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Synthesis of novel bis-thiadiazoles, bis-triazoles and polypyrazole derivatives based on hydrazonoyl halides

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ABSTRACT

A series of novel bis-thiadiazoles and bis-triazoles derivatives were synthesized via the reaction of hydrazonoyl halides with different moieties. Also, the synthesis and mechanism for polypyrazole formation are described via reaction of bis-hydrazonoyl with *p*-benzoquinone. Synthesized compounds were elucidated by elemental analysis and spectral data.

1. Introduction

The interest in the chemistry of hydrazonoyl halides is a consequence of the fact that they undergo a wide variety of reactions, which provide routes to a myriad of both heterocyclic and acyclic compounds. In addition, diverse biological activities, such as anthelmintic, antiviral, antiarthropodal, antimicrobial, fungicidal, herbicidal, antisarcoptic, insecticidal, pesticidal, acaricidal, miticidal, etc., have been found to be associated with hydrazonoyl halids.[1–6] Also, bis-hydrazonoyl dichlorides[7–10] are highly versatile and useful building blocks for the synthesis of a wide variety of heterocyclic. They have also been used as subunits in molecular hosts, such as macrocycles and supermolecular species.[11] Moreover, some bis-heterocycles, such as 2,2′-bis-1,3,4-thiadiazole derivatives exhibit interesting photoluminescence and electroluminescence and are used as thermotropic liquid crystals.[12,13] In addition, 3,3′-bis-1,2,4-triazoles have proved to possess bactericidal, fungicidal and anthelmintic activities.[14] Triazolopyrimidines possess a wide variety of biological activities. For instance, they exhibit in vivo activity against the amastigate stage of leishmaniadonovani,[15,16] have cardiovascular activity,[17–19] are active against *Aspergillus* and *Penicillium* species,[20] and have been tested as bioregulator agents.[21]

Several pyrazoles are important as pharmaceuticals, and have been found to possess analgetic,[22] antipyretic[22,23] and antimicrobial[22,24] properties. They are also useful as biodegradable agrochemicals[25] and as intermediate in the dye industry.[26]

Herein the synthesis of novel bis-thiadiazoles, bis-triazoles and polypyrazole based on bis-hydrazonoyl dichlorides is reported.

2. Results and discussion

A new access to one-pot synthesis of bis-thiadiazoles, bis-triazoles and polypyrazole via reactions of bis-hydrazonoyl dichlorides **1** with thiourea **2**, methylhydrazine-carbodithioate **5**, 2-methylthioketene-*N*,*S*-acetal **12**, 2-methylthiopyrimidine **15a–c** or 2-methylthiobenzimidazole **15d** and also reaction of **20** with *p*-benzoquinone **19** as shown in Chart 1.

Treatment of bis-hydrazonoyl dichlorides **1** with thiourea **2** in DMF under heating to give a single isolated 1,4-bis(3-phenyl-3*H*-[1,3,4]thiadiazol-5-imino) benzene **3** via elimination of HCl and ammonia as shown in Scheme 1.

Benzene-1,4-dicarbaldehyde **4** was reacted with methyl hydrazinecarbodithioate **5** to give dihydrazone **6**, which was reacted with *C*-phenyl-*N*-phenylhydrazonoyl chloride **7** in DMF to give bis-1,3,4-thiadiazoline derivative **10** in a good yield (Scheme 2). Structure **10** was confirmed by elemental analysis, spectra and alternative synthesis; benzene-1,4-dicarbaldehyde **4** was reacted with bis-2,3-dihydro-1,3,4-thiadiazole[27] **11** in DMF affording product identical in all respects (mp, mixed mp and spectra) with **10**.

