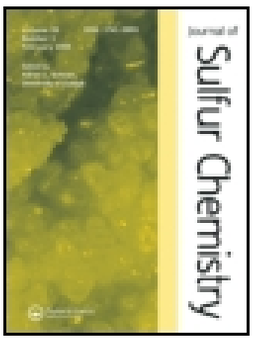

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A convenient synthesis of novel 1,3-phenylene bridged *bis*-heterocyclic compounds

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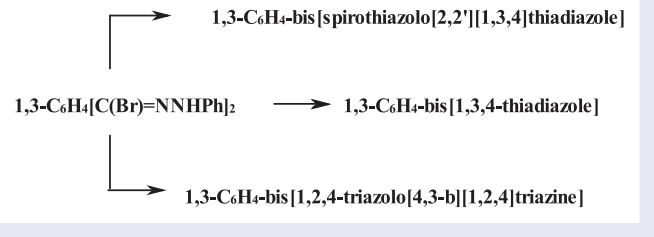
ABSTRACT

Reactions of *bis*-hydrazonoyl bromide 1 with each of phenyl-5-arylidene-2-thioxo-thiazol-4-one, triazinethiones and 4,6-dimethyl-2,6-dioxocyclohexane-1-thiocarboxanilide as sulfur dipolarophilic reagents led to the formation of the hitherto unreported 1,3-phenylene *bis*-heterocycles **4**, **8** and **10**, respectively. The structures of the isolated products were established on the basis of their elemental and spectral analyses. The mechanism and the site selectivity in the studied reactions are discussed.



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1. Introduction

In continuation of our interest in chemistry of hydrazonoyl halides **I** [1–13] and the *bis*-hydrazonoyl halides **II** (Figure 1),[14–16] we thought it is interesting to explore the utility of N′1,N′3-diphenyl-1,3-benzene-*bis*-carbohydrazonoyl bromide **2** as useful precursor in synthesis of new 1,3-phenylene bridged *bis*-heterocycles that have not been reported hitherto. Contrary to 1,4-phenylene bridged *bis*-heterocycles,[17] the target 1,3-phenylene bridged *bis*-heterocycles have received little, if there is any, attention. The interest in synthesis of such new 1,3-phenylene bridged *bis*-heterocycles is due to the fact that several literature reports indicate that some *bis*-heterocyclic compounds exhibit various biological activities, including antibacterial, fungicidal, tuberculostatic, antiamoebic, anthelmintic and plant growth regulative properties.[17–19]

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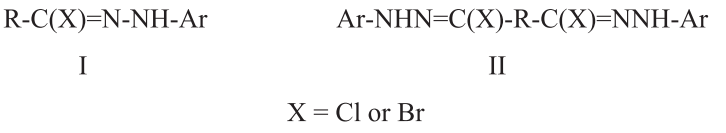


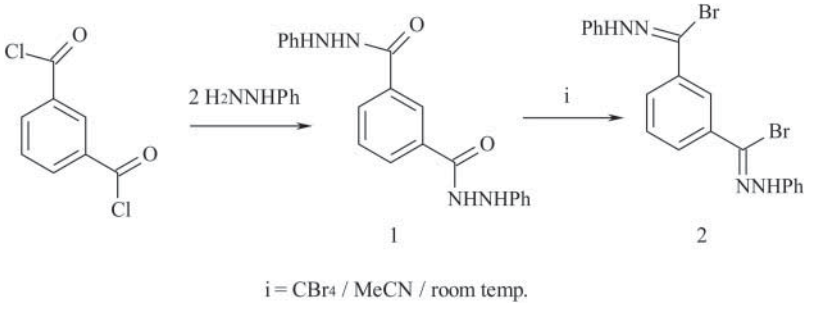
Figure 1. General structure of mono- and bis-hydrazonoyl halides.

