Synthesis and Characterization of Novel Arylaldehyde (Arylketone)-(4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazole-3-yl)-thiol Acetyl Hydrazones

Heng-Wen Zhang (張恒文), Yan-Ping Li* (李燕萍), Chen-Jiang Liu (劉晨江),
Hai-Long Li (李海龍) and Wen-Li Sun (孫文理)
Key Laboratory of Oil and Gas Fine Chemicals of Ministry of Education,
College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi Xinjiang 830046, P. R. China

Fourteen novel arylaldehyde (arylketone)-(4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazole-3-yl)-thiol acetyl hydrazone derivatives (**5a-5g, 6a-6g**) were synthesized by 4-substituted phenyl-5-substituted phenoxy-methyl-1,2,4-triazole-3-thione as starting material according to substructure link principle, followed by thioetherification, hydrazide hydrazone reaction. The structures of these compounds were confirmed by IR, ^{1}H NMR and elemental analysis. Crystal structure of compounds **1b** and **6d** were determined by the X-ray diffraction.

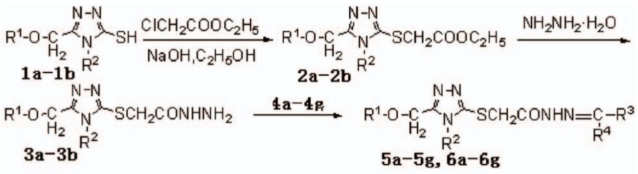
Keywords: Hydrazone derivatives; 1,2,4-Triazole; Synthesis; Crystal structureas.

INTRODUCTION

Acyl hydrazone is a special type of schiff base, it has been shown to exhibit a variety of interesting biological actions, including pesticide, antibacterial, anticancer, antimicrobial, herbicidal and anti-trypanosome activities[1-6] due to the presence of (-CONHN=CH-) moiety. It is also extensively used in coordination chemistry and the metal complexes and it was reported to possess excellent physical and chemical properties,[7-9] which is the hotspot in medicine and materials chemistry areas. In addition, 1,2,4-triazoles have been reported to possess antibacterial, antifungal, antitubercular, antiviral, herbicidal, antihypertensive and insecticidal properties.[10-15]

Some compounds consisting of 1,2,4-triazole rings and acyl hydrazone moiety which have been synthesized by Bayrak[16] showed antimicrobial activities. Prompted by these observations we designed the synthesis of a series of novel arylaldehyde (arylketone)-(4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazole-3-yl)-thiol acetyl hydrazones (**5a-5g**, **6a-6g**) and two single-crystal structures of compounds **1b** and **6d** were obtained. The route of synthesis is shown in Scheme I.

Scheme I



1a,2a,3a,5a-5g	R^1=phenyl ,R^2=*p*-Cl-phenyl
1b,2b,3b,6a-6g	R^1=R^2=*p*-methyl-phenyl
5a-5e,6a-6e	R^3=H; R^4=phenyl, 2-furyl, phenyl-ethylene, 2-hydroxide radical-phenyl, 3-(*p*-Br-phenyl)-1,2,3-triazolyl
5f-5g,6f-6g	R^3=methyl, R^4=phenyl, *p*-methoxyl-phenyl

RESULTS AND DISCUSSION

In the process of the synthesis of these all new compounds, we found that the reaction of acetyl hydrazine with the arylketone could take more time than reaction with the arylaldehyde. The datas of physical properties and elemental analysis of all new compounds are listed in Table 1.

In the IR spectra, all new compounds exhibited medium-strong bands at 3200-3100 cm^{-1}, which assigned to their N-H stretches. The strong bands appeared at around 3000 cm^{-1} were assigned to the group of phenyl and the strong bands appeared at around 1680 cm^{-1} were assigned to the carbonyl group. The bands appeared at around 1620 cm^{-1} were assigned to the C=N in triazole ring.