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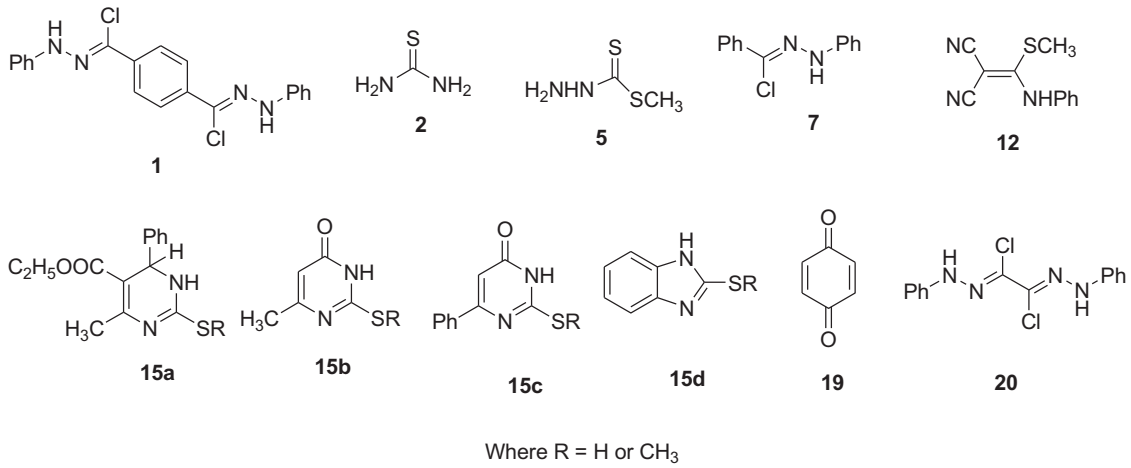
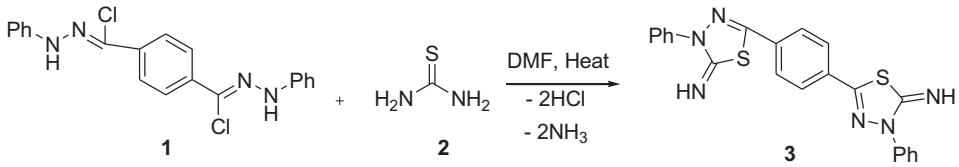
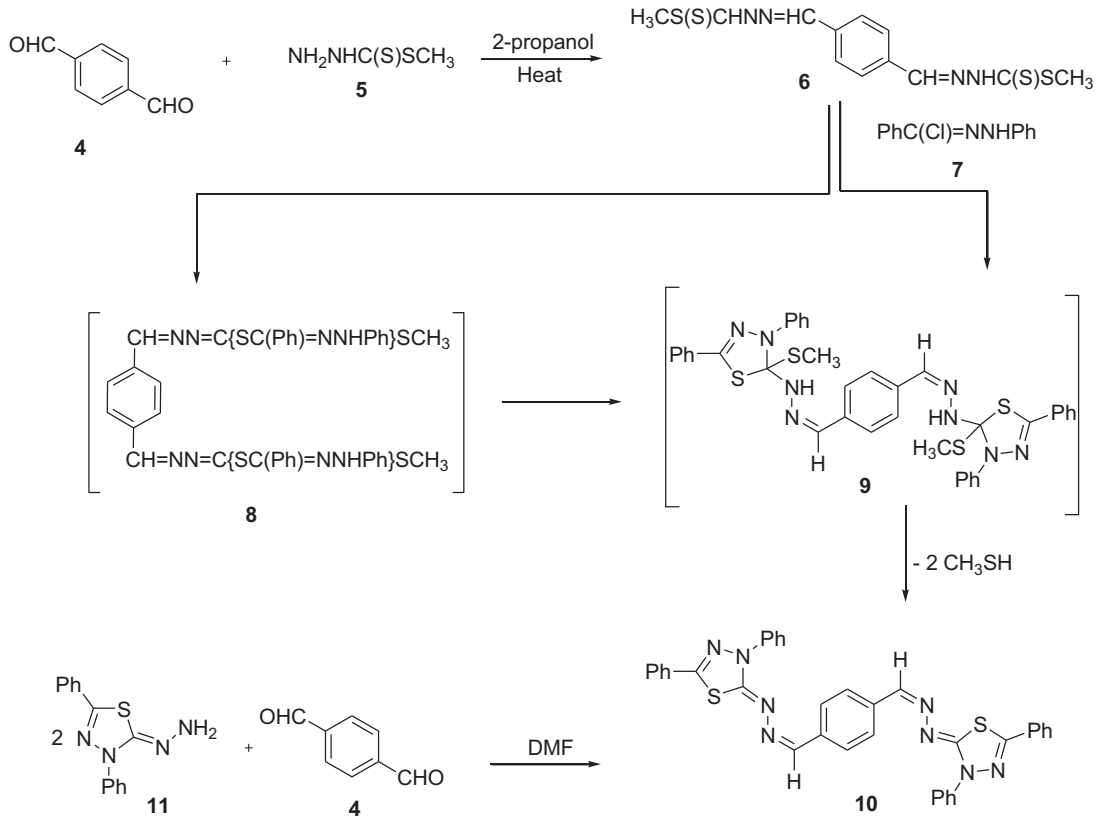


