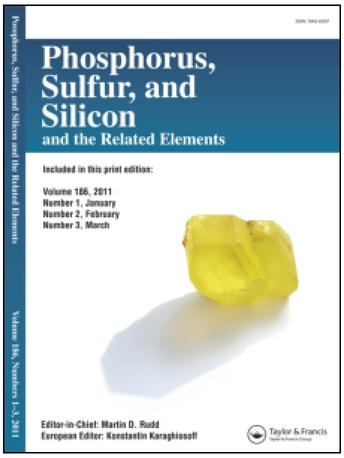

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Solvent-Free Microwave Synthesis of (Aryland Heteroaryl-methylene)-amino Derivatives of 4-Amino-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine and 4-Amino-5-methyl-3-thioxo-2*H*-1,2,4-triazole: Crystal Structure of 6-Methyl-4-(3-nitrobenzylideneamino)5-oxo-3-thioxo-2*H*-1,2,4-triazine

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To cite this Article Tabatabaee, Masoumeh , Ghassemzadeh, Mitra , Zarabi, Behnaz , Heravi, Majid M. , Abbasinejad, Mohammad Anary- and Neumüller, Bernhard(2007) 'Solvent-Free Microwave Synthesis of (Aryland Heteroaryl-methylene)-amino Derivatives of 4-Amino-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine and 4-Amino-5-methyl-3-thioxo-2*H*-1,2,4-triazole: Crystal Structure of 6-Methyl-4-(3-nitrobenzylideneamino)5-oxo-3-thioxo-2*H*-1,2,4-triazine', Phosphorus, Sulfur, and Silicon and the Related Elements, 182: 3, 677 — 686

To link to this Article: DOI: 10.1080/10426500601047461

URL: http://dx.doi.org/10.1080/10426500601047461

Phosphorus, Sulfur, and Silicon, 182:677–686, 2007

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500601047461

Solvent-Free Microwave Synthesis of (Aryl- and Heteroaryl-methylene)-amino Derivatives of 4-Amino-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine and 4-Amino-5-methyl-3-thioxo-2*H*-1,2,4-triazole: Crystal Structure of 6-Methyl-4-(3-nitrobenzylideneamino)-5-oxo-3-thioxo-2*H*-1,2,4-triazine

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*The reaction of 4-amino-6-methyl-5-oxo-3-thioxo-2H-1,2,4-triazine, (AMTTO, **[1]**), and 4-amino-5-methyl-3-thioxo-2H-1,2,4-triazole, (AMTT, **[2]**), with various aldehydes under classical heating and microwave irradiation in a solvent-free system resulted in the formation of the corresponding imines **3a–e** and **4a–d**. The compounds were characterized by their spectroscopic data and elemental analysis. Compound **3a** was also characterized by X-ray diffraction studies. Crystal data for **3a** at −80°C: triclinic, space group P-1, $a = 796.7(2)$, $b = 844.8(2)$, $c = 1073.1(2)$ pm, $\alpha = 88.44(2)^\circ$, $\beta = 76.59(2)^\circ$, $\gamma = 63.42(2)^\circ$, $Z = 2$.*

Received January 7, 2006; accepted August 19, 2006.

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Keywords 1,2,4-triazine; 1,2,4-triazole; schiffbase; microwave synthesis

INTRODUCTION

4-amino-6-methyl-1,2,4-triazine-3-thione-5(2*H*)-one (AMTTO, [**1**]) and 4-amino-5-methyl-1,2,4-triazole-3(4*H*)-thione (AMTT, [**2**]) are well-known heterocyclic thiones. Some of their derivatives exhibit biological activity and have been used for various purposes such as herbicides, neutral antibiotics, antibacterial agents was, etc.[1]

Compound **1** is easily prepared from the reaction between thiocarbohydrazide and pyruvic acid,[2] and **2** was prepared from the reaction of thiocarbohydrazide and acetic acid.[3]

