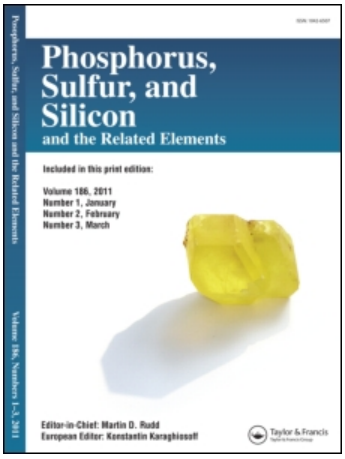

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Reaction of Hydrazonoyl Halides 52:[1] Synthesis and Antimicrobial Activity of Some New Pyrazolines and 1,3,4-Thiadiazolines

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Reaction of Hydrazonoyl Halides 52:[1] Synthesis and Antimicrobial Activity of Some New Pyrazolines and 1,3,4-Thiadiazolines

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[5-Substituted 2-(3-phenyl-5-substituted 2-pyrazolinyl)(1,3-thiazol-4-yl)] phenyldiazene and 2,3-dihydro-1,3,4-thiadiazoles were synthesized via reactions of hydrazonoyl halides with 5-substituted-3-phenyl-4,5-dihydropyrazole-1-carboximidothionic acid and {[2-2-{aza-2-((methylthioxomethyl)-amino]-vinyl}phenyl)-1-azavinyl]amino}methylthiomethane-1-thione, respectively. All structures of the newly synthesized compounds were elucidated by elemental analysis, spectral data, X-ray single crystal, and alternative synthesis methods whenever possible. Some of the new compounds were tested towards bacteria. In general, all tested compounds were capable of a high inhibiting the growth of gram positive and gram negative.

Keywords 2,3-Dihydro-1,3,4-thiadiazoles; arylazothiazoles; hydrazonoyl halides; pyrazolines

INTRODUCTION

Thiosemicarbazones and its derivatives have attracted considerable pharmaceutical interest due to their antiviral,[2] antibacterial,[3–5] and antitumer activities.[6–12] In continuation of our work,[13–16] we report herein the reactivity of hydrazonoyl halides towards 5-substituted-3-phenyl-4,5-dihydropyrazole-1-carboximidothionic acid and {[2-2-{aza-2-[(methylthioxomethyl)-amino]-vinyl}phenyl)-1-aza-vinyl] amino}methylthiomethane-1-thione.

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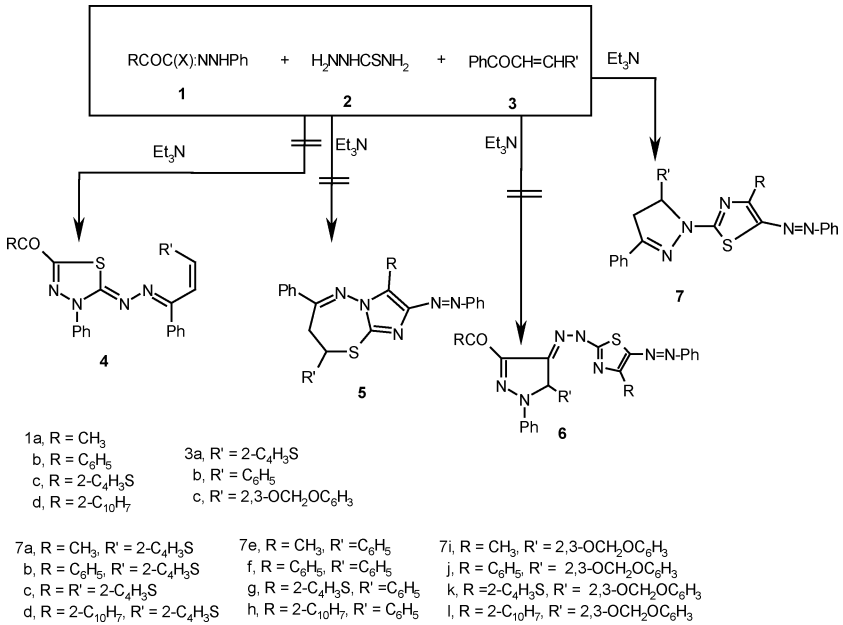
RESULTS AND DISCUSSION