Chart 1. Starting reagents.



Scheme 1. 1,4-Bis-(3-phenyl-3*H*-[1,3,4]thiadiazol-2-imino) benzene **3**.



Scheme 2. Synthesis of dihydrazone **7** and bis-1,3,4-thiadiazoline **10**.

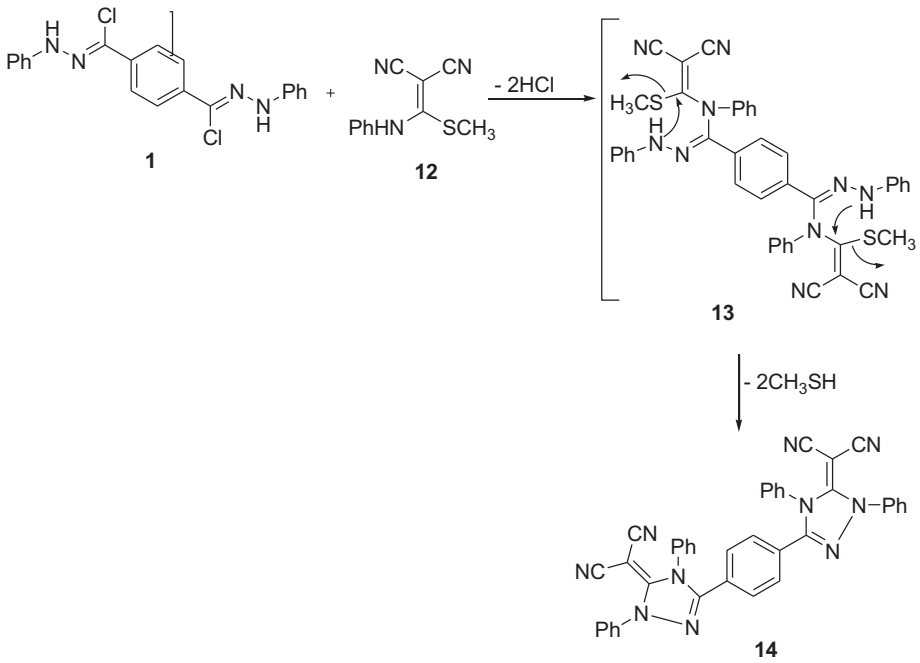
The formation of bis-thiadiazoline **10** can be explained via elimination of methanethiol from cycloadduct **9**, which is assumed to be formed via the 1,3-dipolar cycloaddition of nitrile imide (generate in situ by treatment of **1** with triethylamine) to the C=S double bond of **5** or by a stepwise path involving substitution via 1,3-addition of thiol **5** to nitrile imide to give a cyclic hydrazone **8**, which is then transformed to cyclic intermediate **9**. Cyclization of the latter is achieved by elimination of methanethiol to afford the final product **10**. All attempts to isolate either intermediate hydrazine **8** or cycloadduct **9** were unsuccessful (Scheme 2).