Recently we have reported the synthesis of 1,2,4-triazole[1,5-*d*]-1,2,4-triazine-5-thiones from the reaction of **1** with arylnitriles, showing the reactivity of the amino group of **1** with electrophiles.[4] AMTTO– and AMTT–imine ligands are good candidates for complexation. We have recently reported the synthesis and characterization of a silver(I) complex of 6-methyl-4-[thiophene-2-yl-metylene-amino]-3-thioxo-[1,2,4]-triazin-3,4-dihydro(2*H*)-5-one and copper(I) complexes of 4-(3-methoxybenzylideneamino)-5-methyl-2*H*-1,2,4-triazole-3(4H)-thione.[5,6]

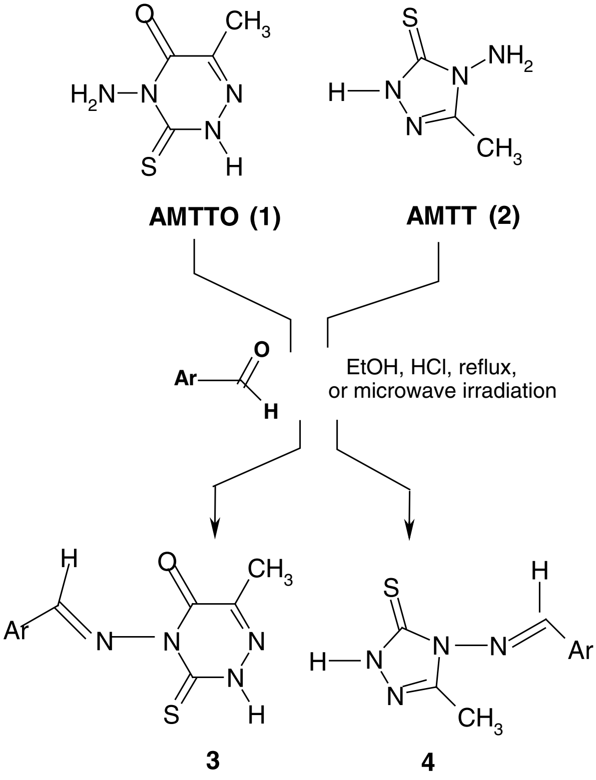
The use of microwave irradiation in organic synthesis has become increasingly popular within the pharmaceutical and academic areas because it is a technology that can accelerate organic reactions. Recent advances in microwave-assisted synthesis have been reviewed in 2004.[7] Recently, microwave-enhanced chemical reactions, especially under solvent-free conditions, have attracted much attention.[8] They offer several advantages over conventional homogeneous and heterogeneous reactions with respect to high reaction rates and yields.

In continuation of our recent work on microwave-assisted reactions under solvent-free conditions,[9] in this communication we report our results on the synthesis of various Schiff-bases derived from AMTTO and AMTT under classical heating and microwave irradiation in a solvent-free system.

RESULTS AND DISCUSSION

AMTTO (**1**) and AMTT (**2**) were heated with a series of aromatic aldehydes in ethanol using HCl as an acid catalyst under reflux to afford the corresponding imines (**3a–f** and **4a–d**) (Scheme 1). The results are listed in Table I.

Organic solvents are often expensive; they are flammable and can be hazardous to the environment. In continuation of our program to



SCHEME 1 The reaction of AMTTO (**1**) and AMTT (**2**) with aromatic aldehydes in refluxing ethanol and solvent-free under microwave irradiation.

TABLE I Synthesis of Imines of AMTTO and AMTT in Refluxing Ethanol and Solvent-free under Microwave Irradiation

		Refluxing EtOH		Solvent-Free	
	Aldehyde	Reaction Time (h)	Yield (%)	Reaction Time (sec)	Yield (%)
3a	3-nitrobenzaldehyde	15	67	220	80
3b	2-bromobenzaldehyde	17	48	210	95
3c	2,4-dichlorobenzaldeyde	17	74	270	83
3d	5-methylthiophen-2-carbaldehyde	15	47	240	64
3e	2-methoxybenzaldehyde	12	55	140	87
3f	3-methoxybenzaldehyde	14	58	180	91
4a	3-nitrobenzaldehyde	15	84	200	86
4b	2-bromobenzaldehyde	13	59	180	80
4c	2,4-dichlorobenzaldeyde	14	76	250	82
4d	5-methylthiophen-2-carbaldehyde	14	72	210	77