C-Acetyl-*N*-phenylhdrazonoyl chloride (**1a**) was reacted with thiosemicarbazide (**2**) and 1-phenyl-3-(2-thienyl)prop-2-ene-1-one (**3a**) in ethanolic triethylamine gave one isolable product according to TLC. The product seemed to be one of the structures **4a**–**7a** (Scheme 1). Its IR

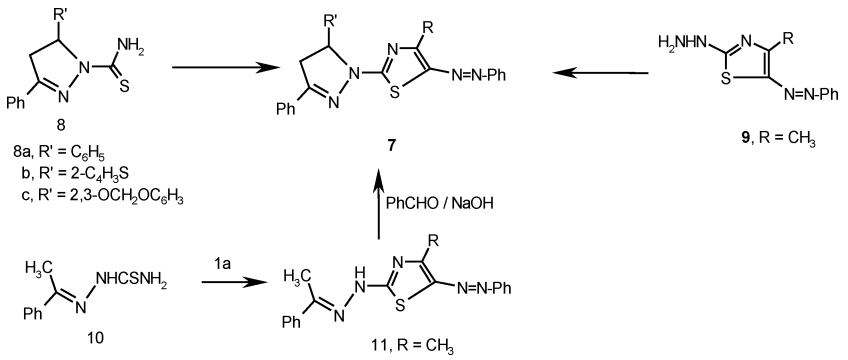


SCHEME 1

spectrum revealed bands at 3048 (CH), 1532 (C=C) and no absorption band between 1650—1800, due the absence of CO group, ^{1}H NMR spectrum showed signals at $\delta = 2.58$ (s, 3H, CH_3), 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 13H, ArH's and thiophene protons) and its X-Ray single crystal showed in Figure 1. Foregoing data the product formulated as [5-methyl-2-(3-phenyl-5-(2-thienyl)(2-pyrazolinyl))(thiazol-4-yl)]phenyldiazene (**7a**).

Also, compound **7a** was elucidated by alternative synthesis. Thus, compound **8b**, which prepared from **2** and **3b**, was reacted with **1a** or reaction of **9a**, which prepared from **1a** and **2**, with 1-phenyl-3-(2-thienyl)prop-2-ene-1-one (**3a**) gave, in each case, product identical in all respects (mp., mixed mp., and spectra) with **7a**.

Analogously, compounds **7b–l** were synthesized by the appropriate hydrazonoyl halides **1a–d** and the appropriate **8a–c** in boiling ethanol containing triethylamine (Scheme 2). Acetophenone thiosemicarbazone



SCHEME 2

(**10**) was reacted **1a** afforded **11a** which reacted with benzaldehyde in sodium hydroxide gave product identical in all respects (mp., mixed mp. and spectra) with **7e**.

On the other hand, benzene-1,2-dicarbaldehyde was reacted with methyl hydrazinecarbodithioate gave {[2-2-aza-{2-[(methylthioxomethyl)amino]-vinyl}phenyl)-1-azavinyl]amino}methylthiomethane-1-thione (**12**). Structure **12** was elucidated by elemental analysis, spectra, and chemical transformation. Thus, **12** was reacted with *C*-ethoxycarbonyl-*N*-phenylhydrazonoyl chloride in ethanolic triethyamine gave ethyl 2-[3-{2-[2,3-diaza-3-[5-ethoxycarbonyl)-3-phenyl(1,3,4-thiadiazolin-2-ylidene)]prop-1-enyl]phenyl}-1,2-diazaprop-2-

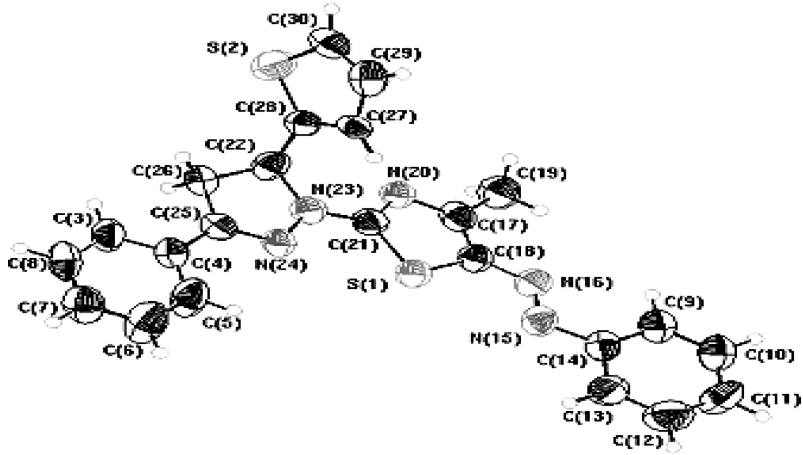


FIGURE 1 X-Ray single crystal of [5-methyl-2-(3-phenyl-5-(2-thienyl)(2-pyrazolinyl))(thiazol-4-yl)]phenyldiazene (**7a**).