The required 2-cyano-3-methylthio-3-phenylaminoacrylonitrile **12** was prepared by the reaction of malononitrile with phenyl isothiocyanate in DMF in the presence of potassium hydroxide and the resulting thiolate was methylated with methyl iodide to give 2-cyano-3-methylthio-3-phenylaminoacrylonitrile **12**.[28] Recently, the synthesis of bis-triazoles[29] from reactions of hydrazonoyl halides with ketene-*N*,*S*-acetal was reported. These principles were extended to the reaction of bis-hydrazonoyl dichlorides **1** with 2 mol equiv of **12** in refluxing DMF/EtOH in the presence of triethylamine proceeded smoothly to give a product that was identified as 3,3′-bis(1,2,4-triazole) derivative **14** (Scheme 3). The structure of the latter product was elucidated on the basis of its microanalysis and spectra as shown in Scheme 3 (see Experimental section).

to afford **17a**–**d**. The mass spectral and the elemental analysis data of the isolated products showed that they are free of sulfur (Scheme 4). ^{13}C NMR spectra for **17b**–**d** could not be recorded. This was due to the poor solubility of the isolated products in the NMR solvents trialled.

The 1,3-dipolar cycloaddition, also known as the Huisgen cycloaddition[31] is a classic reaction in organic chemistry consisting of the reaction of a dipolarophile with a 1,3-dipolar compound that allows the production of various five-membered heterocycles. Most of dipolarophiles are alkenes, alkynes and molecules possessing related heteroatom functional groups (such as carbonyls and nitriles).

Polypyrazoles based on *p*-benzoquinone **20** were formed from 1,3-dipolar cycloaddition polymerization reactions where bis-nitrilimine **18** intermediates, generated in situ by the action of excess triethylamine, with the corresponding bis-hydrazonoyl dichlorides **20**, which cycloadd to *p*-benzoquinone **19** to afford final polymer **21** as shown in Schemes 5 and 6. Chemical Shifts of pyrazoline[32,33] rings disappear because should be appear at 4.64–4.7. Polymer molecular weights for **21** approached 22,000 g/mol with polydispersity indices of approximately 2.34. The structure of the polypyrazole **21** was elucidated on the basis of spectral data.



Scheme 3. Synthesis of 1,4-di[(1,4-diphenyl)-5-dicyanomethylene-1,2,4-triazole)]benzene **14**.

The reactions of hydrazonoyl halides with thioxo or 2-methylthio derivatives have been previously reported.[30] Using these principles, the reactions of bis-hydrazonoyl halides **1** with 2-thioxo or 2-methylthio derivatives **15a**–**d** in 1:2 molar ratios were carried out in DMF/pyridine at reflux. Methanethiol gas evolved during the course of the reaction, accordingly the reaction mixture was refluxed until such a gas ceased to evolve. Bis-(1,2,4-triazoles) **17** formed via *N*-atom **17a**–**d** attacks on the bis-hydrazonoyl dichlorides **1** to give the bis-amidazone intermediate **16a**–**d**, which in turn undergo intermediate intramolecular cyclization via addition of the hydrazone NH group to C=N double bond followed by elimination of hydrogen sulfide or methanethiol gases