TABLE II Crystallographic Data for 3a

Empirical formula	$C_{11}H_9N_5O_3S$	Absorption correction	Numerical
Formula mass	291.28	$\mu_{Mo-K\alpha}(cm^{-1})$	2.7
Crystal size (mm)	0.26 × 0.09 × 0.08	Temperature (K)	193
Crystal system	Triclinic	2θ range	52.54
Space group	P-1	Index range	
a (pm)	796.7(2)	h	−9→9
b (pm)	844.8(2)	k	−9→10
		l	−13→13
c (pm)	1073.1(2)	Reflections collected	6803
$\alpha(^\circ)$	88.44(2)	Unique reflections (R_{int})	2510(0.0588)
$\beta(^\circ)$	76.59(2)	Reflections with $F_o > 4\sigma(Fo)$	1662
$\gamma(^\circ)$	63.42(2)	Parameters	217
Volume($pm^3 \cdot 10^6$)	1275.2(2)	R_1	0.0441
Z	2	wR_2 (all data)	0.1122
$D_{calcd.}(g \cdot cm^{-3})$	1.546	Largest diff. peak and hole $((e \cdot pm^{-3}) \cdot 10^{-6})$	0.35

$w = 1/[\sigma^2(F_o^2) + (0.0656\ P)^2]$; $P = [\max(F_o^2, 0) + 2\ F_c^2]/3$

develop environmentally benign reactions under solvent-free conditions combined with microwave irradiation,[10] AMTTO (**1**) and AMTT (**2**) were thoroughly mixed with 3-nitrobenzaldehyde in a beaker to make an intimate pair. The beaker was placed in a household microwave oven. Progress of the reaction was monitored by TLC, using ethylacetate and petroleum ether (2:1) as an eluent. The imine of AMTTO **3a** was formed in very short time and in a high yield. To establish the generality of this solvent-free method, various aromatic aldehydes were reacted with AMTTO and AMTT to yield the corresponding imines in a very short time and in high yields (Scheme 1). The results are collected in Table I.

The crystallographic data of **3a** and selected bond lengths and angles are given in Tables II and III, respectively. Compound **3a** crystallized in the triclinic space group P-1 (Figure 1). The bond lengths of 166.5(3) pm for S1-C1 and 121.4(3) pm for O1-C2 are indicative of a

TABLE III Selected Bond Lengths (pm) and Bond Angles (°) in 3a

S1-C1	166.5(3)	S1-C1-N1	123.3(2)
C1-N1	137.7(3)	S1-C1-N4	122.8(2)
C1-N4	134.5(3)	C1-N1-N2	116.8(2)
N1-N2	141.7(3)	N1-N2-C5	113.8(2)
N2-C5	126.9(3)	N2-N1-C2	118.6(2)
C5-C6	145.9(3)	N3-N4-C1	127.8(3)
C2-O1	121.4(3)		

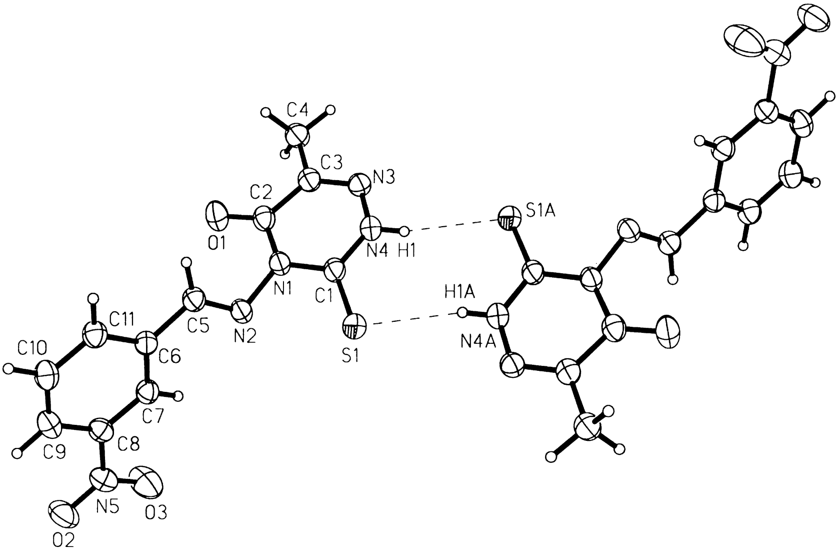


FIGURE 1 The molecular structure of 3a in the crystal. Thermal ellipsoids with 40% probability.

