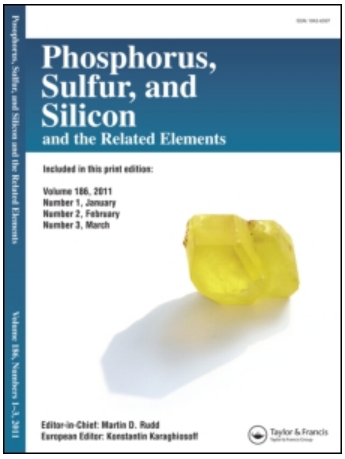

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Synthesis of Some Novel 1,3,4- and 1,2,4-Thiadiazole Derivatives

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Synthesis of Some Novel 1,3,4- and 1,2,4-Thiadiazole Derivatives

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Synthesis and spectral characterization of novel 1,3,4-thiadiazole derivatives including one organo-mercury compound are described. Their structure elucidation was performed by means of spectroscopic and physical methods (IR, ^{1}H NMR, ^{13}C NMR, MS, X-ray).

Keywords Oxadiazole; spectroscopy; thiadiazole; thione

INTRODUCTION

Heterocyclic compounds are commonly used scaffolds on which pharmacophores are arranged to provide potent and selective drugs.[1] This is especially true for five-membered ring heterocyclic compounds, which serve as the core components of a large number of substances that possess a wide range of interesting biological activities. In this family, 1,3,4-oxadiazoles and 1,3,4-thiadiazoles have been used as starting compounds to produce substances of interest in numerous therapeutic areas, such as antiimflammatory,[2] antimicrobial,[3] anticonvulsant,[4] and antihypertensive.[5] In addition, these heterocycles serve as intermediates in the preparation of various biologically important compounds and as optical materials.[6,7]

In this article, the synthesis and characterization of some new 1,3,4- and 1,2,4-thiadiazole derivatives is reported.

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Dr. F. R. Fronczek (Louisiana State University, Baton Rouge, Louisiana, USA) is gratefully acknowledged for X-ray data of compound **7**. CCDC data_Durust21 contains the supplementary crystallographic data for **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223–336-033; or email: depositcdc@cam.ac.uk.

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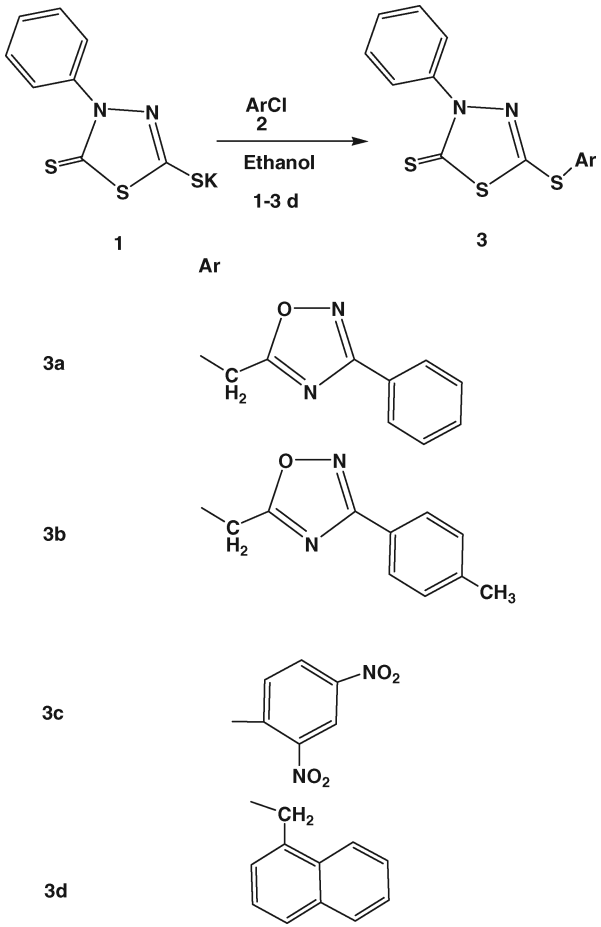
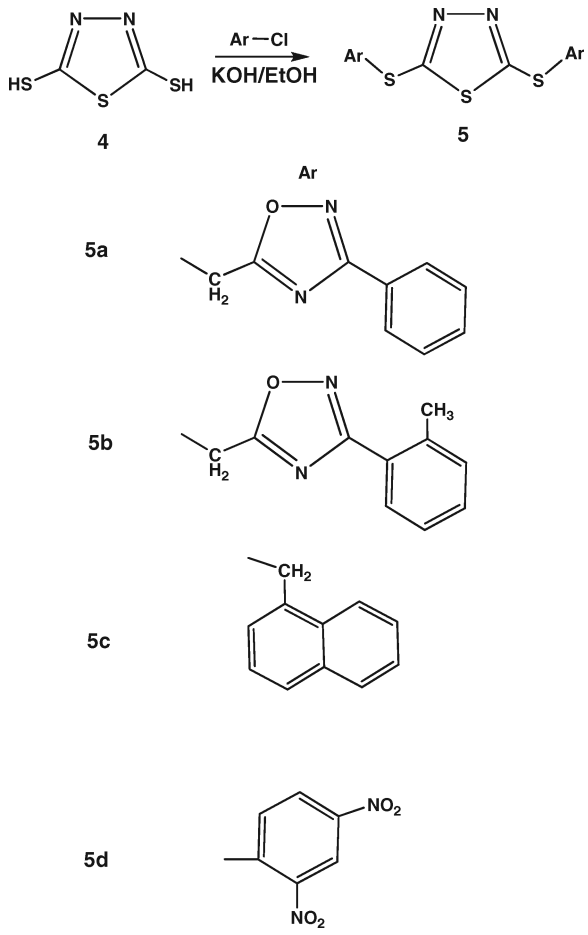
RESULTS AND DISCUSSION