In the ^{1}H NMR spectra, because of coupling with the carbonyl, the proton of NH appeared at around δ 11.7. The signal of N=CH appeared at around δ 8.2, multiple peaks at δ 6.7-8.0 ascribable to aromeric protons, the signal of OCH_2 appeared at around δ 5.0 and S-CH_2 appeared at around δ 3.9, the signal of methyl group protons which

Table 1. Physical datas and Elemental analysis of compounds

No	Formula	Yield (%)	m.p. /°C	Elemental analysis (Calcd.)/%		
				C	H	N
1a	$C_{15}H_{12}ClN_3OS$	84	176-177	56.71 (56.69)	3.85 (3.84)	13.29 (13.22)
1b	$C_{17}H_{17}N_3OS$	99	178-179	65.61 (65.57)	5.45 (5.46)	13.54 (13.49)
2a	$C_{19}H_{18}ClN_3O_3S$	80	96-97	56.52 (56.50)	4.48 (4.49)	10.39 (10.40)
2b	$C_{21}H_{23}N_3O_3S$	76	84-85	63.43 (63.45)	5.84 (5.83)	10.58 (10.57)
3a	$C_{18}H_{20}ClN_5O_2S$	80	177-179	53.22 (53.26)	4.96 (4.97)	17.31 (17.28)
3b	$C_{19}H_{21}N_5O_2S$	84	147-148	59.52 (59.51)	5.52 (5.52)	18.25 (18.26)
5a	$C_{24}H_{20}ClN_5O_2S$	80	148-149	60.30 (60.31)	4.21 (4.22)	14.67 (14.65)
5b	$C_{22}H_{18}ClN_5O_3S$	70	144-146	56.44 (56.47)	3.89 (3.88)	14.99 (14.97)
5c	$C_{26}H_{22}ClN_5O_2S$	86	180-181	61.96 (61.96)	4.41 (4.40)	13.92 (13.90)
5d	$C_{24}H_{20}ClN_5O_3S$	80	191-192	58.38 (58.36)	4.07 (4.08)	14.17 (14.18)
5e	$C_{26}H_{20}BrClN_8O_2S$	75	202-203	50.04 (50.05)	3.22 (3.23)	17.99 (17.96)
5f	$C_{25}H_{22}ClN_5O_2S$	80	175-176	61.03 (61.03)	4.50 (4.51)	14.24 (14.23)
5g	$C_{26}H_{24}ClN_5O_3S$	72	133-135	59.84 (59.82)	4.62 (4.63)	13.41 (13.42)
6a	$C_{26}H_{25}N_5O_2S$	74	186-187	66.23 (66.22)	5.35 (5.34)	14.84 (14.85)
6b	$C_{24}H_{23}N_5O_3S$	70	168-169	62.44 (62.46)	5.03 (5.02)	15.19 (15.17)
6c	$C_{28}H_{27}N_5O_2S$	83	174-176	67.59 (67.58)	5.48 (5.47)	14.06 (14.07)
6d	$C_{26}H_{25}N_5O_3S$	97	194-195	64.03 (64.05)	5.18 (5.17)	14.38 (14.36)
6e	$C_{28}H_{25}BrN_8O_2S$	77	202-203	54.44 (54.46)	4.08 (4.08)	18.17 (18.15)
6f	$C_{27}H_{27}N_5O_2S$	80	167-168	66.77 (66.78)	5.61 (5.60)	14.41 (14.42)
6g	$C_{28}H_{29}N_5O_3S$	82	205-206	65.24 (65.22)	5.66 (5.67)	13.57 (13.58)

connect with benzene ring appeared at around δ 2.3. The datas of the ^{1}H NMR and IR spectra of the new compounds are listed in Table 2.

Two single crystals of compounds **1b** and **6d** were gained by slow evaporation of solvent in their diluted ethanol and trichloromethane solution. The datas of crystals of the compounds are listed in Table 3, Table 4 and Table 5. The molecular structure of **1b** is shown in Fig. 1, and **6d** is shown in Fig. 3. The packing diagram of the unit cell of compound **1b** is shown in Fig. 2, and **6d** is shown in Fig. 4. Complete crystallographic datas for the structural analysis of compounds have been deposited in the Cambridge Crystallographic Data Centre, CCDC numbers of **1b** and **6d** were 710323, 730920 respectively.

X-ray single crystal diffraction analysis indicates that the crystal **1b** belongs to triclinic system with space group *P-1*, Atoms in triazole rings [N(1), N(2), C(10), N(3), C(9)]

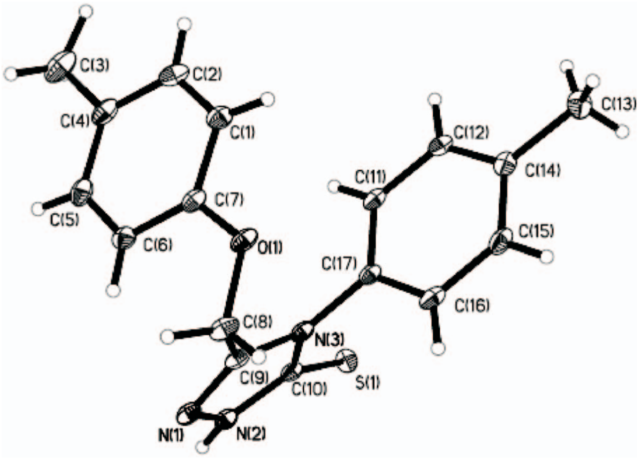


Fig. 1. Molecular structure of compound **1b**. The bonds length (Å): S(1)-C(10), 1.6988(18); N(2)-C(10), 1.515(2).