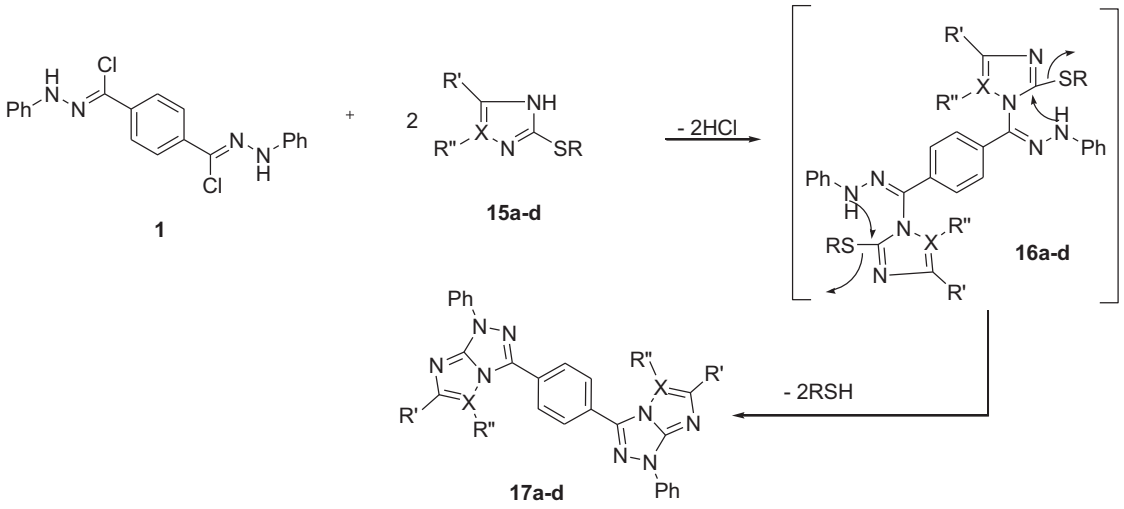
3. Conclusion

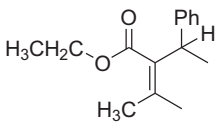
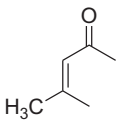
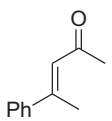
In summary, the synthesis of novel bis-thiadiazoles, bis-triazoles and polypyrazole derivatives based on hydrazonoyl halides is reported.

4. Experimental

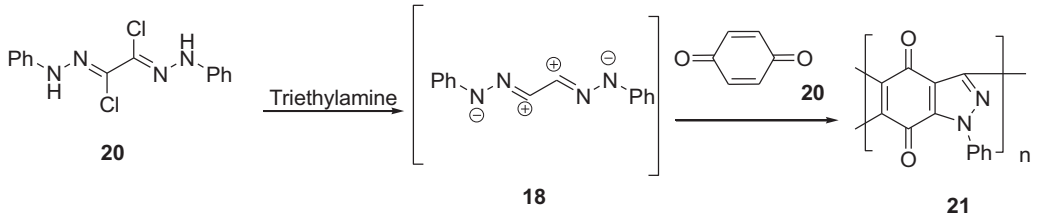
4.1. General

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs)

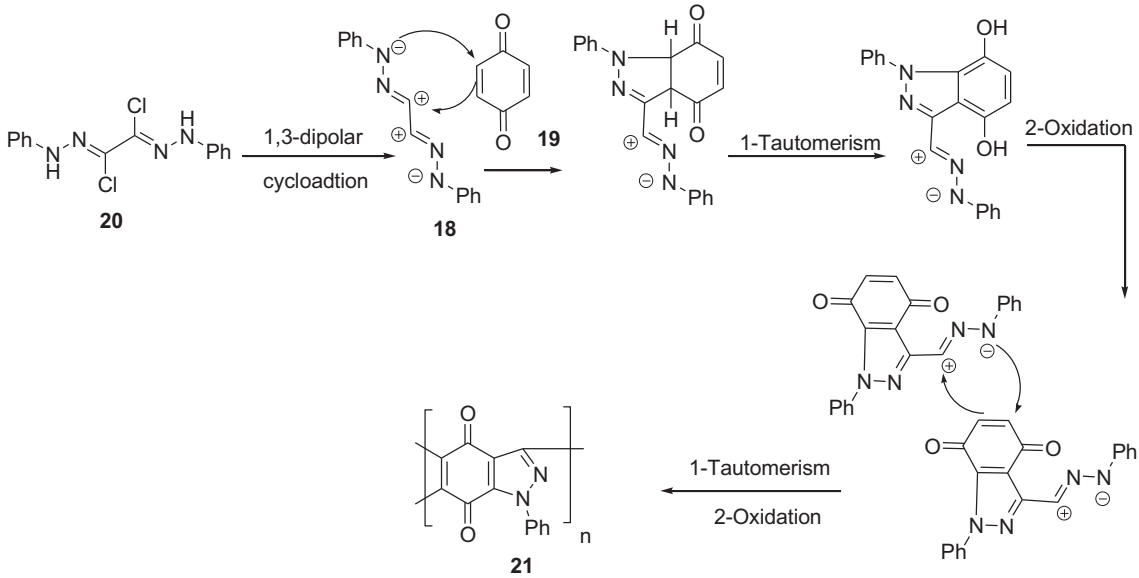


15-17	a	b	c	d
				

Scheme 4. Synthesis of bis-{[1,2,4]triazolo[4,3-*a*]-5(1*H*)-pyrimidinone} **17a**–**c** and bis-{[1,2,4]triazolo[4,5-*a*]benzimidazole} **17d**.



