



Ultrasound assisted synthesis of some new 1,3,4-thiadiazole and bi(1,3,4-thiadiazole) derivatives incorporating pyrazolone moiety

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ABSTRACT

Novel substituted 1,3,4-thiadiazole and bi(1,3,4-thiadiazole) were synthesized from reaction of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarbox-anilide with a series of different hydrazonyl halides or *N,N'*-diphenyl-oxalodihydrazonoyl dichloride. The reactions were carried out under both conventional and ultrasonic irradiation conditions. In general, improvement in rates and yields were observed when reactions were carried out under sonication compared with classical condition. Structures of the products were established on analytical and spectral data.

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1. Introduction

The investigation of the chemistry of pyrazolones has been, and continues to be, one of the most active areas of heterocyclic chemistry [1], specially pyrazolones derivatives among heterocyclic ring systems that have a wide range of unique biological potentialities, some of the pyrazolones derivatives are now included in many of commercialized drugs for brain ischemia [2,3] and myocardial ischemia [4]. On the other hand 1,3,4-thiadiazoles and its derivatives have become very useful compounds in medicine [5–7].

Ultrasound has increasingly been used in organic synthesis in recent years, a large number of organic reactions can be carried out in higher yield, shorter reaction time and milder conditions under ultrasonic irradiation [8,9]. As a part of our interest in the synthesis of a wide range of heterocyclic systems [10–12], and in a continuation of using green chemistry tools in heterocyclic synthesis [12], our current research program is concerned with utility of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarbox-anilides **4** in the synthesis of several new substituted 1,3,4-thiadiazole and bi(1,3,4-thiadiazole) derivatives under both conventional and ultrasonic irradiation conditions.

2. Result and discussion

Ethyl benzoylacetate **1** was treated with methyl hydrazine under ultrasonic irradiation to afford 1-methyl-3-phenyl-2-pyrazo-

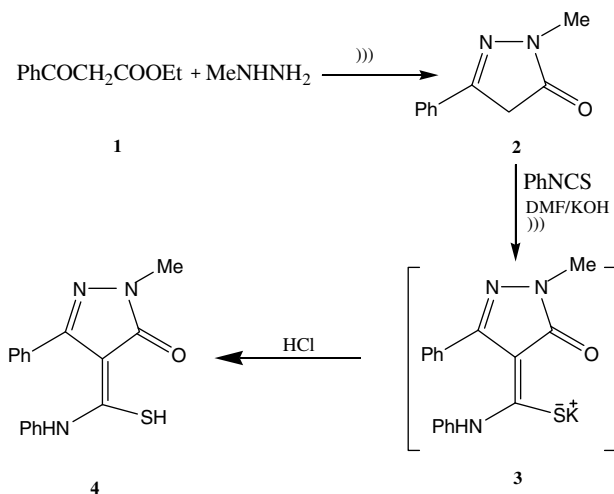
lin-5-one **2** (Scheme 1), which was obtained in excellent yield and shorter reaction time in comparing with conventional condition [13] as shown in Table 1. Thus, when pyrazolone derivative namely 1-methyl-3-phenyl-1*H*-pyrazol-5(4*H*)-one **2** was allowed to react with phenylisothiocyanate, in *N,N*-dimethylformamide in the presence of potassium hydroxide under ultrasound irradiation in an ultrasonic cleaner at 25–30 °C, they afforded the potassium salt of adduct **3**. Treatment of the latter salt with dilute hydrochloric acid afforded the corresponding thiocarboxanilide derivative **4** (Scheme 1). The structure of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarboxanilide **4** was confirmed on basis of its elemental analysis and spectral data. The ¹H NMR spectrum of thioanilide **4** displayed a singlet signal at δ 3.77 due to *N*-methyl proton of pyrazolone and two D₂O exchangeable singlet signals at δ 8.57 and 12.88 due to SH and NH respectively. In addition to multiplet signals at δ 7.20–7.65 due to aromatic protons (see Section 4). Time of reaction and yields of compounds **2** and **4** are shown in Table 1.

Table 1 illustrates that ultrasound technique reduced the time of reactions from several hours to minutes and increasing the yields from 70–80% to 92–97%.