high double-bond character and were also observed in AMTTO.[11] The bond length C5-N2 with 126.9(3) pm lay in the range observed in similar compounds such as 2-acetylthiophene thiosemicarbazone (129.2 [3] pm), 2-acetylthiophene 4-phenyl thiosemicarbazone (128.2 [3] pm),[12] and 4-[(4-chloro-benzylidene)-amino]-6-methyl-3-thioxo[1,2,4]-triazin-3,4-dihydro(2*H*)-5-one (126.5 [3] pm).[13]

Weak hydrogen bonding, which links the sulfur atom of one molecule to the NH-group of the adjacent one (N4-H1···S1A 326.2[2] pm), is responsible for the centrosymmetric geometry of **3a**.

In conclusion, we have developed a facile, efficient, and fast method for the synthesis of imines of AMTTO and AMTT, which are good candidates for complexation with metals.

EXPERIMENTAL

All chemicals and solvents were purchased from (Darmstadt, Germany) or Fluka (Buchs, Switzerland) and were used without further purification or drying. AMTTO (**1**) and AMTT (**2**) were prepared according to literature procedures.[2,3] IR spectra were recorded on a Shimadzu spectrometer 883 (KBr pellets, Nujol mulls, 4000–400 cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer using

TMS as an external standard. For EI mass spectra, a Varian CH7A mass spectrometer (70 eV) was used.

General Procedure for the Reaction of AMTTO (1) and AMTT (2) with Various Aldehydes in Refluxing Ethanol

A solution of **1** or **2** (4 mmol) in EtOH (30 mL) was treated with aldehyde in a molar ratio of 1:1.5, and the resulting mixture was acidified with 37% hydrochloric acid (10 drops). The reaction mixture was refluxed for the indicated time (Table I). The solid residue was filtered, washed with cold ethanol (10 mL), and recrystallized from EtOH.

General Procedure for the Reaction of AMTTO (1) and AMTT (2) with Various Aldehydes Under Microwave Irradiation in a Solvent-Free System

1 or **2** (1 mmol) was mixed in a beaker with aldehyde in a molar ratio of 1:1.5 for solid aldehydes and 1:2 for liquid aldehydes. The beaker was placed in a microwave oven for the appropriate time (Table I). The reaction mixture was dissolved in ethanol or methanol (2 mL), and the solid residue was filtered, washed with cold ethanol (5 mL), and recrystallized from EtOH.

6-Methyl-4-(3-nitrobenzylideneamino)-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3a)

Pale yellow crystals, m.p. 234–235°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3140, CO 1692, CN (imine) 1616 s, CN (triazine) 1564 s;^{1}H NMR (CDCl$_3$), δ: 2.33 (s, 3H, CH$_3$), 7.75 (dd, $J = 7.6, 6.5$ Hz, 1H, Ar), 8.24 (d, $J = 7.6$ Hz, 1H, Ar), 8.44 (d, $J = 6.5$ Hz, 1H, Ar), 8.73 (s, 1H, Ar), 9.16 (s, 1H, CH=N), 10.1 (br, 1H, NH); MS: m/z 291 [M$^+$], 143 ($C_4H_5N_3OS$), 102 ($C_3H_7N_3O^+$), 69, 42 ($C_2H_4N^+$). Anal. calcd. for $C_{11}H_9N_5O_3S$: C, 45.36; H, 3.09; N, 24.05. Found: C, 45.30; H, 3.04; N, 23.98.