In our previous work, we have been involved in the synthesis of thiadiazole derivatives, which were essentially prepared from amidoximes.[8,9] In this study, as starting compounds, 5-mercapto-3-phenyl-1,3,4-thiadiazole-2(*3H*)-thione (potassium salt) **1,**[10] 1,3,4-thiadiazole-2,5-dithiol **4**, and 3-(4-methyphenyl)-1,2,4-thiadiazole-5(*4H*)-thione **6** were utilized to react with aryl chlorides to prepare the new thiadiazoles. The reactions are the type of S-arylation of the heterocyclic thiones,[11] and the products are the first examples carrying 1,2,4-oxadiazole moiety along with the 1,3,4-thiadiazole ring. The structures of the new compounds are shown in Schemes 1–3.



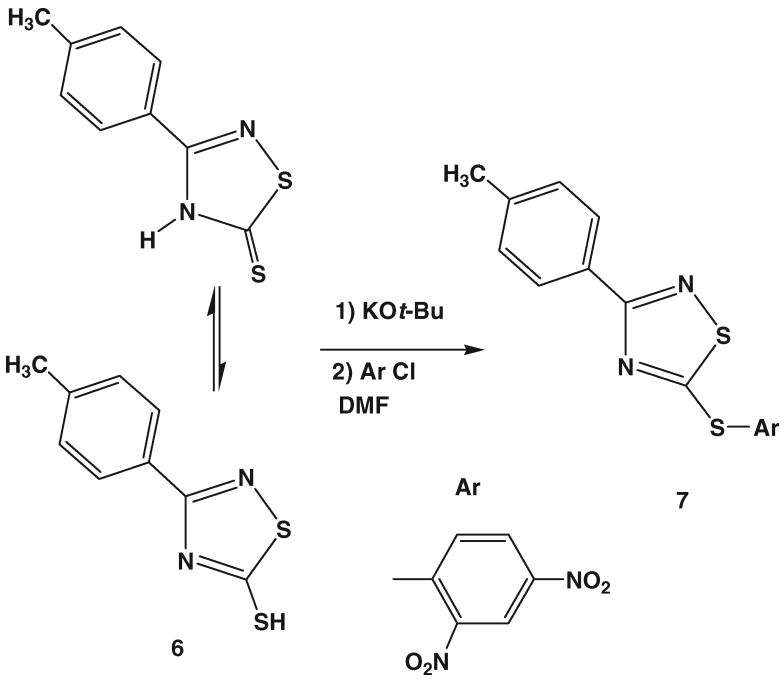
SCHEME 1



SCHEME 2

In addition, a new organo-mercury compound **8** was also obtained from the reaction between potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1**[10] and mercury (II) chloride at refluxing temperature in ethanol (Scheme 4) and characterized by spectral and physical data. The mass spectrum of the compound revealed that loss of mercury would produce peaks related to the disulfide species with m/z (452) and mercury cation with m/z (202).[12]