A series of different hydrazonyl halides **5**, **7a–g** was treated with thioanilide **4** in ethanol in the presence of triethylamine under ultrasonic irradiation (Scheme 2), afforded in each case, only one isolable product (as examined by TLC). The elemental analysis and spectral data of the reaction products were compatible only with the 1,3,4-thiadiazole derivatives **6** or **8a–g**. For example, the IR spectra of 1-methyl-3-phenyl-4-(3,5-diphenyl-1,3,4-thiadiazol-2(3*H*)-ylidene)-1*H*-pyrazol-5(4*H*)-one **6** revealed, the appearance

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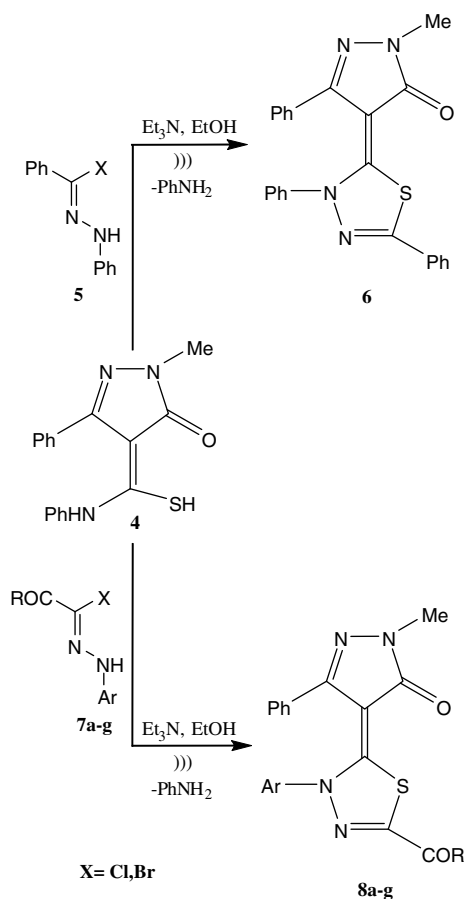
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Scheme 1.

Table 1
Synthesis of pyrazolone **2** and thioanilide derivative **4** under sonication and silent conditions

Compound	Ultrasonic irradiation		Conventional	
	Time (min)	Yield (%)	Time (h)	Yield (%)
2	2	97	1	80
4	60	92	24	70



Scheme 2.

of one carbonyl absorption band near 1632 cm^{-1} in addition, its mass spectrum revealed, a peak corresponding to the molecular ion m/z 410.

To find the specific effect of ultrasound on this reaction, all previously mentioned were carried out under the same conditions in absence of ultrasound irradiations (Table 2).

It was observed that the reaction time increased considerably and the yields of the products decreased in absence of ultrasonic irradiation. Thus, ultrasonic irradiation was found to have beneficial effect on the synthesis of thiadiazole derivatives.

Based on the above findings, we further extend our study to find out the reactivity of thioanilide **4** towards *N,N'*-diphenyl-oxalodihydrizonoyl dichloride **9**. Thus, treatment of thioanilide **4** with *N,N'*-diphenyl-oxalodihydrizonoyl dichloride **9** in ethanol and triethylamine under ultrasonic irradiation afforded 5,5'-bi(3*H*-3-phenyl-2-(1-methyl-5-oxo-3-phenyl-1*H*,4*H*-pyrazol-4-ylidene)-1,3,4-thiadiazole) **10** in 90% yield within 15 min. Similarly, repeating this reaction under the same condition in absence of ultrasonic irradiation decrease the yield into 70% and increase the time up to 3 h (see Scheme 3).

The structures of the latter product was established on the basis of its elemental analysis and spectral data. The IR spectra of the isolated product **10** revealed the appearance of one carbonyl absorption band near 1643 cm^{-1} . In addition, its mass spectrum revealed a peak corresponding to the molecular ion at m/z 665. The elemental analysis and spectral data of compound **10** showed that only one product was separated.

3. Conclusion

We have synthesized a class of novel substituted 1,3,4-thiadiazole **6**, **8a–g** and bi(1,3,4-thiadiazole) **10** under both sonication and classical conditions. In general, improvements in rates and yield of reactions are observed when reactions were carried out under sonication compared with classical condition.