Scheme 5. Synthesis of poly(pyrazole-*p*-benzoquinone) **21**.



Scheme 6. 1,3-Dipolar cycloaddition mechanism of bis-nitrilimine **18** with, *p*-benzoquinone **19**.

on a Shimadzu FT-IR 8201 PC spectrophotometer. ^{1}H NMR spectra were recorded in $CDCl_3$ and $(CD_3)_2SO$ solutions on a Varian Gemini 300 MHz spectrometer and chemical shifts are expressed in δ units using TMS as an internal reference. Mass spectra were recorded on a GC–MS QP 1000 EX Shimadzu. Elemental analyses were carried out at the Microanalytical Canter of the Cairo University.

The starting reagents **1**,[34] **5**,[35] **7**,[36] **15a**,[37] **15bc**,[38] **15d**[39] and **20**[40] were prepared as previously described.

*4.1.1. 1,4-Bis-(3-phenyl-3H-[1,3,4]thiadiazol-2-imino)benzene (**3**).* A mixture of 4-[*N*,*N*′-diphenyl(bis-hydrazonoyl dichlorides)]benzene (1.92 g, 5 mmol) **1** and the appropriate of thiourea (0.76 g, 10 mmol) **2** in DMF(20 mL) was boiled under reflux for 5 h. The cold reaction mixture was then poured onto ice-cold hydrochloric acid with stirring. The solid that precipitated was collected. The resulting solids filtered, washed with water several times, and crystallized from DMF/EtOH; Yellow brown solid; Yield (69%); mp 320 °C; IR: 695 (C–S–C), 1612 (C=N), 3316 (NH) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 7.01–8.13 (m, 16H, ArHs and =NH). ^{13}C NMR (dimethyl sulfoxide-d_6): at 122.7, 126.9, 129.7, 132.1, 133.9, 140.1, 147.9 and 156.2 ppm. *m*/*z* (%)=428 (M^+, 15). Anal. Calcd for $C_{22}H_{16}N_6S_2$ (428.53): C, 61.66; H, 3.76; N, 19.61. Found: C, 61.49; H, 3.87; N, 19.57%.

*4.1.2. 1,4-Bis-(methyl hydrazonecarbodithioate)benzene (**6**).* Benzene-1,4-dicarbaldehyde (0.67 g, 5 mmol) **4** and methyl hydrazinecarbodithioate (1.22 g, 10 mmol) **5** in 2-propanol (40 mL) were refluxed for 30 min. The reaction mixture was cooled and solid formed was collected and recrystallized from DMF/EtOH; Yellow; Yield (85%); mp 226 °C; IR: 3098 (=NH), 1595 (C=N), 1316 (CH_3) cm^{-1}. ^{1}H NMR (dimethyl sulfoxide-d_6): 2.55 (s, 6H, $2CH_3$); 7.81 (d, *J*=8 Hz, 4H, ArHs); 8.26 (s, 2H, =CH) and 10.05 (s, 2H, NH) ppm. ^{13}C NMR (dimethyl sulfoxide-d_6): at 18.0, 130.1, 138.1, 146.1 and 199.6 ppm. *m*/*z* (%)=342 (M^+, 68); Anal. Calcd for $C_{12}H_{14}N_4S_4$ (342.01): C, 42.08; H, 4.12; N, 16.36. Found: C, 42.11; H, 4.30; N, 16.23%.

*4.1.3. 1,4-Bis-{1-benzylidene-2-(3,5-diphenyl-1,3,4-thiadiazol-2(3H)-ylidene)hydrazine} (**10**). Method A.* The appropriate of *C*-phenyl-*N*-phenylhydrazonoyl chlorides (2.31 g, 10 mmol) **7** and dihydrazone (1.71 g, 5 mmol) **6** in DMF (40 mL) was refluxed till no odour of methanthiol was detected by lead acetate (methanthiol is toxic by inhalation). The reaction mixture was cooled and solid formed was collected and recrystallized from DMF/EtOH to give **10**.