2. Results and discussion

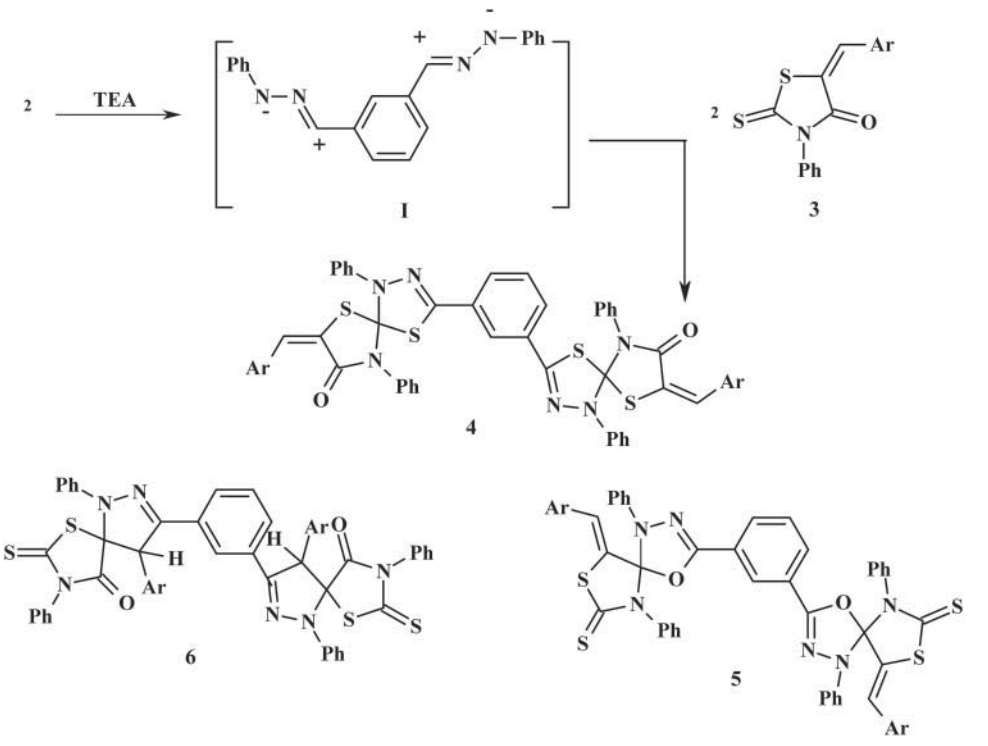
The target new *bis*-hydrazonoyl bromide **2** was prepared in this study, as depicted in Scheme 1, by stirring a mixture of carbon tetrabromide, triphenylphosphine and *N*,*N*′-diphenyl isophthalic hydrazide **1** in acetonitrile at room temperature.[20] Its structure was determined from its elemental and spectroscopic (IR, ^{1}H NMR, ^{13}C NMR and MS) analyses (see Section 3).

Reaction of *bis*-nitrilimine **I**, generated *in situ* by treatment of the *bis*-hydrazonoyl bromide **2** with triethylamine in refluxing chloroform, with two molar equivalents of each 3-phenyl-5-arylidene-2-thioxo-thiazol-4-ones **3** afforded, in each case, a single product as evidenced by TLC analysis. Both the spectral (MS, IR, ^{1}H and ^{13}C NMR) and elemental analysis data (see Section 3) indicated that the isolated products are the corresponding derivatives of 3,3′-(1,3-pheneylene)*bis*-(1,6-diphenyl-7-oxo-8-substituted-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiadiazole)) **4** (Scheme 2). Such products resulted *via* cycloaddition of the generated nitrilimines **I** to the C=S in compounds **2**. On the basis of such a finding, the spirocycloadducts of type **5** and **6**, that result via cycloaddition of the generated nitrilimine intermediate **I** to exocyclic C=C and C=O, respectively, were discarded (Scheme 2). This finding indicates that the C=S is more dipolarophilic than both the exocyclic C=C and C=O groups. This observed site selectivity is also consistent with literature reports on reactions of 3-phenyl-5-arylidene-2-thioxo-thiazol-4-one with mono-nitrilimines.[21,22]

Next, the reaction of **2** with two molar equivalents of each of 6-arylmethylene-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-ones **7a–g** in refluxing chloroform in the presence of triethylamine gave, in each case, a single product as evidenced by TLC analysis of the crude products. Both mass spectra and elemental analyses of the isolated products indicated that they are free of sulfur. The IR spectra of the products, while they are free of NH bands, they revealed two amide-I absorption bands in the region 1670–1660 cm^{-1}. On the basis of these data, the isolated compounds were assigned the structure **8** (Scheme 3).