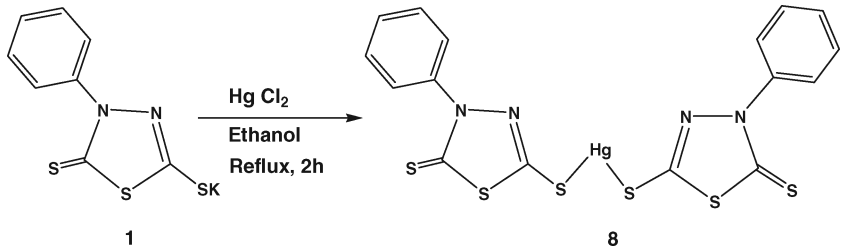
The S-arylated compound 7 was obtained by a slightly modified literature procedure[9] with a higher yield of reaction and more spectral data for this compound were provided herein. The X-ray view of **7** is illustrated in Figure 1. The following software programs were used:



SCHEME 3

data collection: COLLECT[13]; cell refinement: SCALEPACK[14]; data reduction: DENZO[14] and SCALEPACK; programs used to solve structure: SIR97[1]; programs used to refine structure: SHELX97[16]; molecular graphics: ORTEP-3 for Windows[17]; software used to prepare material for publication: SHELXL97 (Tables I and II).

The S1-C1 distance (1.765 Å) is indicative of a single bond, which is in accord with the mean value of 1.761 Å reported for arene thiolates[18] and slightly longer than that of mercury thiolate (1.749 Å).[12] The



SCHEME 4

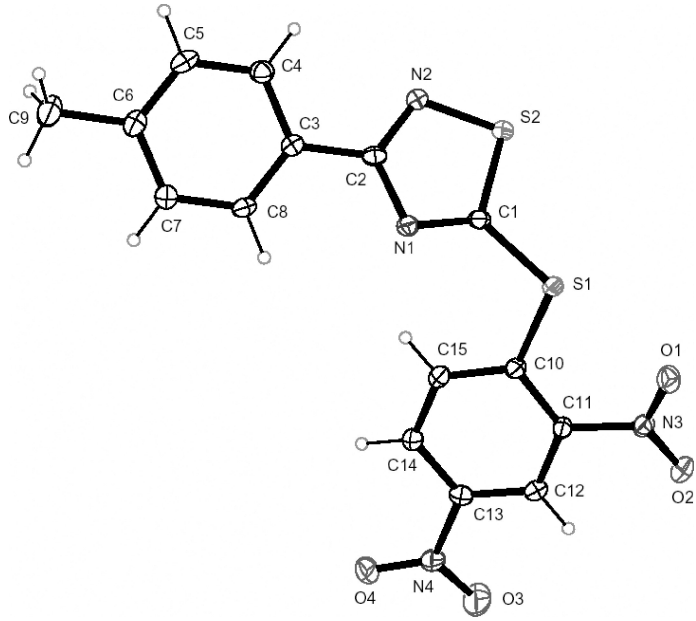


FIGURE 1 ORTEP view of **7**.