Method B. A mixture of benzene-1,4-dicarbaldehyde (0.67 g, 5 mmol) **4** and 2-hydrazino-3,5-diphenyl-1,3,4-thiadiazoline **11** (2.68 g, 10 mmol) **2** in DMF(20 mL) was boiled under reflux for 5 h. The solid that precipitated was collected. The resulting solids filtered, washed with water several times and crystallized from DMF/EtOH to give **10**.

Yellow brown solid; Yield (56%); mp 176 °C; IR: 1632 (C=N), 1587 (C=C) cm^{-1}. ^{1}H NMR (dimethyl sulfoxide-d_6): 6.72–7.83 (m, 24H, ArHs) and 8.43 (s, 2H, =CH) ppm. ^{13}C NMR (dimethyl sulfoxide-d_6): at 113.0, 119.2, 126.1, 129.1, 129.6, 130.2, 131.7, 132.1, 133.1, 134.2, 136.0, 137.6, 146.3 and 162.6 ppm. *m*/*z* (%)=634 (M^+, 34); Anal. Calcd for $C_{36}H_{26}N_8S_2$ (634.17): C, 68.12; H, 4.13; N, 17.65. Found: C, 68.24; H, 4.02; N, 17.71%.

*4.1.4. Synthesis 1,4-di[(1′,4′-diphenyl)-5′-dicyanomethylene-1′,2′,4′-triazole]benzene (**14**).* To a mixture ketene *N*,*S*-acetal (2.15 g, 10 mmol) **12** and bis-hydrazonoyl dichlorides **1** (1.92 g, 5 mmol) in ethanol (30 mL) and DMF (10 mL) was added triethylamine (5 mmol) and the mixture was refluxed till methanethiol ceased to evolve (4–6 h). The precipitate that was formed was filtered off and crystallized from DMF/EtOH mixture to give, respectively, yielded 3,3′-bis(1,2,4-triazole) derivative **14**. Brown solid; Yield (42%); mp >300 °C. IR: 2221 (CN), 2199 (CN) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 6.98–7.43 (m, 24H, ArHs) ppm; *m*/*z* (%)=644 (M^+, 56) Anal. Calcd for $C_{40}H_{24}N_{10}$ (644.22): C, 74.52; H, 3.75; N, 21.73. Found: C, 74.60; H, 3.79; N, 21.65%.

*4.1.5. General procedure for the preparation of bis{[1,2,4]triazolo[4,3-a]-5(1H)-pyrimidinone} (**17a–c**) and bis{[1,2,4]triazolo[4,5-a]benzimidazole} (**17d**).* A mixture of the thioxo or 2-methylthio derivatives (10 mmol) **15a–d** and 4-[*N*,*N*′-diphenyl(bis-hydrazonoyl dichlorides)]benzene (1.92 g, 5 mmol) **1** were refluxed in DMF/pyridine till hydrogen sulfide or methanthiol ceased to evolve (12–14 h) and cooled. The cold reaction mixture was then poured onto ice-cold hydrochloric acid with stirring. The solid that precipitated was collected, washed with water several times; dried and recrystallized from DMF/EtOH to give final products **17a–d** as shown in Scheme 4.

*4.1.6. Ethyl 3-(4-(6-(ethoxycarbonyl)-1,7-dihydro-5-methyl-1,7-diphenyl-[1,2,4]triazolo[4,3-a]pyrimidin-3-yl)phenyl)-1,5-dihydro-7-methyl-1,5-diphenyl-[1,2,4]triazolo[4,3-a]pyrimidine-6-carboxylate (**17a**).* Brown solid from DMF/EtOH; Yield (43%); mp 248 °C; IR: 1733 (C=O), 1611 (C=N) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 1.23 (t, 6H, $2OCH_2CH_3$), 2.37 (s, *J*=7 Hz, 6H, $2CH_3$), 4.12 (q, *J*=7 Hz, 4H, $2OCH_2CH_3$); 5.36 (s, 2H, two pyrimidine–H) and 6.96–8.18 (m, 24H, ArHs) ppm. ^{13}C NMR (dimethyl sulfoxide-d_6): 13.9, 25.05, 57.95, 59.97, 99.54, 113.06, 119.98, 126.09, 128.06, 128.97, 129.54, 130.12, 133.45, 138.32, 142.01, 143.99, 150.01, 160.11, 167.59 ppm. *m*/*z* (%)=794 (M^+, 14) Anal. Calcd for $C_{48}H_{42}N_8O_4$ (794.9); C, 72.53; H, 5.33; N, 14.10. Found: C, 72.41; H, 5.26; N, 13.89%.