Scheme 1. Synthesis of *bis*-hydrazonoyl bromide.

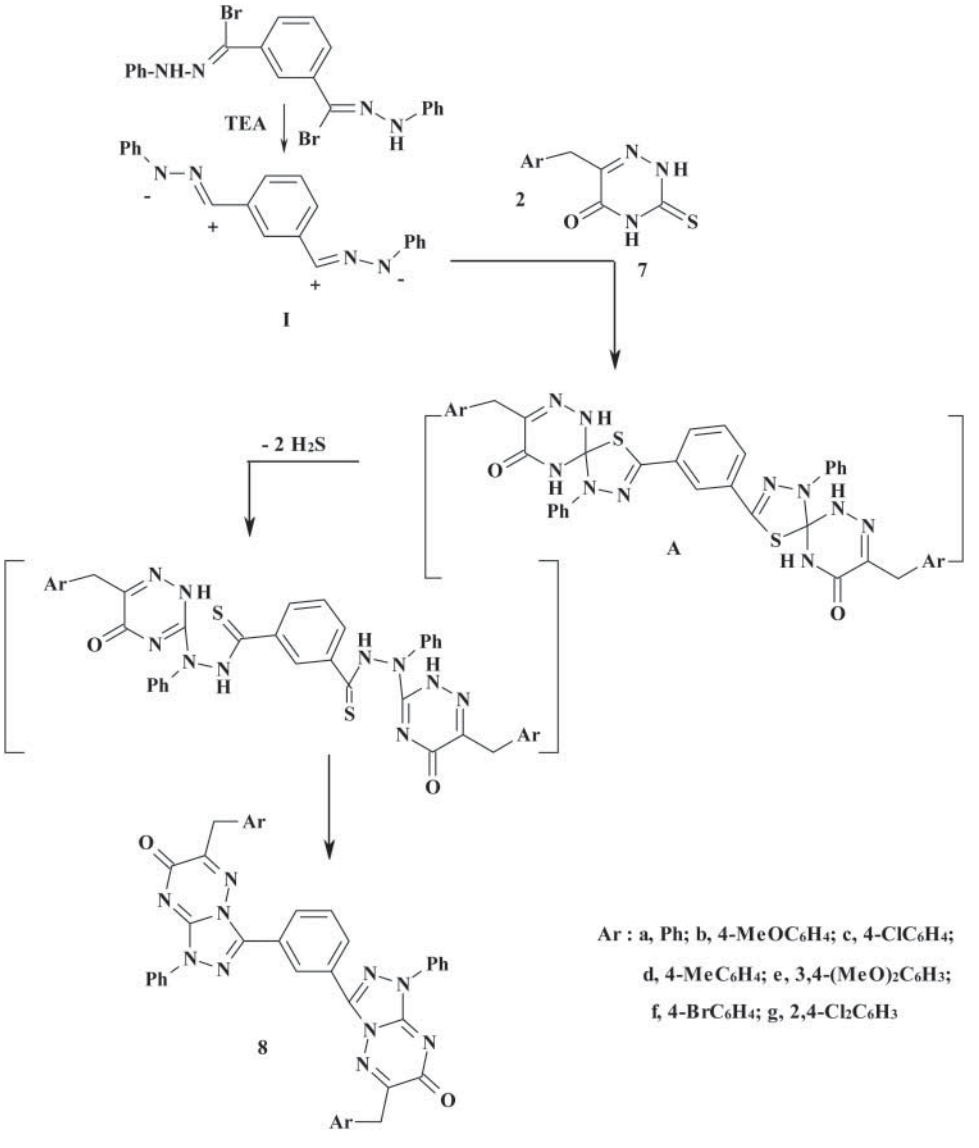


Scheme 2. Synthesis of *bis*-spiro compounds.

To account for the formation of latter, it is suggested as depicted in Scheme 3, that the reaction involves an initial cycloaddition of the *bis*-nitrilimine to C=S of **7** to give the *bis*-cycloadduct **A** which undergo *in situ* tandem ring opening, recyclization and elimination of H_2S to give **8** as end products.