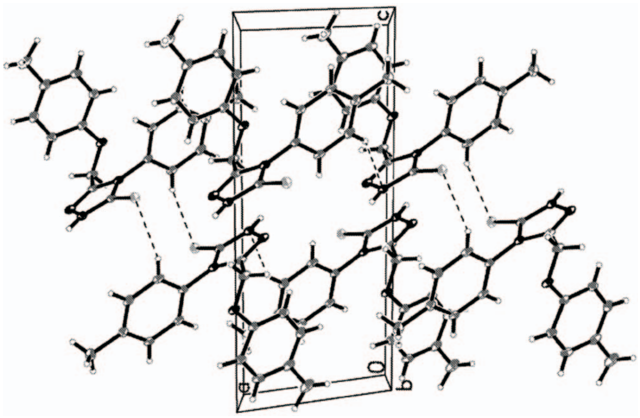


Fig. 2. Packing diagram of the unit cell of compound **1b**. Two intermolecular hydrogen bonds are shown.

Table 2. ^{1}H NMR, IR data of compounds

No.	^{1}H NMR δ	IR (KBr) ν/cm^{-1}
1a	11.40 (s, br, 1H, S-H), 7.42-6.87 (m, 9H, Ar-H), 4.91 (s, 2H, CH_2)	3075, 3020, 2890, 2550, 1590
1b	11.38 (s, br, 1H, S-H), 7.42-6.46 (m, 8H, Ar-H), 4.52 (s, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.17 (s, 3H, CH_3)	3079, 3032, 2891, 2593, 1583
2a	7.32-6.78 (m, 9H, Ar-H), 5.00 (s, 2H, OCH_2), 4.21 (q, 2H, $COOCH_2$), 4.07 (s, 2H, SCH_2), 1.28 (t, 3H, CH_3)	3041, 1746, 1610
2b	7.31-6.77 (m, 8H, Ar-H), 5.01 (s, 2H, OCH_2), 4.20 (q, 2H, $COOCH_2$), 4.08 (s, 2H, SCH_2), 2.42 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.27 (t, 3H, CH_3)	3044, 1745, 1614
3a	6.86-7.50 (m, 9H, Ar-H), 5.05 (s, 2H, OCH_2), 3.86 (s, 2H, SCH_2)	3331, 3241, 1680, 1619
3b	6.87-7.53 (m, 8H, Ar-H), 5.07 (s, 2H, OCH_2), 3.89 (s, 2H, SCH_2), 2.44 (s, 3H, CH_3), 2.27 (s, 3H, CH_3)	3333, 3245, 1681, 1621
5a	11.70 (s, 1H, NH), 8.19 (s, 1H, N=CH), 6.74-7.80 (m, 14H, Ar-H), 5.03 (s, 2H, OCH_2), 3.96 (s, 2H, SCH_2)	3190, 3076, 1685, 1620
5b	11.80 (s, 1H, NH), 8.22 (s, 1H, N=CH), 6.72-7.55 (m, 12H, Ar-H and furan-CH), 5.01 (s, 2H, OCH_2), 3.98 (s, 2H, SCH_2)	3186, 3005, 1674, 1625
5c	11.48 (s, 1H, NH), 7.92 (s, 1H, N=CH), 6.85-7.52 (m, 16H, Ar-H and CH=CH), 5.07 (s, 2H, OCH_2), 3.93 (s, 2H, SCH_2)	3177, 3000, 1681, 1622
5d	11.82 (s, 1H, NH), 11.15 (s, 1H, OH), 8.17 (s, 1H, N=CH), 6.87-7.36 (m, 13H, Ar-H), 5.04 (s, 2H, OCH_2), 3.92 (s, 2H, SCH_2)	3270, 3069, 1679, 1618
5e	11.81 (s, 1H, NH), 8.40 (s, 1H, triazole-CH), 8.32 (s, 1H, N=CH), 6.82-7.99 (m, 13H, Ar-H), 5.08 (s, 2H, OCH_2), 3.94 (s, 2H, SCH_2)	3178, 3061, 1681, 1624
5f	11.33 (s, 1H, NH), 8.6 (s, 1H, N=CH), 6.81-7.98 (m, 14H, Ar-H), 5.07 (s, 2H, OCH_2), 3.98 (s, 2H, SCH_2), 2.41 (s, 3H, CH_3)	3190, 3076, 1685, 1614
5g	11.33 (s, 1H, NH), 8.5 (s, 1H, N=CH), 6.81-7.98 (m, 13H, Ar-H), 5.07 (s, 2H, OCH_2), 3.96 (s, 2H, SCH_2), 2.40 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3)	3201, 3069, 1692, 1620
6a	11.65 (s, 1H, NH), 8.15 (s, 1H, N=CH), 6.76-7.79 (m, 13H, Ar-H), 5.02 (s, 2H, OCH_2), 3.94 (s, 2H, SCH_2), 2.43 (s, 3H, CH_3), 2.26 (s, 3H, CH_3)	3190, 3076, 1685, 1616