4-(2-Bromobenzylideneamino)-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3b)

Colorless powder, m.p. 210–212°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3145, CO 1694, CN (imine) 1602, CN (triazine) 1559; ^{1}H NMR (d$_6$-DMSO), δ: 2.19 (s, 3H, CH$_3$), 7.58–7.60 (m, 2H, Ar), 7.81 (m, 1H, Ar), 8.18 (m, 1H, Ar), 8.95 (s, 1H, CH=N), 13.69 (br, 1H, NH); ^{13}C NMR (d$_6$-DMSO), δ: 17.3 (CH$_3$), 125.8, 128.9, 129.9 (CH, Ar), 131.2 (C, Ar), 134.1 (CH, Ar), 135.2 (C, Ar), 147.9 (C=N, imine), 150.2 (C=N, triazine), 170.9 (C=O), 172.1 (C=S). MS: m/z 324 [M^+], 182 (C_7H_4BrN), 143 ($C_4H_5N_3OS$), 102 ($C_3H_7N_3O^+$), 69, 42 ($C_2H_4N^+$). Anal. calcd. for $C_{11}H_9BrN_4OS$: C, 40.61; H, 2.76; N, 17.23. Found: C, 40.56; H, 2.71; N, 17.19.

4-(2,4-Dichlorobenzylideneamino)-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3c)

Colorless powder, m.p. 222–224°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3145, CO 1694, CN (imine) 1605, CN (triazine) 1585;^{1}H NMR (d_6-DMSO), δ: 2.18 (s, 3H, CH_3), 7.65 (d, $J = 8.5$ Hz, 1H, Ar), 7.87 (s, 1H, Ar), 8.18 (d, $J = 8.5$ Hz, 1H, Ar) 8.99 (s, 1H, CH=N), 13.7 (s, 1H, NH);^{13}C NMR (d_6-DMSO), δ: 17.3 (CH_3), 128.7 (C, Ar), 129.0, 130.0, 130.4 (CH, Ar), 136.5, 139.0 (C, Ar), 147.9 (C=N, imine), 150.1 (C=N, triazine), 169.0 (C=O), 170.9 (C=S). MS: m/z 314 [M^+], 172 ($C_7H_3Cl_2N$), 143 ($C_4H_5N_3OS$), 102 ($C_3H_7N_3O^+$), 69. Anal. calcd. for $C_{11}H_8Cl_2N_4OS$: C, 41.90; H, 2.54; N, 17.78. Found: C, 41.76; H, 2.51; N, 17.73.

6-Methyl-4-(3-methylthiophen-2-ylmethylenamino)-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3d)

Colorless powder, m.p. 226–229°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3095, CO 1694, CN (imine) 1612, CN (triazine) 1587;^{1}H NMR (d_6-DMSO), δ: 2.19 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 7.10 (d, $J = 5.0$ Hz, 1H, thiophene), 7.80 (d, $J = 5.0$ Hz, 1H, thiophene), 8.85 (s, 1H, CH=N), 13.35 (br, 1H, NH); ^{13}C NMR (d_6-DMSO), δ: 14.3 (CH_3, thiophene), 17.3 (CH_3, triazine), 130.1, 131.8, 132.9 (CH, thiophene), 146.7 (C, thiophene), 147.6 (C=N, imine), 150.5 (C=N, triazine), 166.1 (C=O), 171.3 (C=S). MS: m/z 267 [M^+], 143 ($C_4H_5N_3OS$), 122 (C_6H_5NS), 102 ($C_3H_7N_3O^+$), 69, 42($C_2H_4N^+$). Anal. calcd. for $C_{10}H_{10}N_4OS_2$: C, 45.1; H, 3.76; N, 21.05. Found: C, 45.03; H, 3.64; N, 20.96.

4-(2-Methoxybenzylideneamino)-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3e)

Colorless crystals, m.p. 212–215°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3140, CO 1657, CN (imine) 1600, CN (triazine) 1572;^{1}H NMR ($CDCl_3$), δ: 2.34 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 7.95 (m, 2H, Ar), 7.55 (m, 1H, Ar), 8.23 (m, 1H, Ar), 8.88 (s, 1H, CH=N), 10.7 (s, 1H, NH); MS: m/z 276 [M^+], 143 ($C_4H_5N_3OS$), 133 (C_8H_7NO), 102 ($C_3H_7N_3O^+$), 69, 42 ($C_2H_4N^+$). Anal. calcd. for $C_{12}H_{12}N_4O_2S$: C, 52.17; H, 4.36; N, 20.25. Found: C, 52.09; H, 4.22; N, 20.13.