The differences recorded between reactions of **2** with each of **3** and **7** is due to the absence of NH in the former **3** that facilitates ring opening of the initially formed thiadiazole cycloadduct. This rationalization is evidenced by the following result of the reaction of **2** with the thioanilide **9**.

Treatment of *bis*-hydrazonoyl bromide **2** with 4,4-dimethyl-2,6-dioxocyclohexanethiocarboxanilide **9** in refluxing chloroform in the presence of triethylamine gave a single product that proved to be 5,5′-(1,3-phenylene)*bis*[2-(5,5-dimethylcyclohexane-1,3-dione)-3-phenyl-3H-[1,3,4]thiadiazole] **10** (Scheme 4). The structure of product **10** was established on the basis of its spectra (MS, IR, ^{1}H and ^{13}C NMR) and elemental analyses data. Thus, its IR spectrum displayed an absorption band at ν 1645 (CO) cm^{-1} and its ^{1}H NMR spectrum exhibited, in addition to aromatic proton multiplet, a characteristic two singlet signals at δ 1.07 and 2.38 assignable to the $4CH_3$ and $4CH_2$ groups, respectively. The formation of the latter product **10** seems to result also *via* initial cycloaddition of the nitrilimine **I** to the C=S bond to the corresponding cycloadduct which in turn undergoes *in situ* tandem ring opening, recyclization and elimination of H_2NPh to give **10** as end

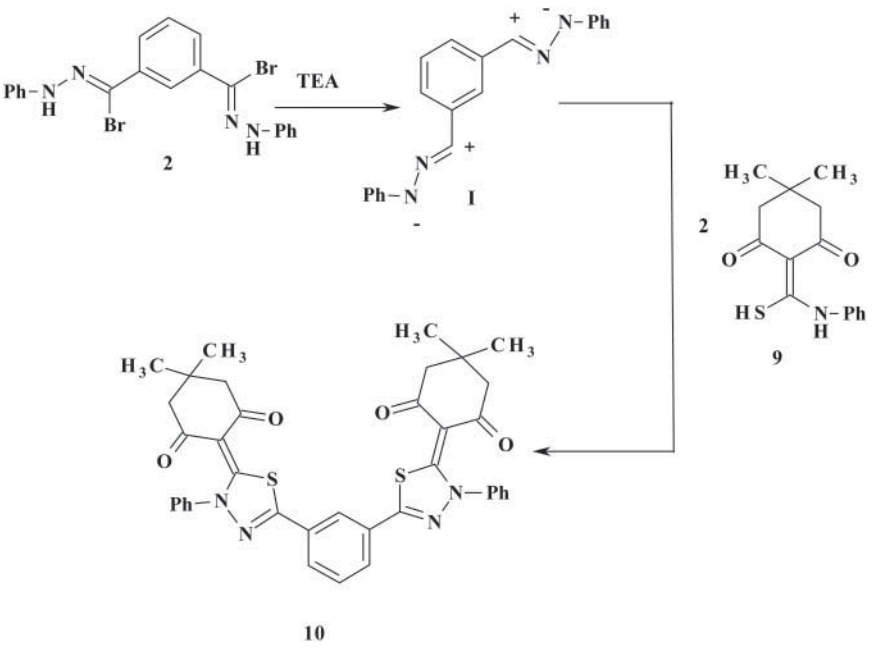


Scheme 3. Synthesis of *bis*-1,2,4-triazolo-[4,3-*b*]-triazine derivatives.

products. Such a sequence is consistent with literature reports on reactions of thioanilides with hydrazonoyl halides.[23,24]

3. Experimental section

Melting points were determined on a Stuart melting point apparatus and are uncorrected. The IR spectra were measured as KBr pellets on a FTIR Bruker-Vector 22 spectrophotometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or [d_6] DMSO on a Varian Mercury VXR 300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz



Scheme 4. Synthesis of *bis*-5,5-dimethylcyclohexane-[1,3,4]-thiadiazole.

for ^{13}C NMR) using TMS as internal standard. Mass spectra were measured on a Shimadzu GCMS-Q-1000 EX mass spectrometer at 70 eV. The elemental analyses were carried out at the Microanalytical Center, Cairo University using Automated analyzer CHNS, Vario EL III, Elementar, Germany.

