{-1} (KBr) 1701, 1659 (CO); ^{1}H NMR (DMSO-d_6):$\delta = 4.75$ (m, 2H, H-6, H-6′), 5.12 (d, 2H, $J = 6$ Hz, H-5, H-5′), 5.18 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 6.53–7.70 (m, 22H, Ar). Anal. Calcd $C_{46}H_{28}Cl_2N_4O_6S_4$ (931.89): C, 59.29; H, 3.03; Cl, 7.61; N, 6.01; S, 13.76. Found: C, 59.48; H, 3.20; Cl, 7.44; N, 6.25; S, 13.94.

4.5.1.5. *7,7′-(1,4-Phenylene)bis(2-oxo-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano-[2,3-d] thiazole-6-carbonitrile)* ***(11a)***. Pale yellow crystals (56%); m.p. 210°C; ν_{max}/cm^{-1} (KBr) 2218 (CN), 1663 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 3.42$–3.47 (m, 4H, H-5, H-5′), 4.16–4.20 (m, 2H, H-6, H-6′), 4.62–4.67 (m, 2H, H-7, H-7′), 7.40–7.76 (m, 14H, Ar). Anal. Calcd. $C_{32}H_{22}N_4O_2S_4$ (622.79): C, 61.71; H, 3.56; N, 9.00; S, 20.59. Found: C, 61.89; H, 3.74; N, 9.22; S, 20.78.

4.5.1.6. *Diethyl 7,7′-(1,4-phenylene)bis(2-oxo-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano [2,3-d] thiazole-6-carboxylate) (11b).* Pale yellow crystals (52%); m.p. 195°C; ν_{max}/cm^{-1} (KBr) 1720, 1616 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.13$ (t, 6H, $J = 7.2$ Hz, $2CH_3$), 3.21–3.33 (m, 4H, H-5, H-5′), 3.38 (q, 4H, $J = 7.2$ Hz, $2CH_2$), 3.99–4.01 (m, 2H, H-6, H-6′), 4.40 (d, 2H, $J = 8.1$ Hz, H-7, H-7′), 6.90–7.82 (m, 14H, Ar). *m/z* = 716 (M^+, 17.8%), 607 (22.2%), 568 (21.6%), 453 (18.2%), 309 (48.6%), 255 (21.6%), 156 (18.2%), 103 (27.5%), 77 (100%). Anal. Calcd $C_{36}H_{32}N_2O_6S_4$: C, 60.31; H, 4.50; N, 3.91; S, 17.89. Found: C, 60.50; H, 4.67; N, 3.65; S, 17.72.

4.6. *Preparation of compounds 13 and 14*

To a solution of 1 (0.01 mol) in glacial acetic acid (25 ml) and anhydrous sodium acetate (1.64 g, 0.02 mol), 4,4′-(pentan-1-diybisoxy)dibenzaldehyde 12 (0.01 mol) was added. The reaction mixture was refluxed for 1 h, cooled and then poured into cold water. The solid so formed was filtered off and crystallized from ethanol to afford mono compound **13** and the insoluble compound is recrystallized from an ethanol and dioxane mixture to afford compound **14**.

4.6.1. *4-((5-(4-((2-Oxo-3-phenyl-4-thioxothiazolidin-5-ylidene)methyl)phenoxy)-pentyl)oxy)-benzaldehyde* ***(13)***

Orange crystals (30%); m.p. 110°C; ν_{max}/cm^{-1} (KBr) 2869 (CHO), 1714 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.81$ (m, 2H, CH_2), 1.89 (m, 4H, $2CH_2$), 4.10 (m, 4H, $2CH_2$), 7.10–7.87 (m, 13H, Ar), 8.30 (s, 1H, CH), 9.86 (s, 1H, CHO); *m/z* = 503 (M^+, 12%), 443 (12%), 415 (18.1%), 312 (38.6%), 297 (9.6%), 284 (10.8%), 193 (26.5%), 163 (21.7%), 150 (67.5%), 121 (51.8%), 105 (34.9%), 77 (61.4%), 69 (100%). Anal. Calcd. $C_{28}H_{25}NO_4S_2$: C, 66.78; H, 5.0; N, 2.78; S, 12.73. Found: C, 66.95; H, 5.20; N, 2.50; S, 12.91.

4.6.2. *5,5′-(((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))-bis(3-phenyl-4-thioxo-2-thiazolidinone) (**14**)*

Red crystals (46%); m.p. 165°C; ν_{max}/cm^{-1} (KBr) 1714 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.82$ (m, 2H, CH_2), 1.84 (m, 4H, $2CH_2$), 4.10 (m, 4H, $2CH_2$), 7.11–7.70 (m, 18H, Ar), 8.26 (s, 2H, 2CH); $m/z = 694$ (M^+, 18.8%), 380 (3.1%), 313 (10.7%), 284 (10.7%), 209 (13.8%), 193 (10.7%), 165 (3.6%), 150 (24.1%), 135 (32.1%), 119 (38.4%), 104 (37.1%), 91 (36.2%), 77 (100%). Anal. Calcd $C_{37}H_{30}N_2O_4S_4$: C, 63.95; H, 4.35; N, 4.03; S, 18.45. Found: C, 63.77; H, 4.54; N, 4.31; S, 18.65.