enylidene]-3-phenyl-1,3,4-thiadiazoline-5-carboxylate (**15**) in a good yield (Scheme 3). Structure **15** was confirmed by elemental analysis, spectra and alternative synthesis route. Thus, benzene-1,2-dicarbaldehyde was reacted with 2,3-dihydro-1,3,4-thiadiazole **16**[17] in ethanol afforded product identical in all respects (mp., mixed mp. and spectra) with **15a**.

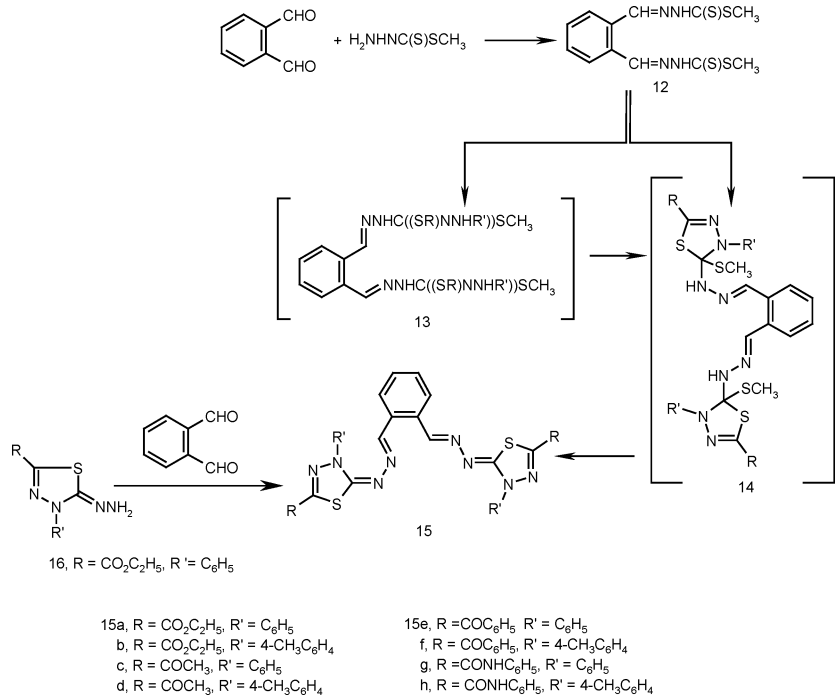


FIGURE 2

The formation of thiadiazoline **15a** can be explained via elimination of methanethiol from cycloadduct **14a**, which is assumed to be formed via 1,3-dipolar cycloaddition of nitrile imide (generate in situ by treatment of **1a** with triethylamine) to C=S double bond of **12** or by its stepwise path involving substitution via 1,3–addition of thiol **12** to nitrile imide to give a cyclic hydrazone **13a**, which transformed to cyclic intermediate **14a**. Cyclization of the latter is achieved by elimination of methanethiol to afford the final product **15**. All attempts to isolate either intermediate hydrazone **13a** or cycloadduct **14a** were unsuccessful (c.f., Scheme 3).

Similar, compound **12** was reacted with the appropriate hydrazonoyl halides **1b–h** in ethanol containing triethylamine gave 2,3-dihydro-1,3,4-thiadiazoles **15b**–**h**, respectively.