3.1. Synthesis of N′1,N′3-diphenylisophthalohydrazide (1)

To a solution of phenylhydrazine (108.0 g, 1.0 mol) in cold ether (400 mL), the solution of isophthaloyl dichloride (100 g, 0.5 mol) in cold ether (50 mL) was added dropwise with stirring. The addition took 30 min. The reaction mixture was stirred for further 1 h and the precipitated solid was collected, washed with water and crystallized from DMF to give N′1,N′3-diphenylisophthalohydrazide in 70% yield; m.p. 280–282°C [Lit. m.p. 260–262°C].[20]

3.2. Synthesis of N′1,N′3-diphenyl-1,3-benzene-bis-carbohydrazonoyl bromide (2)

To a solution of N′1,N′3-diphenylisophthalohydrazide **1** (3.5 g, 10.0 mmol) in acetonitrile (40 mL), the triphenylphosphine (6.4 g) and carbon tetrabromide (6.8 g) were added. The reaction mixture was stirred overnight at room temperature. The solid product was collected, washed with ethanol and crystallized from acetonitrile to give product **2** as white crystals, m.p. 240°C, yield (4.02 g, 84%). IR (KBr) ν 3280 (NH), 1595 (C=N) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90–8.40 (m, 14H) and 8.60 (s, 2H, 2NH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.9, 122.4, 128.4, 128.9, 129.5, 131.3, 131.5, 143.0, 155.2. GC/MS (*m/z*): 472

(M^+). Anal. Calcd. for $C_{20}H_{16}Br_2N_4$ (472.21): C, 50.87; H, 3.42; Br, 33.85; N, 11.87. Found: C, 50.76; H, 3.30; Br, 33.87; N, 11.89.

3.3. Synthesis of 3,3′-(1,3-pheneylene)bis-(1,6-diphenyl-7-oxo-8-substituted-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiadiazole)) derivatives (4a–j)

To a mixture of *N*,*N*′-biphenyl-1,3-benzene-bis-carbohydrazonoyl bromide **2** (1.15 g, 3.0 mmol) and the appropriate 3-phenyl-5-arylidene-2-thioxo-thiazol-4-ones **3** (6.0 mmol) in chloroform (20 mL), triethylamine (0.6 mL, 6.0 mmol) was added at room temperature. The reaction mixture was refluxed for 6 h and then cooled, the excess chloroform was removed under reduced pressure and the residue was treated with ethanol (10 mL). The solid that precipitated was collected and crystallized from acetonitrile to give the corresponding product **4**. The compounds **4a–j** prepared together with their physical properties are listed below.

3.3.1. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(4-methoxybenzylidene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4a)

Yellow crystals, m.p. 188–190°C, yield (2.49 g, 90%); IR (KBr) ν 1692 (CO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 6H, $2CH_3O$), 7.09–7.50 (m, 32H) and 7.79 (s, 2H, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 101.2, 114.2, 116.7, 120.8, 121.0, 124.1, 127.5, 128.0, 128.9, 129.5, 130.2, 130.7, 131.5, 138.8, 139.1, 141.8, 143.8, 159.8, 162.3. GC/MS (*m/z*): 964 (M^+). Anal. Calcd. for $C_{54}H_{40}N_6O_4S_4$ (964.95): C, 67.20; H, 4.18; N, 8.71; S, 13.29. Found: C, 67.28; H, 4.10; N, 8.69; S, 13.26.

3.3.2. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(4-chlorobenzylidene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole (4b)

Yellow crystals, m.p. 194–196°C, yield (2.48 g, 89%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.99–7.50 (m, 32H) and 7.60 (s, 2H, 2CH). GC/MS (*m/z*): 973 (M^+). Anal. Calcd. for $C_{52}H_{34}Cl_2N_6O_2S_4$ (973.80): C, 64.12; H, 3.52; Cl, 7.28; N, 8.63; S, 13.17. Found: C, 64.21; H, 3.53; Cl, 7.25; N, 8.61; S, 13.20.