4.7. *Preparation of compounds 15a–15d and 16a,b*

4.7.1. *General procedure*

To compound 14 (0.01 mol), suspended in glacial acetic acid (20 ml), *N*-arylmaleimides **4a–4d**, acrylonitrile **6a** or ethyl acrylate **6b** (0.02 mol) was added. The mixture was refluxed for 30 min or till decolorization took place, then it was left overnight at room temperature. The solid so formed was filtered off and recrystallized from an ethanol and dioxane mixture.

4.7.1.1. *8,8′-((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(3,6-diphenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione) (**15a**).* Pale yellow crystals (56%); m.p. 176°C; ν_{max}/cm^{-1} (KBr) 1710, 1661 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.78$–1.80 (m, 2H, CH_2), 1.84–1.90 (m, 4H, $2CH_2$), 4.01–4.04 (m, 4H, $2CH_2$), 4.07–4.411 (m, 2H, H-6, H-6′), 4.57 (d, 2H, $J = 5.7$ Hz, H-5, H-5′), 5.16 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 6.67–7.55 (m, 28H, Ar). Anal. Calcd $C_{57}H_{44}N_4O_8S_4$ (1041.24): C, 65.75; H, 4.26; N, 5.38; S, 12.32. Found: C, 65.95; H, 4.45; N, 5.12; S, 12.49.

4.7.1.2. *8,8′-((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(3-phenyl-6-(4-methyl-phenyl)-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione) (**15b**).* Pale yellow crystals (58%); m.p. 156°C; ν_{max}/cm^{-1} (KBr) 1710, 1664 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.78$–1.80 (m, 2H, CH_2), 1.85–1.93 (m, 4H, $2CH_2$), 2.37 (s, 6H, $2CH_3$), 4.0–4.01 (m, 4H, $2CH_2$), 4.06–4.18 (m, 2H, H-6, H-6′), 4.54 (d, 2H, $J = 5.7$ Hz, H-5, H-5′), 5.14 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 6.69–7.59 (m, 26H, Ar). Anal. Calcd $C_{59}H_{48}N_4O_8S_4$ (1069.29): C, 66.27; H, 4.52; N, 5.24; S, 11.99. Found: C, 66.45; H, 4.35; N, 5.49; S, 12.18.

4.7.1.3. *8,8′-((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(6-(4-methoxyphenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione) (**15c**).* Pale yellow crystals in a yield of 56%; m.p. 160°C; IR (KBr, ν cm^{-1}):1718, 1660 (CO); ^{1}H NMR (DMSO-d_6) $\delta = 1.80$–1.86 (m, 2H, CH_2), 1.89–1.92 (m, 4H, $2CH_2$), 3.87 (s, 6H, $2OCH_3$), 4.04–4.06 (m, 4H, $2CH_2$), 4.09–4.12 (m, 2H, H-6, H-6′), 4.57 (d, 2H, $J = 5.7$ Hz, H-5, H-5′), 5.13 (d, 2H, $J = 8.7$ Hz, H-7, H-7′), 6.70–7.61 (m, 26H, Ar). Anal. Calcd. $C_{59}H_{48}N_4O_{10}S_4$ (1101.29): C, 64.35; H, 4.39; N, 5.09; S, 11.64. Found: C, 64.54; H, 4.21; N, 5.36; S, 11.48.

4.7.1.4. *8,8′-((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(6-(4-chlorophenyl)-3-phenyl-3,4a,7a,8-tetrahydro-pyrrolo[3′,4′:5,6]thiopyrano[2,3-d]thiazole-2,5,7(6H)-trione) (**15d**).* Pale yellow crystals (60%); m.p. 186°C; ν_{max}/cm^{-1} (KBr) 1716, 1618 (CO); ^{1}H NMR (DMSO-d_6):$\delta = 1.79$–1.86 (m, 2H, CH_2), 1.91–2.09 (m, 4H, $2CH_2$), 4.01–4.04 (m, 4H, $2CH_2$), 4.07–4.11 (m, 2H, H-6, H-6′), 4.61 (d, 2H, $J = 5.7$ Hz, H-5, H-5′), 5.17 (d, 2H, $J = 8.4$ Hz, H-7, H-7′), 6.73–7.62 (m, 26H, Ar); $m/z = 1108$ (M^+, 20.7%), 979 (19.2%), 693 (17.2%), 328 (20.7%),

255 (17.2%), 194 (17.2%), 127 (27.6%), 97 (34.5%), 71 (34.5%), 63 (100%). Anal. Calcd $C_{57}H_{42}Cl_2N_4O_8S_4$: C, 61.67; H, 3.81; Cl, 6.39, N, 5.05; S, 11.55. Found: C, 61.85; H, 3.63; Cl, 6.20; N, 5.32; S, 11.75.