4-(3-Methoxy-benzylideneamino)-6-methyl-5-oxo-3-thioxo-2*H*-1,2,4-triazine (3f)

Colerless powder, m.p. 167–169°C; IR (KBr), $\tilde{\upsilon}(\text{cm}^{-1})$: NH 3145, CO 1690, CN (imine) 1617, CN (triazine) 1575;^{1}H NMR ($CDCl_3$) δ: 2.33 (s, 3H, CH_3), 3.87 (s, 3H, OCH_3), 7.15 (m, 1H, Ar), 7.36–7.41 (m, 2H, Ar), 7.52 (m, 1H, Ar), 8.42 (s, 1H, CH=N), 10.89 (s, 1H, NH); MS: m/z 276 [M^+], 143 ($C_4H_5N_3OS$), 133 (C_8H_7NO), 102 ($C_3H_7N_3O^+$), 77, 69, 42 ($C_2H_4N^+$). Anal. calcd. for $C_{12}H_{12}N_4O_2S$: C, 52.17; H, 4.36; N, 20.25. Found: C, 52.06; H, 4.21; N, 20.11.

5-Methyl-4-(3-nitrobenzylideneamino)-3-thioxo-2*H*-1,2,4-triazole (4a)

Pale yellow powder, m.p. 220°; IR (KBr), $\tilde{\upsilon}(\text{cm}^{-1})$: NH 3105b, CN (imine) 1614 s, CN (triazole) 1590 s, 1524–1351;^{1}H NMR (d_6-DMSO), δ: 2.37 (s, 3H, CH_3), 7.85 (t, $J = 8.0$ Hz, 1H, Ar), 8.35 (d, $J = 8.0$ Hz, 1H, Ar), 8.43 (dd,$J = 8.0$, 1.6, Hz, 1H, Ar), 8.69 (d, $J = 1.6$ Hz, 1H, Ar), 10.2 (s, 1H, CH=N), 13.8 (br, 1H, NH);^{13}C NMR (d_6-DMSO), δ: 11.3 (CH_3, triazole), 122.9 (CH, Ar), 127.0 (C, Ar), 131.3 (CH, Ar), 134.4, 134.9 (CH, Ar), 137.9 (C, Ar), 148.7 (C=N, imine), 149.0 (C=N, triazole), 161.8 (C=S). MS: m/z 264 [M^++1], 114 ($C_3H_5N_3S^+$), 74, 56 ($C_2N_2H_4^+$), 42 ($C_2H_4N^+$). Anal. calcd. for $C_{10}H_9N_5O_2S$: C, 45.62; H, 3.42; N, 26.61. Found: C, 45.46; H, 3.38; N, 26.54.

4-(2-Bromobenzylideneamino)- 5-methyl -3-thioxo-2*H*-1,2,4-triazole (4b)

Colorless powder, m.p. 210°C; IR (KBr), $\tilde{\upsilon}(\text{cm}^{-1})$: NH 3105 b, CN (imine) 1610 s, CN (triazole) 1589s; ^{1}H NMR (d_6-DMSO), δ: 2.38 (s, 3H, CH_3), 7.48-7.56 (m, 2H, Ar), 7.77 (m, 1H, Ar), 8.12 (m, 1H, Ar), 10.82 (s, 1H, CH=N), 13.8 (br, 1H, NH);^{13}C NMR (d_6-DMSO), δ: 11.2 (CH_3, triazole), 125.8, 128.3, 128.8 (CH, Ar), 132.1 (C, Ar), 133.9 (CH, Ar), 134.4 (C, Ar), 149.5 (C=N, imine), 150.1 (C=N, triazole), 161.8 (C=S). MS: m/z 297 [M^++1], 115 ($C_3H_4N_3S$), 74, 56 ($C_2N_2H_4^+$), 42 ($C_2H_4N^+$). Anal. calcd. for $C_{10}H_9BrN_4S$: C, 40.40; H, 3.03; N, 18.85. Found: C, 40.51; H, 3.14; N, 18.43.