S2-N2 distance (1.6425 Å) is somewhat shorter than that of 3-methylthio 5-chloro 1,2,4-thiadiazole (1.6629 Å).[19] Bond distances and bond angles within the 1,2,4-thiadiazole ring are consistent with those of our previous report.[12]

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Bruker and Varıan spectrometers (300 and 400 MHz for proton, 75 and 100 MHz for carbon). IR spectra were recorded on Jasco 430 FTIR and Shimadzu FTIR-8000S instruments (KBr pellet). Mass spectra were measured on an Agilent GC 6890N gas chromatograph with mass detector MS 5975. Melting points were determined on a Meltemp apparatus and are uncorrected. Flash column chromatography was performed using silica gel (Merck, 230–400 mesh ASTM). TLC was performed using precoated plates with fluorescent indicator (Merck 5735). The stain solutions of permanganate, *p*-anisaldehyde, and iodine were used for visualization of the TLC spots.

1,3,4-thiadiazole-2,5-dithiol **4** was purchased from Aldrich and used without purification. 5-Chloromethyl-3-phenyl-1,2,4-oxadiazole **2a**,

TABLE I Crystal Data of 7

$C_{15}H_{10}N_4O_4S_2$	$V = 761.0\ (4)\ Å^3$
$Mr = 374.39$	$Z = 2$
Triclinic	$Dx = 1.634\ Mg\ m^{-3}$
$P\bar{1}$	D_m not measured
$a = 4.4874\ (15)\ Å$	Mo $K\alpha$ radiation
$b = 11.497\ (4)\ Å$	$\Lambda = 0.71073\ Å$
$c = 15.154\ (5)\ Å$	Cell parameters from 2765 reflections
$\alpha = 101.160\ (16)^\circ$	$\theta = 2.5–29.8^\circ$
$\beta = 95.41\ (2)^\circ$	$\mu = 0.381\ mm^{-1}$
$\gamma = 93.61\ (2)^\circ$	
$T = 110\ K$	$T_{min} = 0.853,\ T_{max} = 0.970$
Needle	9387 measured reflections
Yellow	4076 independent reflections
$0.43 \times 0.12 \times 0.08\ mm$	2956 reflections with $I > 2\sigma(I)$
Data collection	$R_{int} = 0.035$
Nonius KappaCCD (with Oxford Cryostream) diffractometer	$\theta_{max} = 29.8^\circ$
ω scans with κ offsets	$h = -6 \rightarrow 6$
Absorption correction:	$k = -15 \rightarrow 15$
multi-scan HKL Scalepack (Otwinowski & Minor 1997)	$l = -21 \rightarrow 21$
Refinement	intensity decay: <2%
Refinement on F^2	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\ \sigma(F^2)] = 0.044$	$(\Delta/\sigma)_{max} = 0.001$
$\omega R(F^2) = 0.103$	$\Delta\rho_{max} = 0.69\ e\ Å^{-3}$
$S = 1.021$	$\Delta\rho_{min} = -0.52\ e\ Å^{-3}$
4076 reflections	Extinction correction: SHELXL
228 parameters	Extinction coefficient: 0.005 (2)
H-atom parameters constrained	Scattering factors from *International Tables for Crystallography* (Vol. C)
$\omega = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.4038P]$	

5-(chloromethyl)-3-*p*-tolyl-1,2,4-oxadiazole **2b**, and potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1** were synthesized according to the procedures previously described in the literature.[89]

3-Phenyl-5-{(3-phenyl-1,2,4-oxadiazol-5-yl)methylthio}-1,3,4-thiadiazole-2(3H)-thione (3a)

5-Chloromethyl-3-phenyl-1,2,4-oxadiazole **2a**[8] (1 mmol) in THF (5 mL) was added dropwise to potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1**[10] (1 mmol) in THF (5 mL). A yellow solution

TABLE II Selected Geometric Parameters (Å, °)