4. Experimental

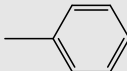
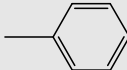
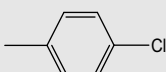
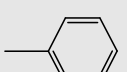
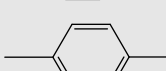
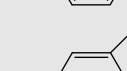


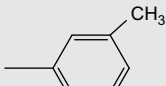
4.1. Materials and methods

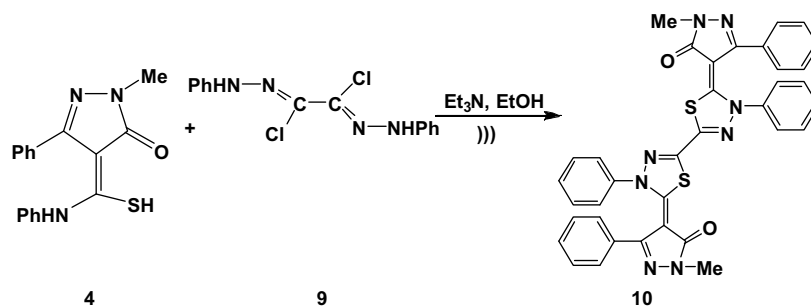
All organic solvents were purchased from commercial sources and used as received or dried using standard procedures, unless otherwise stated. All chemicals were purchased from Aldrich or Across and used without further purification, Analytical thin-layer chromatography (TLC) was performed on precoated Merck 60 GF254 silica gel plates with a fluorescent indicator, and detection by means of UV light at 254 and 360 nm. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded in KBr disks on a pye Unicam SP 3300 and Shimadzu FT-IR 8101 PC infrared spectrophotometers. The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. ^1H spectra were run at 300 MHz and ^{13}C spectra were run at 75.46 MHz in deuterated chloroform (CDCl_3) or dimethyl sulphoxide (DMSO-d_6). Chemical shifts were related to that of the solvent. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX mass spectrometer at 70 eV. Elemental analyses were carried out at the Micro analytical Center of Cairo University, Giza, Egypt.

Sonication was performed by Fisher sonicator (with a frequency of 25 kHz and a nominal power 600 W).

1-methyl-3-phenyl-1*H*-pyrazol-5-one **2** [13], hydrazonyl halides **6** [14], **7a–g** [15–17] and *N,N'*-diphenyloxalodihydrizonoyl dichloride **10** [18] were prepared according to the reported literature.

Table 2
Synthesis of 1,3,4-thiadiazole derivatives under sonication and conventional conditions

Compound	R	Ar	Ultrasonic irradiation		Conventional	
			Time (min)	Yield (%)	Time (h)	Yield (%)
6	Ph		7	93	3	73
8a	Me		7	92	3	72
8b	Me		5	95	3	75
8c	EtO		5	90	3	70
8d	EtO		3	92	3	75
8e	PhNH		15	90	3	70
8f	Ph		13	92	3	71
8g			15	90	3	67



Scheme 3.

4.2. General procedure

4.2.1. Silent reactions

4.2.1.1. Synthesis of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarbox-anilides (4). To a stirred suspension of potassium hydroxide (0.56 g, 10 mmol) in *N,N*-dimethylformamide (20 ml) the pyrazolone **2** (10 mmol) was added. To the resulting solution phenyl isothiocyanate (10 mmol) was added. The reaction mixture was stirred for 24 h at room temperature. The potassium salt intermediate formed **3**. The solution was acidified with dilute hydrochloric acid (30 ml, 10%). The solid formed was collected, washed with water and recrystallized from ethanol to give thioanilide derivative **4**.

4.2.1.2. synthesis of 2,3-dihydro-1,3,4-thiadiazole derivatives 6, 8a–g. To a stirred mixture of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-

thiocarbox-anilides **4** (0.33 g, 1 mmol) and the appropriate hydrazonoyl halides **5** or **7a–g** (1 mmol) in ethanol (20 ml), 3 drops of triethylamine was added then the mixture was heated under reflux for 3 h. After completion of the reaction as indicated by TLC, the solvent was evaporated under reduced pressure and the formed solid was collected, washed with ethanol and recrystallized from a mixture of DMF/EtOH (1:20) to get pure 1,3,4-thiadiazole derivatives **6** and **8a–g**. The yields of the products are given in **Table 2**, and the spectral data are given below.

4.2.1.3. Synthesis of 5,5'-bi(3H-3-phenyl-2-(1-methyl-5-oxo-3-phenyl-1H,4H-pyrazol-4-ylidene)-1,3,4-thiadiazole) (10). A mixture of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarbox-anilides **4** (10 mmol) and *N,N'*-diphenylodihydrazonoyl dichloride **9** (5 mmole) and triethylamine (2 ml) in ethanol (20 ml) was heated under reflux condition for 3 h. After completion of the

reaction as indicated by TLC, the solvent was evaporated under reduced pressure and the formed solid was collected, washed with ethanol and recrystallized from the mixture of DMF/EtOH (1:20) to give the corresponding compound **10**.