*4.1.7. 3-(4-(1,7-Dihydro-5-methyl-7-oxo-1-phenyl-[1,2,4]triazolo[4,3-a]pyrimidin-3-yl)phenyl)-7-methyl-1-phenyl-[1,2,4]triazolo[4,3-a]pyrimidin-5(1H)-one (**17b**).* Pale yellow solid from DMF/EtOH; Yield 25%; mp >300 °C; IR: 1693 (C=O), 1605 (C=N) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 2.31 (s, 6H, $2CH_3$); 6.18 (s, 2H, two pyrimidine–H); 7.01–8.43 (m, 14H, ArHs) ppm. *m*/*z* (%)=526 (M^+, 61) Anal. Calcd for $C_{30}H_{22}N_8O_2$(526.55); C, 68.43; H, 4.21; N, 21.28. Found: C, 68.39; H, 4.19; N, 21.31%.

*4.1.8. 3-(4-(1,7-Dihydro-7-oxo-1,5-diphenyl-[1,2,4]triazolo[4,3-a]pyrimidin-3-yl)phenyl)-1,7-diphenyl-[1,2,4]triazolo[4,3-a]pyrimidin-5(1H)-one(**17c**).* Brown solid from DMF/EtOH; Yield 36%; mp >300 °C; IR: 1698 (C=O), 1611 (C=N) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 6.58 (s, 2H, two pyrimidine–H); 7.13–8.69 (m, 24H, ArHs) ppm. *m*/*z* (%)=650 (M^+, 42) Anal. Calcd for $C_{40}H_{26}N_8O_2$ (650.69); C, 73.83; H, 4.03; N, 17.22. Found: C, 73.79; H, 4.10; N, 17.19%.

*4.1.9. 1,4-Bis{1-phenyl-[1,2,4]triazolo[4,5-a]benzimidazole}benzene (**17d**).* Brown from DMF/EtOH; Yield 68%; mp >300 °C; IR: 1608 (C=N) cm^{-1}; ^{1}H NMR (dimethyl sulfoxide-d_6): 7.19–8.23 (m, 22H, ArHs) ppm. *m*/*z* (%)=542 (M^+, 74) Anal. Calcd for $C_{34}H_{22}N_8$ (542.59); C, 75.26; H, 4.09; N, 20.65. Found: C, 75.21; H, 4.13; N, 21.01%.

*4.1.10. Synthesis of poly{1-phenyl-3-phenylpyrazoline-1,4-benzoquinone} (**21**).* To an oven-dried round bottom flask were added *p*-benzoquinone (0.54 g, 5 mmol) **19** and bis-hydrazonoyl dichlorides (1.54 g, 5 mmol) **20** and 20 mL dry chloroform and 4 mL DMF in the presence of excess triethylamine (1.52 g, 15 mmol). The round bottom flask was attached to a reflux condenser. The reaction mixture solution was heated to reflux for 12 h. The cold reaction mixture was then poured onto ice-cold hydrochloric acid with stirring. The solid that precipitated was collected, washed with water several times to give final product **21**, dried to open air. The structure of the polypyrazole **21** was elucidated on the basis of spectral data. Polymer molecular weights approached 22,000 g/mol

with polydispersity indices of approximately 2.379. Deep green solid; Yield (55%); IR: 1674 (C=O), 1594 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): 6.82–8.01 (m, ArHs) ppm. ^{13}C NMR ($CDCl_3$): 113.12, 124.01, 125.93, 128.14, 130.16, 132.11, 139.15, 143.51 and 174.16 ppm.

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