Bond lengths	
	O4—N4 1.224 (2)
S1—C1 1.765 (2)	N1—C1 1.315 (3)
S1—C10 1.767 (2)	N1—C2 1.384 (3)
S2—N2 1.6425 (18)	N2—C2 1.327 (3)
S2—C1 1.716 (2)	N3—C11 1.470 (3)
O1—N3 1.227 (2)	N4—C13 1.466 (3)
O2—N3 1.228 (2)	C2—C3 1.473 (3)
O3—N4 1.227 (3)	C6—C9 1.508 (3)
Bond Angles	
C1—S1—C10 104.51 (9)	N2—S2—C1—S1 −173.25 (12)
N2—S2—C1 92.04 (10)	C10—S1—C1—N1 51.0 (2)
C1—N1—C2 108.01 (17)	C10—S1—C1—S2 −136.28 (12)
C2—N2—S2 108.97 (14)	S2—N2—C2—N1 1.8 (2)
N1—C1—S2 112.85 (15)	S2—N2—C2—C3 −178.89 (15)
N1—C1—S1 128.94 (15)	C1—N1—C2—N2 −1.4 (2)
S2—C1—S1 117.86 (12)	C1—N1—C2—C3 179.31 (17)
N2—C2—N1 118.10 (18)	N2—C2—C3—C8 166.56 (19)
N2—C2—C3 121.42 (18)	N1—C2—C3—C8 −14.2 (3)
N1—C2—C3 120.48 (17)	N2—C2—C3—C4 −13.1 (3)
C15—C10—S1 122.68 (15)	N1—C2—C3—C4 166.18 (18)
C11—C10—S1 120.81 (15)	C1—S1—C10—C15 −14.00 (19)
C1—S2—N2—C2 −1.30 (14)	C1—S1—C10—C11 166.05 (16)
C2—N1—C1—S2 0.3 (2)	S1—C10—C11—C12 −179.51 (16)
C2—N1—C1—S1 173.29 (15)	S1—C10—C11—N3 −0.2 (3)
N2—S2—C1—N1 0.58 (15)	S1—C10—C15—C14 −179.75 (17)

appeared. The reaction mixture was stirred at room temperature for 1 day. A white precipitate that formed (KCl) was filtered off. The solvent was removed under reduced pressure. The crude product was crystallized from benzene as pale yellow needles to give compound **3a** (400 mg, 78%), mp 84–85°C. R_f: 0.57 (ethanol:*n*-hexane, 3:1). IR (KBr) v (cm^{-1}): 1591, 1566, 1492, 1444, 1359, 1228. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 8.09 (d, 2H, J = 6.1 Hz), 7.63 (d, 2H, J = 3.7 Hz), 7.55–7.39 (m, 6H), 4.58 (s,2H).^{13}C NMR ($CDCl_3$, 100 MHz).: 185.6 (C = S), 174.2,168.7, 151.9, 138.2, 131.4, 128.9, 128.8, 127.5, 126.2, 125.3, 96.1, 26.7.MS (m/z,%): 383 (M^+, 44), 135 (14), 105 (31), 77 (100), 64 (13), 51 (16). Anal. Calcd for $C_{17}H_{12}N_4OS_3$:C, 53.10; H, 3.15; N, 14.57; S, 25.02.Found. 53.39; H, 3.01; N,14.50; S,25.90.

3-Phenyl-5-{(3-p-tolyl-1,2,4-oxadiazol-5-yl)methylthio}-1,3,4-thiadiazole-2(3H)-thione (3b)

5-Chloromethyl-3-*p*-tolyl-1,2,4-oxadiazole **2b**[8] (1 mmol) in THF (5 mL) was added to potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-

thiadiazole-2-thiolate **1**[10] (1mmol) in THF (5 mL). A yellow solution appeared. The reaction mixture was stirred at room temperature for 3 days. A white precipitate that formed (KCl) was filtered off. The solvent was removed under reduced pressure. The crude product was crystallized from hexane as white flocculent crystals to give compound **3b** (quantitative). Mp 84–86°C. R_f: 0.67 (EtOAc:hexane, 1:3). IR (KBr) v (cm^{-1}):1590, 1494, 1227, 1041. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 7.98 (d, 2H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.0 Hz), 7.42 (m, 3H), 7.29 (m, 2H), 4.66 (s, 2H), 2.45 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ: 185.6 (C=S), 174.0, 168.6, 151.9, 141.6, 138.2, 129.6, 128.8, 127.4, 125.3, 123.4, 96.1, 26.7, 21.6. MS (m/z,%): 397 (M^+, 97), 135 (18), 117 (10), 105 (49), 91 (35), 77 (100), 64 (13), 51 (18). Anal.Calcd for $C_{18}H_{14}N_4OS_3$ C, 54.25; H, 3.54; N, 14.06; S, 24.14.Found. C,54.67;H, 4.07; N, 14.01; S, 25.19.