4.2.2. Sonicated reactions

4.2.2.1. Synthesis of 1-methyl-3-phenyl-1H-pyrazol-5-one (2). An equimolar amount of Ethylbenzoylacetate **1** (25 mmol) and methylhydrazine (28 mmol) were added in 50 ml Erlenmeyer flask. The mixture was subjected to ultrasound irradiation for 2 min at 25–30 °C (to avoid increase vapor pressure of ethanol and to achieve effective cavitations in this solvent, bath 25 kHz). The precipitate was filtered off, washed with ethanol and recrystallized from ethanol to afford the corresponding pyrazolone derivative **2**. The synthesized compound was confirmed by melting point and mixed melting point [13].

4.2.2.2. Synthesis of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarboxanilide 4. To irradiated solution of potassium hydroxide (0.56 g, 10 mmol) in dimethylformamide (20 ml), 2-pyrazoline-5-one **2** (10 mmol) were added in 50 ml Erlenmeyer flask. After irradiated for 10 min, phenyl isothiocyanate (1.35 g, 10 mmol) was added to the resulting mixture. Ultrasonic Irradiation was continued for 1 h then poured over crushed ice containing diluted hydrochloric acid (30 ml, 10%). The solid product so-formed was filtered off, washed with water, dried and recrystallized from mixture of DMF/EtOH (1:20) to afford 5-Oxo-2-pyrazolin-4-thiocarboxanilide derivative **4**.

4.2.2.3. Synthesis of 2,3-dihydro-1,3,4-thiadiazole derivatives 6, 8a–g. To a solution of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarboxanilides **4** (0.33 g, 1 mmol) in ethanol (20 ml), and the appropriate hydrazonoyl halides **5** or **7a–g** (1 mmol), triethylamine (0.5 ml) were added in 50 ml Erlenmeyer flask. The reaction mixture was subjected to ultrasonic irradiation at 25–30 °C for the appropriate time until completion of the reaction (monitored by TLC). The formed solid was filtered off, washed with ethanol and recrystallized from DMF/EtOH (1:20) to afford the corresponding 1,3,4-thiadiazole derivatives **6** and **8a–g**. The yields of the products are given in Table 2, and the spectra data are given below.

4.2.2.4. Synthesis of 5,5'-bi(3H-3-phenyl-2-(1-methyl-5-oxo-3-phenyl-1H,4H-pyrazol-4-ylidene)-1,3,4-thiadiazole) 10. To a solution of 1-methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarboxanilides **4** (10 mmol) in ethanol (20 ml), and the appropriate *N,N'*-diphenylloxalodihydrazonoyl dichloride **9** (5 mmol), triethylamine (0.5 ml) were added in 50 ml Erlenmeyer flask. The reaction mixture was subjected to ultrasound irradiation at 25–30 °C for the appropriate time until completion of the reaction (monitored by TLC). The formed solid was filtered off, washed with ethanol and recrystallized from a mixture of DMF/EtOH (1:20) to afford the corresponding bis-1,3,4-thiadiazole **10** in 90% yield. The synthesized compound with their physical data are listed below.

4.2.2.4.1. 1-Methyl-5-oxo-3-phenyl-2-pyrazolin-4-thiocarboxanilide 4. m.p. = 117–118 °C; IR (KBr): 3175 (NH), 3023 (SH), 1587 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.77 (s, 3H, NCH_3), 7.20–7.65 (m, 10H, ArH's), 8.57 (s, 1H, SH, D_2O -exchangeable), 12.88 (s, 1H, NH, D_2O -exchangeable); ^{13}C NMR (75.46 MHz, CDCl_3) δ : 35.50, 96.25, 121.21–145.59 (10 signals arom), 149.87, 155.42, 169.40; MS (m/z): 309 M^+ . (Found: C, 66.11; H, 4.85; N, 13.56; S, 10.31. $\text{C}_{17}\text{H}_{15}\text{N}_3\text{OS}$ requires C, 66.00; H, 4.89; N, 13.58; S, 10.36).