3.3.3. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(2-thienylmethylene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4c)

Yellow crystals, m.p. 182–184°C, yield (2.45 g, 93%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.90–8.20 (m, 32H). GC/MS (*m/z*): 916 (M^+). Anal. Calcd. for $C_{48}H_{32}N_6O_2S_6$ (916.82): C, 62.86; H, 3.52; N, 9.16; S, 20.98. Found: C, 62.91; H, 3.49; N, 9.19; S, 20.95.

3.3.4. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(2,4-dichlorobenzylidene)-spiro (5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4d)

Yellow crystals, m.p. 192–194°C, yield (2.83 g, 95%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.00–7.76 (m, 30H) and 7.80 (s, 2H, 2CH). GC/MS (*m/z*): 1042 (M^+). Anal. Calcd. for $C_{52}H_{32}Cl_4N_6O_2S_4$ (1042.70): C, 59.89; H, 3.09; Cl, 13.60; N, 8.06; S 12.30. Found: C, 59.96; H, 3.03; Cl, 13.61; N, 8.02; S 12.32.

3.3.5. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(benzylidene-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4e)

Yellow crystals, m.p. 168–170°C, yield (2.44 g, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.13–7.52 (m, 34H) and 7.84 (s, 2H, 2CH). GC/MS (*m/z*): 904 (M^+). Anal. Calcd. for $C_{52}H_{36}N_6O_2S_4$ (904.90): C, 69.00; H, 4.01; N, 9.28; S, 14.17. Found: C, 69.05; H, 3.98; N, 9.22; S, 14.20.

3.3.6. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(4-methylbenzylidene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4f)

Yellow crystals, m.p. 180–182°C, yield (2.44 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.40 (s, 6H, $2CH_3$), 6.71–7.40 (m, 32H) and 7.80 (s, 2H, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.6, 101.2, 116.7, 120.8, 121.0, 124.1, 127.5, 128.0, 128.5, 128.7, 128.9, 129.2, 129.5, 130.7, 131.5, 132.2, 137.6, 138.8, 139.1, 141.8, 162.3. GC/MS (*m/z*): 932 (M^+). Anal. Calcd. for $C_{54}H_{40}N_6O_2S_4$ (932.94): C, 69.50; H, 4.32; N, 9.01; S, 13.74. Found: C, 69.53; H, 4.35; N, 8.98; S, 13.76.

3.3.7. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-((cinnamylmethylene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4g)

Yellow crystals, m.p. 190–192°C, yield (2.44 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.70 (d, 2H, 2CH), 7.02 (d, 2H, 2CH) and 6.90–7.50 (m, 36H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 101.3, 116.7, 118.5, 120.8, 121.0, 125.2, 127.5, 127.9, 128.0, 128.5, 128.6, 128.9, 129.5, 130.7, 131.5, 125.2, 138.4, 139.1, 141.8, 142.8, 143.8, 162.3. GC/MS (*m/z*): 956 (M^+). Anal. Calcd. for $C_{56}H_{40}N_6O_2S_4$ (956.98): C, 70.27; H, 4.21; N, 8.78; S, 13.40. Found: C, 70.30; H, 4.19; N, 8.76; S, 13.43.

3.3.8. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(2-furylmethylene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4h)

Yellow crystals, m.p. 176–178°C, yield (2.23 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.8–8.10 (m, 32H). GC/MS (*m/z*): 884 (M^+). Anal. Calcd. for $C_{48}H_{32}N_6O_4S_4$ (884.82): C, 65.14; H, 3.64; N, 9.50; S, 14.49. Found: C, 65.19; H, 3.61; N, 9.48; S, 14.43.

3.3.9. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-(4-dimethylamino-benzylidene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4i)

Orange crystals, m.p. 196–198°C, yield (2.62 g, 92%); IR (KBr) ν 1665 (CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.10 (s, 12H, $4CH_3$), 6.71–8.23 (m, 32H, ArH) and 8.49 (s, 2H, 2CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 41.3, 101.2, 111.7, 116.7, 121.0, 120.8, 124.1, 124.7, 127.5, 128.0, 128.9, 129.5, 129.7, 138.8, 139.1, 141.8, 143.8, 150.3. GC/MS (*m/z*): 991 (M^+). Anal. Calcd. for $C_{56}H_{46}N_8O_2S_4$ (991.04): C, 67.85; H, 4.68; N, 11.30; S, 12.94. Found: C, 67.89; H, 4.63; N, 11.28; S, 12.90.