5-(2,4-Dinitrophenylthio)-3-phenyl-1,3,4-thiadiazole-2(3H)-thione (3c)

1-Chloro-2,4-dinitrobenzene **2c** (303 mg, 1.5 mmol) in THF (5 mL) was added to potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1**[10] (396 mg, 1.5 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 1 day. The reaction mixture was was taken into water and extracted with CH_2Cl_2 (3 × 25 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was crystallized from hexane as pale yellow needles to give compound **3c** (quantitative). Mp 173–175°C. R_f: 0.24 (ethanol:*n*-hexane, 2:1). IR (KBr) v, (cm^{-1}):1600, 1535, 1337, 1223, 1025, 908, 730. ^{1}H NMR ($CDCl_3$, 400 MHz): δ: 9.64 (s, 1H), 8.59 (s, 1H), 7.70 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ:188.4, 147.4, 146.2, 145.3, 140.4, 137.6, 129.7, 129.2, 128.0, 125.6, 121.6. MS (m/z,%): 391 (M^+,20), 183 (13), 135 (17), 77 (100), 64 (22), 51 (16). Anal. Calcd for $C_{14}H_8N_4O_4S_3$: C, 42.85; H, 2.05; N, 14.28; S, 24.51. Found C,43.47;H,2.02; N, 14.24; S, 26.21.

5-(Naphthalen-1-ylmethylthio)-3-phenyl-1,3,4-thiadiazole-2(3H)-thione (3d)

1-Chloromethyl naphthalene **2d** (110.5 mg, 0.5 mmol) in THF (5 mL) was added to potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1**[10] (133 mg, 0.5 mmol) in THF (5 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated, and the crude material was crystallized from petroleum ether as white flocculent plates to give compound **3d** (151 mg,

41%). Mp 100–101°C. R_f: 0.96 (*n*-hexane:ethyl acetate, 2:1). IR (KBr) v (cm^{-1}):1594, 1495, 1342, 1245, 1050, 820, 744, 683. ^1H NMR ($CDCl_3$, 400 MHz): δ: 7.88–7.46 (m, 12H), 4.48 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ:185.9, 155.2, 138.4, 133.1, 132.9, 132.32, 129.0, 128.9, 128.8, 128.5, 127.8, 127.7, 126.6, 126.5, 126.5, 125.6, 37.8. MS (m/z,%): 365 (M^+,5), 141 (100), 115 (20), 77 (14), 64 (3), 51 (13). Calculated for $C_{19}H_{14}N_2S_3$ C, 62.26; H, 3.85; N, 7.64; S, 26.25 Found C, 62.84; H, 4.40; N, 7.67; S, 26.96.

3-Phenyl-5-{(5-((3-phenyl-1,2,4-oxadiazol-5-yl)methylthio}-1,3,4-thiadiazol-2-ylthio)methyl)-1,2,4-oxadiazole (5a)

5-(Chloromethyl)-3-phenyl-1,2,4-oxadiazole **2a**[8] (260 mg, 1.34 mmol) in THF (5 mL) was added dropwise into a solution of 1,3,4-thiadiazole-2,5-dithiol **4** (100 mg, 0.67mmol) in EtOH (5 mL) containing KOH (75 mg, 1.34 mmol) and stirred at room temperature for 1 day. The mixture was evaporated to dryness. The yellow solid was taken into the water (50 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic fractions were dried over anhydrous Na_2SO_4, and after evaporation of the solvent, the remaining solid was crystallized from EtOH to give **5a** (0.211 g, 67.1%). Mp 103–105°C. IR (KBr) v (cm^{-1}): 1592, 1568, 1446, 1385, 1359, 1049, 908, 713, 687. ^1H NMR (DMSO-d_6, 400 MHz): δ: 8.11 (m, 4H), 7.75 (m, 6H), 4.96 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 189.2, 176.9, 168.3, 164.6, 155.8, 132.6, 1342.2, 132.1, 129.7, 128.7, 127.4, 126.3, 126.2, 28.4, 127.9. MS (m/z,%): 466 (M^+, 10), 307 (16), 191 (9), 159 (23), 145 (24), 129 (96), 103 (100), 91 (37), 76 (74), 64 (45), 51 (62). Calculated for $C_{20}H_{14}N_6O_2S_3.H_2O$ C, 49.57; H, 3.33; N, 17.34; S, 19.85. Found C, 49.36; H, 3.60; N, 17.69; S, 20.01.