4.2.2.4.2. 1-Methyl-3-phenyl-4-(3,5-diphenyl-1,3,4-thiadiazol-2(3H)-ylidene)-1H-pyrazol-5(4H)-one 6. m.p. = 208–210 °C; IR (KBr): 1632 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.61 (s, 3H, NCH_3), 7.02–7.88 (m, 15H, ArH's); ^{13}C NMR (75.46 MHz, CDCl_3) δ : 33.2, 90.03, 120.34–140.38 (18 signals arom), 141.76, 153.12, 158.60,

163.27 (CO). MS (m/z): 410 M^+ . (Found: C, 70.20; H, 4.49; N, 13.67; S, 7.74. $\text{C}_{24}\text{H}_{18}\text{N}_4\text{OS}$ requires C, 70.22; H, 4.42; N, 13.65; S, 7.81).

4.2.2.4.3. 4-(5-Acetyl-3-phenyl-1,3,4-thiadiazol-2(3H)-ylidene)-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one 8a. m.p. = 200–201 °C; IR (KBr): 1680 (CO), 1610 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.64 (s, 3H, NCH_3), 2.68 (s, 3H, COCH_3), 6.80–8.16 (m, 10H, ArH's); ^{13}C NMR (75.46 MHz, CDCl_3) δ : 20.25, 34.24, 95.64, 120.11–137.47 (12 signals arom), 139.98, 149.65, 156.64, 166.43 (CO), 170.74 (CO). MS (m/z): 376 M^+ . (Found: C, 63.79; H, 4.25; N, 14.89; S, 8.56. $\text{C}_{20}\text{H}_{16}\text{N}_4\text{O}_2\text{S}$ requires C, 63.81; H, 4.28; N, 14.88; S, 8.52).

4.2.2.4.4. 4-(5-Acetyl-3-(4-chlorophenyl)-1,3,4-thiadiazol-2(3H)-ylidene)-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one 8b. m.p. = 190–192 °C; IR (KBr): 1675 (CO), 1618 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.21 (s, 3H, NCH_3), 2.71 (s, 3H, COCH_3), 6.52–8.10 (m, 9H, ArH's); ^{13}C NMR (75.46 MHz, CDCl_3) δ : 21.30, 36.54, 99.21, 122.31–135.30 (12 signals arom), 140.33, 151.23, 157.31, 169.40 (CO), 179.54 (CO); MS (m/z): 410.00 M^+ . (Found: C, 58.51; H, 3.71; N, 13.60; S, 7.76. $\text{C}_{20}\text{H}_{15}\text{ClN}_4\text{O}_2\text{S}$ requires C, 58.46; H, 3.68; N, 13.64; S, 7.80).

4.2.2.4.5. Ethyl 4,5-dihydro-5-(1-methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-4-phenyl-1,3,4-thiadiazole-2-carboxylate 8c. m.p. = 240–242 °C; IR (KBr): 1738 (CO), 1636 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 1.45 (t, 3H, $J = 7.2$ Hz, CH_3 ester), 3.61 (s, 3H, NCH_3), 4.52 (q, 2H, $J = 7.2$ Hz, CH_2 ester), 6.73–7.27 (m, 10H, ArH's). ^{13}C NMR (75.46 MHz, CDCl_3) δ : 13.88, 31.62, 63.29, 92.05, 120.87–144.38 (12 signals arom), 138.87, 150.06, 157.80, 160.30 (CO), 165.45 (CO ester); MS (m/z): 406 M^+ . (Found: C, 62.10; H, 4.50; N, 13.79; S, 7.80. $\text{C}_{21}\text{H}_{18}\text{N}_4\text{O}_3\text{S}$ requires C, 62.05; H, 4.46; N, 13.78; S, 7.89).

4.2.2.4.6. Ethyl 4-(4-chlorophenyl)-4,5-dihydro-5-(1-methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-1,3,4-thiadiazole-2-carboxylate 8d. m.p. = 230–231 °C; IR (KBr): 1725 (CO), 1655 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 1.47 (t, 3H, $J = 7.2$ Hz, CH_3 ester), 3.66 (s, 3H, NCH_3), 4.46 (q, 2H, $J = 7.2$ Hz, CH_2 ester), 6.71–7.29 (m, 9H, ArH's). ^{13}C NMR (75.46 MHz, CDCl_3) δ : 15.92, 33.70, 66.42, 98.19, 121.76–146.64 (12 signals arom), 148.75, 153.43, 159.89, 163.30 (CO), 170.32 (CO ester); MS (m/z): 440 M^+ . (Found: C, 57.19; H, 3.87; N, 12.70; S, 7.32. $\text{C}_{21}\text{H}_{17}\text{ClN}_4\text{O}_3\text{S}$ requires C, 57.21; H, 3.89; N, 12.71; S, 7.27).