3.3.10. 3,3′-(1,3-Phenylene)bis(1,6-diphenyl-7-oxo-8-((4-florobenzylidene)-spiro(5H-thiazolo[2,2′]-3H-1,3,4-thiazole) (4j)

Yellow crystals, m.p. 188–190°C, yield (2.53 g, 94%). GC/MS (*m/z*): 940 (M^+). Anal. Calcd. for $C_{52}H_{34}F_2N_6O_2S_4$ (940.88): C, 66.36; H, 3.64; F, 4.04; N, 8.93; S, 13.63. Found: C, 66.41; H, 3.60; F, 3.99; N, 8.90; S, 13.65.

3.4. Synthesis of 3,3′-(1,3-phenylene)bis(1-phenyl-6-(aryl)-7-oxo-1,2,4-triazolo-[4,3-b]-triazine) derivatives (8a–g)

To a mixture of *N*,*N*′-biphenyl-1,3-benzene-bis-carbohydrazonoyl bromide **2** (1.15 g, 3.0 mmol) and the appropriate 6-benzyl-2,3-dihydro-3-thioxo-1,2,4-triazin-5(4H)-ones **7** (6.0 mmol) in chloroform (20 mL), triethylamine (0.6 mL, 6.0 mmol) was added at room temperature. The reaction mixture was refluxed for 6 h and then cooled, the excess chloroform was removed under reduced pressure and the residue was treated with ethanol (10 mL). The solid that precipitated was collected and crystallized from a suitable solvent to give the corresponding product **8**. The compounds **8a–g** prepared together with their physical properties are listed below:

3.4.1. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-benzyl-7-oxo-1,2,4-triazolo[4,3-b]triazine) (8a)

Orange crystals, m.p. 278–280°C (DMF), yield (1.56 g, 80%). IR (KBr) ν 1660 (CO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.07 (s, 4H, $2CH_2$) and 7.09–8.37 (m, 24H). GC/MS (*m*/*z*): 680 (M^+). Anal. Calcd. for $C_{40}H_{28}N_{10}O_2$ (680.73): C, 70.58; H, 4.15; N, 20.58. Found: C, 70.61; H, 4.10; N, 20.55.

3.4.2. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(p-methoxybenzyl)-7-oxo-1,2,4-triazolo[4,3-b]triazine) (8b)

Beige crystals, m.p. 270–272°C (DMF), yield (1.89 g, 87%). IR (KBr) ν 1656 (CO) cm^{-1}. ^1H NMR (300 MHz, DMSO): δ 3.30 (s, 6H, $2CH_3O$), 3.99 (s, 4H, $2CH_2$) and 7.21–8.40 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.4, 56.7, 122.3, 123.2, 127.1, 127.3, 128.1, 128.9, 129.1, 130.9, 133.8, 134.6, 135.8, 140.4, 148.9, 152.4, 164.8. GC/MS (*m*/*z*): 740 (M^+). Anal. Calcd. for $C_{42}H_{32}N_{10}O_4$ (740.78): C, 68.10; H, 4.35; N, 18.91. Found: C, 68.16; H, 4.31; N, 18.94.

3.4.3. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(p-chlorobenzyl-7-oxo-1,2,4-triazolo[4,3-b]triazine) (8c)

Beige crystals, m.p. 296–298°C (DMF), yield (1.80 g, 84%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 4H, $2CH_2$) and 7.40–8.26 (m, 22H). GC/MS (*m*/*z*): 749 (M^+). Anal. Calcd. for $C_{40}H_{26}Cl_2N_{10}O_2$ (749.63): C, 64.09; H, 3.50; Cl, 9.46; N, 18.69. Found: C, 64.13; H, 3.52; Cl, 9.42; N, 18.66.