3-*o*-Tolyl-5-{(5-(3-*o*-tolyl-1,2,4-oxadiazol-5-yl)methylthio)-1,3,4-thiadiazol-2-ylthio)methyl}-1,2,4-oxadiazole (5b)

5-(Chloromethyl)-3-*p*-tolyl-1,2,4-oxadiazole **2b**[8] (490 mg, 2.40 mmol) in THF (5 mL) was added dropwise into a solution of 1,3,4-thiadiazole-2,5-dithiol **4** (180 mg, 1.20 mmol) in EtOH (5 mL) containing NaOH (96 mg, 2.40 mmol) and stirred at room temperature for 1 day. The mixture was evaporated to dryness and extracted with ethyl acetate. NaCl was filtered off. The crude reaction product was crystallized from petroleum ether to give **5b** (679 mg, 77%). Mp 98–100°C. IR (KBr) v (cm^{-1}): 1594, 1592, 1567, 1560, 1345, 1051, 905, 902, 739, 726. ^1H NMR (DMSO-d_6, 400 MHz): δ: 8.11 (m, 4H), 7.75 (m, 6H), 4.96 (s, 4H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 173.6, 169.3, 163.3, 138.3, 131.4, 130.8,

130.1, 126.0, 125.5, 27.8, 22.1. MS (m/z,%): 321 (M^+-173, 6), 159 (100), 131 (27), 116 (48), 104 (10), 89 (22), 77 (23), 63 (14), 51 (9). Calculated for $C_{22}H_{18}N_6O_2S_3$ C, 53.42; H, 3.67; N, 16.99; S, 19.45 Found C, 53.12; H, 3.63; N,16.76; S,19.45.

2,5-Bis(naphthalen-1-ylmethylthio)-1,3,4-thiadiazole (5c)

A mixture of 2,5-dimercapto-1,3,4-thiadiazole **4** (150.2 mg, 1 mmol) in an aqueous solution of NaOH (80 mg, 2 mmol) and 1-chloromethyl naphthalene (442 mg, 2 mmol) was stirred at room temperature overnight. The solvent was evaporated to dryness. The remaining solid was extracted with benzene, then successively with ethyl acetate and ethanol. The combined organic fractions were evaporated, and the remaining solid was finally crystallized from benzene-petroleum ether (50–70°C) to give **5c** as flocculent shiny plates (370 mg, 86%). Mp 131–133°C. IR (KBr) v (cm^{-1}): 1594, 1505, 1383, 1051, 831, 752. ^{1}H NMR ($CDCl_3$, 400 MHz): δ:7.86–7.80 (m, 8H), 7.53–7.49 (m, 6H), 4.42 (s, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 164.7, 133.2, 133.1, 132.8, 128.6, 128.2, 127.8, 127.7, 126.8, 126.4, 126.3, 38.7. MS (m/z,%): 430 (M^+, 9), 396 (6), 198 (9), 141 (100), 115 (24). Anal Calcd for $C_{24}H_{18}N_2S_3$ C, 66.94; H, 4.21; N, 6.51; S, 22.34.Found. C,67.13;H,3.77;N,6.50; S,22.38.