Antimicrobial Activity

The tested microorganisms were gram +ve bacteria, gram -ve bacteria, and some fungal plants. Sensitivity of the selected microorganisms to some synthesized compounds were determined in vitro culture that were dissolved in chloroform, the tests were carried out using the filter paper and hole plate method.[18,19] Studies on the biological activity of compounds in comparison with Ampicillin and tetracycline showed in Table I. In general all tested compounds were capable of a high inhibiting the growth of gram positive and gram

TABLE I Response of Various Microorganisms to Some Synthesized Compounds in vitro (Culture)

Microorganisms/ compound no.	*Staphylococcus albus*(G^+)	*Streptococcus faecalis*(G^+)	*Bacillus subtilis* (G^+)	*Echerichia coli* (G^-)	*Aspergills flvus (Fungus)*	*Candida albicans (fungus)*
Ampicillin/ tetracycline	34R/27	37/31	33/30	39/34	0.0/0.0	20/37
7a	13	14	14	14	0.0	14
7b	14	14	15	14	0.0	14
7c	13	14	14	14	0.0	15
7d	13	14	14	14	0.0	15
7e	13	13	13	14	0.0	14
7f	14	14	14	13	0.0	15
7g	13	13	12	14	0.0	14
7h	14	15	14	15	0.0	15
7i	14	13	14	13	0.0	14
7k	15	14	13	13	0.0	15
7l	14	15	15	14	0.0	15
9	18	18	20	18	14	18
11	17	16	18	18	0.0	17
15a	14	14	15	15	12	14
15b	13	13	15	12	0.0	13
15c	13	14	13	14	0.0	13
15e	14	15	14	13	0.0	14
15f	15	15	15	15	0.0	13
15g	13	13	14	14	0.0	14
15h	14	14	13	13	0.0	13

St. Reference standard; Chloramphenicol was used as a standard antibacterial agent; Terbinafin was used as a standard antifungal agent. Values show zone of inhibition in mm. Diameter of the inhibition zones were: high (11–15 mm), moderate (6–10 mm), slight (1–5 mm), and negative (0).

negative. Also, Table I showed the tested compounds were a high inhibition towards *Candida albicans (Fungus) and negative Aspergills flvus (Fungus).*

EXPERIMENTAL

All melting points were determined on an electrothermal apparatus and are uncorrected. IR spectra were recorded (KBr discs) 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. X-ray single crystals analysis was obtained from the National Research Centre, Dokki, Cairo, Egypt. Hydrazonoyl halides were prepared as previously reported.[20–25]

Synthesis of [5-Substituted-2-(3-phenyl-5-(2-substituted)(2-pyrazolinyl))(thiazol-4-yl)]phenyldiazene (7a–l), General Method

Equimolar amounts of the appropriate hydrazonoyl halides **1a–d** (5 mmol), thiosemicarbazide (0.46 g, 5 mmol), the appropriate of 1-phenyl-3-(2-substituted)prop-2-ene-1-one (**3a–c**), and triethylamine (0.75 mL, 5 mmol) in ethanol (20 mL) were heated under reflux for 3 h. The resulting solid was collected and recrystallized from acetic acid to give **7a–l** (Tables II and III).

Synthesis of [5-Methyl-2-(3-phenyl-5-(2-thienyl)(2-pyrazolinyl))(thiazol-4-yl)]phenyldiazene (7a)

Method A. A mixture of amino(3-phenyl-5-(2-thienyl)(2-pyrazolinyl))methane-1-thione (**8a**) (1.40 g, 5 mmol), *C*-acetyl-*N*-phenylhdrazonoyl chloride **1a** (0.98 g, 5 mmol), and triethylamine (0.75 mL, 5 mmol) in ethanol (20 mL) was boiled under reflux for 2 h. The resulting solid was collected and recrystallized from acetic acid to give **7a** (Tables II and III).

Method B. A mixture of (2-hydrazino-4-methyl)(1,3-thiazol-5-yl))phenyldiazene (**9a**, 1.16 g, 5 mmol) and 1-phenyl-3-(2-thienyl)prop-2-ene-1-one (**3a)** (1.16 g, 5 mmol)) in ethanol (20 mL) was boiled under reflux for 2 h. The result solid was collected and recrystallized to give identical product with**7a**.