3.4.4. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(p-methylbenzyl)-7-oxo-1,2,4-triazolo[4,3-b]triazine) (8d)

Beige crystals, m.p. 268–270°C (DMF), yield (1.61 g, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ 2.22 (s, 6H, $2CH_3$), 4.17 (s, 4H, $2CH_2$) and 6.99–9.07 (m, 22H).^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 25.4, 122.3, 123.1, 127.0, 127.3, 128.3, 128.9, 129.2, 130.4, 131.3, 133.7, 134.8, 135.4, 141.3, 149.9, 153.4, 164.6. GC/MS (*m*/*z*): 708 (M^+). Anal. Calcd. for $C_{42}H_{32}N_{10}O_2$ (708.79): C, 71.17; H, 4.55; N, 19.76. Found: C, 71.21; H, 4.52; N, 19.79.

3.4.5. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(3,4-dimethoxybenzyl)-7-oxo-1,2,4-triazolo [4,3-b]triazine) (8e)

Beige crystals, m.p. 258–260°C (CH_3CN), yield (2.02 g, 82%). IR (KBr) ν 1667 (CO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.67 (s, 6H, $2CH_3O$), 3.73 (s, 4H, $2CH_2$), 4.12 (s, 4H, $2CH_2$) and 6.67–9.11 (m, 22H). GC/MS (*m/z*): 800 (M^+). Anal. Calcd. for $C_{44}H_{36}N_{10}O_6$ (800.84): C, 65.99; H, 4.53; N, 17.49. Found: C, 66.02; H, 4.50; N, 17.46.

3.4.6. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(p-bromobenzyl)-7-oxo-1,2,4-triazolo[4,3-b] triazine) (8f)

Beige crystals, m.p. 300–302°C (DMF), yield (1.95 g, 81%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 4H, $2CH_2$) and 7.30–8.20 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.3, 120.1, 122.2, 122.4, 126.8, 128.7, 128.9, 129.5, 129.6, 129.9, 131.1, 131.5, 140.4, 146.0, 148.9, 152.0, 161.1. GC/MS (*m/z*): 838 (M^+). Anal. Calcd. for $C_{40}H_{26}Br_2N_{10}O_2$ (838.55): C, 57.30; H, 3.13; Br, 19.06; N, 16.70. Found: C, 57.36; H, 3.10; Br, 19.02; N, 16.72.

3.4.7. 3,3′-(1,3-Phenylene)bis(1-phenyl-6-(2,4-dichlorobenzyl)-7-oxo-1,2,4-triazolo[4,3-b]triazine) (8g)

Beige crystals, m.p. 284–286°C (DMF), yield (2.02 g, 86%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 4H, $2CH_2$) and 7.23–8.26 (m, 20H). GC/MS (*m/z*): 818 (M^+). Anal. Calcd. for $C_{40}H_{24}Cl_4N_{10}O_2$ (818.53): C, 58.70; H, 2.96; Cl, 17.33; N, 17.11. Found: C, 58.78; H, 2.92; Cl, 17.30; N, 17.18.

3.5. Synthesis of 5,5′-(1,3-phenylene)bis[2-(5,5-dimethylcyclohexane-1,3-dione)-3-phenyl-3H-[1,3,4]thiadiazole] (10)

To a solution of hydrazonoyl bromide **2** (1.15 g, 3.0 mmol) and N-phenyl 4,4-dimethyl-2,6-dioxocyclohexane-thiocarboxamide **9** (1.7 g, 6.0 mmol) in chloroform (50 mL), triethyl amine (2 mL) was added. The reaction mixture was refluxed for 6 h. The excess chloroform was removed under reduced pressure and the residue was treated with ethanol (10 mL). The resulting solid product was collected, washed with ethanol and crystallized from DMF to give compound **10**, as yellow crystals, m.p. 334–336°C, yield (1.94 g, 84%). IR (KBr) ν 1645 (CO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.07 (s, 12H, $4CH_3$), 2.38 (s, 8H, $4CH_2$) and 7.27–8.46 (m, 14H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9, 31.5, 53.2, 106.2, 120.4, 122.5, 122.6, 126.9, 128.2, 130.4, 131.5, 148.4, 155.2, 166.4, 191.3. GC/MS (*m/z*): 674 (M^+). Anal. Calcd. for $C_{38}H_{34}N_4O_4S_2$ (674.71): C, 67.63; H, 5.08; N, 8.30; S, 9.50. Found: C, 67.69; H, 5.07; N, 8.28; S, 9.47.

Disclosure statement

No potential conflict of interest was reported by the authors.

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