4.2.2.4.7. 4-(3-Chlorophenyl)-4,5-dihydro-5-(1-methyl-5-oxo-3-phenyl-1H-pyrazol-4(5H)-ylidene)-N-phenyl-1,3,4-thiadiazole-2-carboxamide 8e. m.p. = 230–231 °C; IR (KBr): 3395 (NH), 1680 (CO), 1665 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.76 (s, 3H, NCH_3), 7.02–8.15 (m, 14H, ArH's), 8.46 (s, 1H, NH, D_2O -exchangeable). ^{13}C NMR (75.46 MHz, CDCl_3) δ : 35.64, 92.63, 123.34–142.45 (18 signals arom), 143.76, 155.54, 159.35, 163.27 (CO), 165.89 (CO). MS (m/z): 487 M^+ . (Found: C, 61.50; H, 3.96; N, 14.40; S, 6.52. $\text{C}_{25}\text{H}_{18}\text{ClN}_5\text{O}_2\text{S}$ requires C, 61.54; H, 3.72; N, 14.35; S, 6.57).

4.2.2.4.8. 4-(5-Benzoyl-3-(4-chlorophenyl)-1,3,4-thiadiazol-2(3H)-ylidene)-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one 8f. m.p. = 245–247 °C; IR (KBr): 1663 (CO), 1624 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 3.65 (s, 3H, NCH_3), 7.13–8.43 (m, 14H, ArH's); ^{13}C NMR (75.46 MHz, CDCl_3) δ : 36.32, 98.65, 120.29–141.98 (18 signals arom), 142.84, 156.34, 160.24, 164.67 (CO), 166.58 (CO). MS (m/z): 472 M^+ . (Found: C, 63.44; H, 3.67; N, 11.87; S, 6.76. $\text{C}_{25}\text{H}_{17}\text{ClN}_4\text{O}_2\text{S}$ requires C, 63.49; H, 3.62; N, 11.85; S, 6.78).

4.2.2.4.9. 4-(5-Thien-2-oyl-3-(3-methylphenyl)-1,3,4-thiadiazol-2(3H)-ylidene)-1-methyl-3-phenyl-1H-pyrazol-5(4H)-one 8g. m.p. = 237–238 °C; IR (KBr): 1645 (CO), 1612 (CO) cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ : 2.17 (s, 3H, CH_3), 3.62 (s, 3H, NCH_3), 6.81–7.10 (m, 9H, ArH's), 7.83 (d, 1H, $J = 5.6$ Hz thiophen-5-CH), 8.40 (d, 1H, $J = 3.9$ Hz thiophen-3-CH), 7.21 (dd, $J = 3.9$ Hz, $J = 5.6$ Hz, 1H, thiophen-4-CH). ^{13}C NMR (75.46 MHz, CDCl_3) δ : 28.68, 37.54, 94.61, 121.54–140.63 (12 signals arom), 131.31–145.93, 144.65, 157.76,

162.76, 166.87 (CO), 175.95 (CO). MS (m/z): 458 M^+ . (Found: C, 62.80; H, 3.90; N, 12.32; S, 14.01 $C_{24}H_{18}N_4O_2S_2$ requires C, 62.86; H, 3.96; N, 12.22; S, 13.99).

4.2.2.4.10. 5,5'-bi((3*H*-3-phenyl-2-(1-methyl-5-oxo-3-phenyl-1*H*,4*H*-pyrazol-4-ylidene)-1,3,4-thiadiazole) 10. m.p. = 295–297 °C; IR (KBr): 1643 (CO) cm^{-1} ; 1H NMR ($CDCl_3$): δ (300 MHz, DMSO- d_6) δ : 3.56 (s, 6H, 2CH₃), 6.93–7.37 (m, 20H, ArH's). ^{13}C NMR (75.46 MHz, DMSO- d_6) δ : 36.67, 99.72, 118.63–142.78 (24 signals arom), 143.42, 159.83, 163.32, 168.91 (2CO), MS (m/z): 666 M^+ . (Found: C, 64.80; H, 3.90; N, 16.85; S, 9.67 $C_{36}H_{26}N_8O_2S_2$ requires C, 64.85; H, 3.93; N, 16.81; S, 9.62).

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