TABLE II Characterization Data of the Newly Synthesized Compounds

Compd. no.	Mp.,°C solvent	Yield % colour	Mol. formula mol. wt.	% Analyses, calcd./found			
				C	H	N	S
7a	200–201 Acetic	82 Red	$C_{23}H_{19}N_5S_2$ 429.57	64.31 64.22	4.46 4.46	16.30 16.20	14.93 15.10
7b	242–244 Acetic	84 Red	$C_{28}H_{21}N_5S_2$ 491.64	68.41 68.51	4.31 4.42	14.24 14.40	13.04 12.90
7c	220–221 Acetic	85 Red	$C_{26}H_{19}N_5S_3$ 497.67	62.75 62.85	3.85 4.00	14.07 14.12	19.33 19.53
7d	224–225 Acetic	78 Red	$C_{32}H_{23}N_5S_2$ 541.70	70.95 71.10	4.28 4.30	12.93 13.20	11.84 11.95
7e	210–211 Acetic	79 Red	$C_{25}H_{21}N_5S$ 423.54	70.90 71.10	5.00 5.10	16.54 16.58	7.57 7.61
7f	270–272 Acetic	81 Red	$C_{30}H_{23}N_5S$ 485.60	74.20 74.32	4.77 4.85	14.42 14.35	6.60 6.42
7g	255–256 Acetic	80 Red	$C_{28}H_{21}N_5S_2$ 491.64	68.41 68.24	4.31 4.32	14.24 14.32	13.04 12.85
7h	235–236 Acetic	69 Red	$C_{34}H_{25}N_5S$ 535.68	76.24 76.42	4.70 4.85	13.07 12.95	5.99 6.12
7i	180–182 Acetic	67 Red	$C_{26}H_{21}N_5O_2S$ 467.55	66.79 66.92	4.53 4.35	14.98 14.89	6.86 6.72
7j	253–255 Acetic	69 Red	$C_{31}H_{23}N_5O_2S$ 529.63	70.30 70.20	4.38 4.24	13.22 13.42	6.05 6.12
7k	203–205 Acetic	72 Red	$C_{29}H_{21}N_5O_2S_2$ 535.65	65.03 65.15	3.95 3.78	13.07 13.24	11.97 12.12
7l	199–201 Acetic	75 Red	$C_{35}H_{25}N_5O_2S$ 579.69	72.52 72.65	4.35 4.53	12.08 12.12	5.53 5.74
8a	201–203 EtOH	68 Pale yellow	$C_{16}H_{15}N_3S$ 281.38	68.30 68.20	5.37 5.24	14.93 15.12	11.40 11.20
8b	195–197 EtOH	72 Orange	$C_{14}H_{13}N_3S_2$ 287.41	58.51 58.35	4.56 4.65	14.62 14.56	22.31 22.22
8c	196–197 EtOH	66 Yellow	$C_{17}H_{15}N_3O_2S$ 325.39	62.75 62.85	4.65 4.56	12.91 13.20	9.85 10.12
9	177–179 EtOH	85 Red	$C_{10}H_{11}N_5S$ 233.30	51.48 51.65	4.75 4.85	30.02 29.90	13.74 13.60
11	159–161 EtOH	78 Red	$C_{18}H_{17}N_5S$ 335.43	64.45 64.54	5.11 5.18	20.88 20.95	9.56 9.75
12	149–150 EtOH	74 Black	$C_{12}H_{14}N_4S_4$ 342.53	42.08 41.97	4.12 4.35	16.36 16.58	37.45 37.79
15a	200–201 Dioxan	78 Yellow	$C_{30}H_{26}N_8O_4S_2$ 626.72	57.50 57.56	4.18 4.30	17.88 17.60	10.23 10.32
15b	253–254 Dioxan	80 Yellow	$C_{32}H_{30}N_8O_4S_2$ 654.78	58.70 58.60	4.62 4.70	17.11 16.95	9.79 9.84
15c	230–231 Dioxan	82 Yellow	$C_{28}H_{22}N_8O_2S_2$ 566.66	59.35 59.26	3.91 4.11	19.77 19.85	11.32 11.51
15d	240–242 Dioxan	85 Brown	$C_{30}H_{26}N_8O_2S_2$ 594.71	60.59 60.72	4.41 4.68	18.89 18.75	10.78 11.00
15e	238–240 Dioxan	79 Brown	$C_{38}H_{26}N_8O_2S_2$ 690.81	66.07 66.21	3.79 3.52	16.22 16.16	9.28 9.23
15f	210–212 Dioxan	78 Brown	$C_{40}H_{30}N_8O_2S_2$ 718.87	66.83 68.68	4.21 4.42	15.59 15.75	8.92 9.10
15g	245–247 Dioxan	82 Yellow	$C_{38}H_{28}N_{10}O_2S_2$ 720.84	63.32 63.23	3.92 4.12	19.43 19.34	8.90 9.10
15h	280–282 Dioxan	85 Yellow	$C_{40}H_{32}N_{10}O_2S_2$ 748.89	64.15 64.32	4.31 4.23	18.70 18.60	8.56 8.62