4.7.1.5. *7,7′-((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(2-oxo-3-phenyl-3,5,6,7-tetrahydro-2H-thiopyrano[2,3-d]thiazole-6-carbonitrile) (**16a**).* Pale yellow crystals (58%); m.p. 117°C; ν_{max}/cm^{-1} (KBr) 2218 (CN), 1624 (CO); ^{1}H NMR (DMSO-d_6) δ = 1.80–1.84 (m, 2H, CH_2), 1.89–1.92 (m, 4H, $2CH_2$), 4.01–4.05 (m, 4H, $2CH_2$), 4.08–4.11 (m, 4H, H-5, H-5′), 4.41–4.54 (m, 2H, H-6, H-6′), 4.92 (d, 2H, J = 8.7 Hz, H-7, H-7′), 6.73–7.62 (m, 18H, Ar). Anal. Calcd $C_{43}H_{36}N_4O_4S_4$ (801.02): C, 64.47; H, 4.53; N, 6.99; S, 16.01. Found: C, 64.30; H, 4.70; N, 6.73; S, 16.20.

4.7.1.6. *Diethyl 7,7′-((pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(2-oxo-3-phen-yl-3,5,6,7-tetrahydro-2H-thiopyrano[2,3-d]thiazole-6-carboxylate) (**16b**).* Pale yellow crystals (54%); m.p. 127°C; ν_{max}/cm^{-1} (KBr) 1720, 1630 (CO); ^{1}H NMR (DMSO-d_6) δ = 1.11 (t, 6H, J = 7.2 Hz, $2CH_3$), 1.59–1.62 (m, 2H, CH_2), 1.79–1.81 (m, 4H, $2CH_2$), 3.11–3.15 (m, 4H, H-5, H-5′), 3.37–3.41 (m, 4H, CH_2), 3.39 (q, 4H, J = 4.8 Hz, $2CH_2$), 3.97–3.99 (m, 2H, H-6, H-6′), 4.42 (d, 2H, J = 8.1 Hz, H-7, H-7′), 6.88–7.55 (m, 18H, Ar). Anal. Calcd. $C_{47}H_{46}N_2O_8S_4$ (894.21): C, 63.06; H, 5.18; N, 3.13; S, 14.33. Found: C, 62.78; H, 5.37; N, 3.40; S, 14.16.

4.8. *Preparation of compounds 17 and 14*

To compound 13 (0.01 mol), suspended in glacial acetic acid (20 ml), each of 2-thioxo-4-thiazolidinone or 3-phenyl-4-thioxo-2-thiazolidinone (0.01 mol) was added. The mixture was refluxed for 30 min and then it was left overnight at room temperature. The precipitate so formed was filtered off and recrystallized from ethanol and/or dimethylformamide.

5,5′-(((Pentane-1,5-diylbis(oxy))bis(4,1-phenylene))bis(methanylylidene))-bis(3-phenyl-4-thioxo-2-thiazolidinone) (14): Red crystals (64%); m.p. 165°C.

4.8.1. *5-(4-((5-(4-((4-Oxo-2-thioxothiazolidin-5-ylidene)methyl)phenoxy)pentyl)-oxy)benzylid-ene)-3-phenyl-4-thioxo-2-thiazolidinone (**17**)*

Red crystals (54%); m.p. 266°C; ν_{max}/cm^{-1} (KBr) 3223 (NH), 1680, 1645 (CO); ^{1}H NMR (DMSO-d_6) δ = 1.64–1.69 (m, 2H, CH_2), 1.79–1.89 (m, 4H, $2CH_2$), 3.37–3.46 (m, 4H, $2CH_2$), 7.07–7.94 (m, 15H, Ar), 8.40 (s, 2H, 2CH), 12.50 (s, 1H, NH). Anal. Calcd $C_{31}H_{26}N_2O_4S_4$ (618.80): C, 60.17; H, 4.24; N, 4.53; S, 20.72. Found: C, 60.35; H, 4.42; N, 4.79; S, 20.54.

5. Computational method

Molecular orbital calculations were carried out using the Gaussian 09W package.[30] Geometries of the studied 4-thiazolidinone derivatives were fully optimized using Becke's hybrid Hartree–Fock (HF) density functional method [31,32] with the Lee–Yang–Parr (LYP) correlation functional [33] and the 6-31G(d) basis set [B3LYP/6-31G(d)]. Vibrational frequency calculations were performed at the same level of theory to confirm the local minima. Solvation effect was introduced by the self consistent reaction field method, *via* the polarizable continuum model [34] implemented in the Gaussian program.

Disclosure statement

No potential conflict of interest was reported by the authors.

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