4-(2,4-Dichlorobenzylideneamino)-5-methyl-3-thioxo-2*H*-1,2,4-triazole (4c)

Colorless powder, m.p. 242–244°C; IR (KBr), $\tilde{\upsilon}(\text{cm}^{-1})$: NH 3055 b, CN (imine) 1619 s, CN (triazole) 1585s; ^{1}H NMR (d_6-DMSO), δ: 2.37 (s, 3H, CH_3), 7.56 (dd, $J = 8.5$, 1.9 Hz 1H, Ar), 7.78 (d,$J = 1.9$ Hz, 1H, Ar), 8.12 (d, $J = 8.5$ Hz, 1H, Ar), 10.89 (s, 1H, CH=N), 13.8 (br, 1H, NH);^{13}C

NMR (d$_6$-DMSO), δ: 11.2 (CH$_3$, triazole), 128.7, 129.1 (CH, Ar), 129.6 (C, Ar), 130.2 (CH, Ar), 136.2, 138.0 (C, Ar), 149.5 (C=N, imine), 154.8 (C=N, triazole), 161.6 (C=S). MS: m/z 287 [M$^+$], 115 ($C_3H_4N_3S$), 74, 56 ($C_2N_2H_4^+$), 42 ($C_2H_4N^+$). Anal. calcd. for $C_{10}H_8Cl_2N_4S$: C, 41.81; H, 2.78; N, 19.51. Found: C, 41.72; H, 2.71; N, 19.40.

5-Methyl-4-(3-methylthiophen-2-ylmethylenamino)-3-thioxo-2*H*-1,2,4-triazole (4d)

Colorless crystals**,** m.p. 200–202°C; IR (KBr), $\tilde{\upsilon}$(cm^{-1}): NH 3065, CN (imine) 1602, CN (triazole) 1578 cm^{-1};^{1}H-NMR (d$_6$-DMSO), δ: 2.19 (s, 3H, CH$_3$), 2.47 (s, 3H, CH$_3$), 6.96 (d, $J = 5.0$ Hz, 1H, thiophene), 7.28 (s, 1H, CH=N) 7.49 (d, $J = 5.0$ Hz, 1H, thiophene), 10.69 (br, 1H, NH);^{13}C NMR (d$_6$-DMSO), δ: 11.1 (CH$_3$, thiophene), 14.3 (CH$_3$, triazole), 130.6, 131.8, 132.3 (CH, thiophene), 145.9 (C, thiophene), 148.6 (C=N, imine), 157.0 (C=N, triazole), 161.6 (C=S). MS: m/z 239 [M$^+$+1], 115 ($C_3H_4N_3S$), 74, 56 ($C_2N_2H_4^+$), 42 ($C_2H_4N^+$). Anal. calcd. for $C_9H_{10}N_4S_2$: C, 45.35; H, 4.23; N, 23.15. Found: C, 45.26; H, 4.16; N, 23.01.

Crystal Structure Analysis of 3a

The crystal of **3a** was covered with perfluorinated oil and mounted on top of a glass capillary under a flow of cold gaseous nitrogen. The orientation matrix and preliminary unit cell dimensions were determined from ca. 3000 reflections (diffractometer: Stoe IPDS II; graphite-monochromated Mo-Kα radiation; $\lambda = 71.073$ pm). Intensities were corrected for Lorentz and polarization effects. In addition, a numerical absorption correction was applied. The structure of **3a** was solved by direct methods using SHELXS-97[14] and refined against F^2 by full-matrix least-squares using SHELXL-97. [15] The positions of carbon-bonded hydrogen atoms (except for H1) in **3a** were calculated for ideal positions and refined with a common displacement parameter. The H1 atom in **3a** was subjected to free refinement. The programs used were SHELXS-97, [14] SHELXL-97, [15] SHELXTL-Plus, [16] ORTEP, [17] and PLATON. [18] Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K., (Fax: + 44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk) quoting depository no. CCDC 615769.

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