2,5-Bis(2,4-dinitrophenylthio)-1,3,4-thiadiazole (5d)

An aqueous alcoholic solution of 2,5-dimercapto-1,3,4-thiadiazole **4** (225 mg, 1.5 mmol), NaOH (120 mg, 3 mmol), and 2,4-dinitro chloro benzene (607 mg, 3 mmol) was mixed and stirred at room temperature overnight. The reaction mixture was evaporated to dryness, and the remaining material was taken into water (50 mL). The pale yellow precipitate was filtered and crystallized from ethanol as a pale yellow powder **5d**. Mp 236–237°C (710 mg, 98%).R_f:0.35 (EtOAc:*n*-hexane, 1:2) IR (KBr) v (cm^{-1}): 1591, 1516, 1346, 1049, 833, 736. ^{1}H NMR (DMSO-d_6 +$CDCl_3$, 400 MHz):δ: 8.96 (d, J = 2.4 Hz, 2H), 8.44 (dd, J = 8.9 2.5 Hz, 2H), 8.23 (s, 1H), 7.67 (d, J = 2.4 Hz, 2H). ^{13}C NMR (DMSO-d_6+ $CDCl_3$, 100 MHz):δ: 165.0, 146.2, 131.4, 128.8, 121.5. MS (m/z,%): 436 (M^+, 17), 183 (58), 137 (100), 95 (63), 63 (76), 51 (14). Calculated for $C_{14}H_6N_6O_8S_3$ C, 34.85; H, 1.25; N, 17.42; S, 19.94. Found. 35.16; H, 1.37; N, 17.39; S, 19.56.

(2,4-Dinitrophenylthio)-3-(4-methylphenyl)-1,2,4-thiadiazole (7)

To a stirring solution of 3-(4-methyphenyl)-1,2,4-thiadiazole-5(*4H*)-thione **6** (208 mg,1 mmol) in *N*,*N*-dimethylformamide (10 mL) at room

temperature, potassium *tert*-butoxide (120 mg, 1 mmol) was added. After stirring for 25 min, 2,4-dinitrochlorobenzene (202 mg, 1 mmol) in *N,N*-dimethylformamide (5 mL) was added, and the reaction mixture was stirred for further 24 h at room temperature. After the disappearance of the starting materials (TLC monitoring), the reaction mixture was quenched with brine (50 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Crystallization from benzene:petroleum ether (1:1) gave **7** as yellow needles. Mp 169–171°C (Lit.[11] 168–170°C) (82%). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 178.8, 175.0, 146.0, 145.6, 141.7, 140.1, 130.8, 129.1, 128.3, 127.6, 121.3, 21.5. MS (m/z,%): 374 (M^+, 35), 328 (7), 149 (100), 117 (32), 91 (13), 63 (6).

3-Phenyl-5-{(4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazol-2-ylthio)mercuriothio}-1,3,4-thiadiazole-2(3H)-thione (8)

An aqueous ethanolic solution of mercury (II) chloride (197 mg, 0.5 mmol) (10 mL) was added dropwise to a solution of potassium 4-phenyl-5-thioxo-4,5-dihydro-1,3,4-thiadiazole-2-thiolate **1**[10] (264 mg, 1 mmol) in ethanol (5 mL). The reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure. The remaining solid material was dissolved in THF and filtered to remove solid parts (KCl). After the evaporation of solvent, crude material was crystallized from ethanol to give **8** as yellow powder (0.435 g, 65%). Mp 186–187°C. IR (KBr) v (cm^{-1}): 1628 (C=N), 1492, 1429, 1365, 1230, 1020, 842, 759, 682, 607. ^1H NMR (DMSO-d_6, 400 MHz): δ: 7.95–7.58 (m, 4H), 7.58–7.25 (m, 6H).^{13}C NMR (DMSO-d_6, 100 MHz) δ: 186.9 (C=S), 159.7, 138.4, 129.4, 126.0.MS (m/z,%): 450 (M-Hg, 9), 314 (4), 226 (9), 202 (6), 135 (36), 105 (28), 77 (100), 63 (95), 51 (26). Calculated for $C_{16}H_{10}HgN_4S_6$ C, 29.51; H, 1.55; N, 8.60; S, 29.54 found C, 30.14; H, 1.66; N, 8.55; S, 29.08.

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