TABLE III ^{1}H NMR Spectra of Some Newly Synthesized Compounds

Comp. no.	Spectral data
7a	^{1}H NMR: 2.58 (s, 3H, CH_3), 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 13H, ArH's, and thiophene protons)
7b	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 18H, ArH's, and thiophene protons)
7c	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 16H, ArH's, and thiophene protons)
7d	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 20H, ArH's, and thiophene protons)
7e	^{1}H NMR: 2.58 (s, 3H, CH_3), 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 15H, ArH's)
7f	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 20H, ArH's)
7g	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 18H, ArH's, and thiophene protons)
7h	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 22H, ArH's)
7i	^{1}H NMR: 2.58 (s, 3H, CH_3), 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 5.92 (s, 2H, CH_2), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 13H, ArH's, and thiophene protons)
7j	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 5.92 (s, 2H, CH_2), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 18H, ArH's)
7k	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 5.92 (s, 2H, CH_2), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 16H, ArH's, and thiophene protons)
71	^{1}H NMR: 3.66 (dd, 1H, $CH_{2(pyraz)}$), 4.01 (dd, 1H, $CH_{(pyraz)}$), 6.15 (d, 1H, $CH_{2(pyraz)}$), and 7.00–7.82 (m, 20H, ArH's)
8a	^{1}H NMR: 3.66 (dd, 1H), 4.01 (dd, 1H), 4.6 (s, br., 2H, NH_2), 6.15 (d, 1H), 7.00–7.82 (m, 10H, ArH's), and 9.34 (s, br., 1H, NH)
8b	3.66 (dd, 1H), 4.01 (dd, 1H), 4.6 (s, br., 2H, NH_2), 6.15 (d, 1H), and 7.00–7.82 (m, 8H, ArH's, and thiophene protons).
8c	^{1}H NMR: 3.66 (dd, 1H), 4.01 (dd, 1H), 4.6 (s, br., 2H, NH_2), 5.92 (s, 2H, CH_2), 6.15 (d, 1H), and 7.00–7.82 (m, 8H, ArH's).
9	2.47 (s, 3H, CH_3), 4.34 (s, 2H, NH_2), 7.00–7.32 (m, 5H, ArH's), and 9.23 (s, br., 1H, NH)
11	^{1}H NMR: 1.12 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), and 7.23–8.24 (m, 11H, ArH's, and NH proton)
12	^{1}H NMR: 2.31 (s, 6H, $2CH_3$) and 7.51–7.92 (8H, ArH,s and NH).
15a	^{1}H NMR: 1.30 (t, 6H, 2 CH_2CH_3), 4.22 (q, 4H, 2 CH_2CH_3), 6.46–7.92 (m, 14 H, ArH's), and 8.42 (s, 2H, 2 CH vinyl)
15b	^{1}H NMR: 1.30 (t, 6H, 2 CH_2CH_3), 2.35 (s, 6H, 2 CH_3), 4.22 (q, 4H, 2 CH_2CH_3), 6.46–7.92 (m, 12 H, ArH's), and 8.42 (s, 2H, 2 CH vinyl)
15c	^{1}H NMR: 2.21 (s, 6H, 2 CH_3), 6.46–7.92 (m, 14 H, ArH's), and 8.42 (s, 2H, 2 CH vinyl)
15d	^{1}H NMR: 2.20 (s, 6H, 2 CH_3), 2.35 (s, 6H, 2 CH_3), 6.46–7.92 (m, 12 H, ArH's), and 8.42 (s, 2H, 2 CH vinyl)
15e	^{1}H NMR: 6.46–7.92 (m, 24 H, ArH's) and 8.42 (s, 2H, 2 CH vinyl)
15f	^{1}H NMR: 2.35 (s, 6H, 2 CH_3), 6.46-7.92 (m, 22 H, ArH's), and 8.42 (s, 2H, 2 CH vinyl)
15g	^{1}H NMR: 6.46–7.92 (m, 24 H, ArH's), 8.21 (s, br., 2H, 2NH), and 8.42 (s, 2H, 2 CH vinyl)
15h	^{1}H NMR: 2.35 (s, 6H, 2 CH_3), 6.46–7.92 (m, 22 H, ArH's), 8.21 (s, br., 2H, 2NH), and 8.42 (s, 2H, 2 CH vinyl)

Synthesis of [5-Methyl-2-(3-phenyl-5-(2-phenyl)(2-pyrazolinyl))(thiazol-4-yl)]phenyldiazene (7e)

Equimolar amounts of (1-aza-2-phenylprop-1-enyl)[4-methyl-5-(phenyldiazenyl)(1,3-thiazol-2-yl)]amine (**11**) (1.60 g, 5 mmol) and benzaldehyde (0.53 g, 5 mmol) in ethanol (20 mL) was cooled at 5°C then added sodium hydroxide solution (4N, 10 mL) portion wise while stirring. The resulting solid was collected and recrystallized from acetic acid to give **7e**.

Synthesis of Amino(3-Phenyl-5-substituted (2-pyrazolinyl))methane-1-thione (8a–c)

A mixture of the appropriate **3a–c** (5 mmol) and thiosemicarbazide (0.46 g, 5 mmol) in ethanol (20 mL) was heated under refluxed for 3 h. The resulting solid was collected and recrystallized from ethanol to give **8a–c**, respectively (Tables II and III).

Synthesis of (2-Hydrazino-4-methyl)(1,3-thiazol-5-yl))phenyldiazene (9a)

A mixture of *C*-acetyl-*N*-phenylhdrazonoyl chloride **1a** (0.98 g, 5 mmol), thisemicarbazide (0.5 g, 5 mmol), and triethylamine (0.75 mL, 5 mmol) in ethanol (20 mL) was boiled under reflux for 2 h. The resulting solid was collected and recrystallized from ethanol to give **9a** (Tables II and III).

Synthesis of (1-Aza-2-phenylprop-1-enyl)[4-methyl-5-(phenyldiazenyl)(1,3-thiazol-2-yl)]amine (11)

A mixture of *C*-acetyl-*N*-phenylhdrazonoyl chloride (**1a**) (0.98 g, 5 mmol) and [(-1-aza-2-phenylprop-1-enyl)amino]aminometane-1-thione (**10**) (0.96 g, 5 mmol) and triethylamine (0.75 mL, 5 mmol) in ethanol (20 mL) was heated under reflux for 2 h. The resulting solid was collected and recrystallized to give **11** (Tables II and III).

Synthesis of[2-2-Aza-2-[(methylthioxomethyl)amino]-vinylphenyl)-1-azavinyl]-aminomethylthiomethane-1-thione (12)

Equimolar amount of benzene-1,2-dicarbaldehyde (0.67 g, 5 mmol) and methyl hydrazinecarbodithioate (0.66 g, 5 mmol) in 2-propanol (40 mL) was refluxed for 30 min. The reaction mixture was cooled and solid formed was collected and recrystallized from ethanol to give **12** (Tables I and II).

Synthesis of Ethyl 2-[3-2-[2,3-Diaza-3-[3,5-disubstituted (1,3,4-Thiadiazolin-2-ylidene)]prop-1-enyl]phenyl-1,2-diazaprop-2-enylidene]-3,5-disubstituted 1,3,4-thiadiazoline 15a–h

Equimolar amount of the appropriate of hydrazonoyl halides (5 mmol) and {[2-2-aza-2-[(methylthioxomethyl)amino]-vinyl}phenyl)-1-azavinyl]aminomethylthio-methane-1-thione (**12)** (1.7 g, 5 mmol) in ethanol (40 ml) was stirred for 2 h. The resulting solid was collected and recrystallized from dioxan to give **15a–h**, respectively (Tables II and III).

X-Ray Structural Analysis of Compound 7a

Crystal data $C_{23}H_{19}N_5S_2$, M = 429.57, triclinic. PT, a = 10.4778 (4)A°, b = 10.6635 (4)A°, c = 11.0283 (6)A°, α = 63.852 (2)°, β = 86.687 (2)°, γ = 74.257 (2)°, V = 1061.87 (8)^{3}A, Z = 2.

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