6b	11.80 (s, 1H, NH), 8.12 (s, 1H, N=CH), 6.69-7.52 (m, 11H, Ar-H and furan-CH), 5.02 (s, OCH_2), 4.00 (s, 2H, SCH_2), 2.44 (s, 3H, CH_3), 2.26 (s, 3H, CH_3)	3186, 3005, 1674, 1619
6c	11.52 (s, 1H, NH), 8.02 (s, 1H, N=CH), 6.75-7.51 (m, 15H, Ar-H and CH=CH), 5.03 (s, 2H, OCH_2), 3.90 (s, 2H, SCH_2), 2.43 (s, 3H, CH_3), 2.26 (s, 3H, CH_3)	3177, 3000, 1681, 1628
6d	11.84 (s, 1H, NH), 6.77-7.34 (m, 12H, Ar-H), 5.03 (s, 2H, OCH_2), 2.27 (s, 3H, CH_3), 3.92 (s, 2H, SCH_2), 2.43 (s, 3H, CH_3), 2.27 (s, 3H, CH_3)	3270, 3069, 1694, 1616
6e	11.80 (s, 1H, NH), 8.32 (s, 1H, triazole-CH), 8.12 (s, 1H, N=CH), 6.88-7.99 (m, 12H, Ar-H), 5.05 (s, 2H, OCH_2), 3.92 (s, 2H, SCH_2), 2.45 (s, 3H, CH_3), 2.26 (s, 3H, CH_3)	3268, 3065, 1692, 1621
6f	11.21 (s, 1H, NH), 6.84-8.02 (m, 13H, Ar-H), 5.04 (s, 2H, OCH_2), 3.92 (s, 2H, SCH_2), 2.41 (s, 3H, CH_3), 2.33 (s, 3H, CH_3)	3274, 3064, 1690, 1617
6g	11.36 (s, 1H, NH), 6.81-7.80 (m, 12H, Ar-H), 5.01 (s, 2H, OCH_2), 3.83 (s, 2H, SCH_2), 2.41 (s, H, OCH_3), 2.24 (s, 3H, CH_3)	3271, 3073, 1695, 1622

are quite planar, and the deviation from the least squares plane through the ring atom is 0.0039 Å, the plane equation is 4.440 x + 3.447 y + 13.541 z = 6.9493. And atoms in benzene ring [C(11), C(12), C(14), C(15), C(16), C(17)] are also quite planar, the deviation from the least squares plane through the ring atom is 0.0011 Å, the plane equation is 0.748 x + 6.425 y – 2.350 z = 1.4534. The dihedral angle between the plane of triazole group and the plane of the benzene ring [C(11), C(12), C(14), C(15), C(16), C(17)] is 92.2°. Some kinds of hydrogen bonds of intermolecular *H*-bond (C-H···S, N-H···S and C-H···N) exist in the crystal lattice, and the structure is stabilized by the hydrogen bond. The molecule exists in the thione tautomeric form with an S(1)–C(10) distance of 1.6988(18) Å, which indicates substantial double bond character whereas bond N(2)–C(10) distance of 1.515(2) Å is typical for a single bond. Bond lengths observed in the thione fragment are in agreement with the values found in analogues compounds.[17,18]

X-ray single crystal diffraction analysis indicates that

Table 3. Crystal data and structure refinement for **1b** and **6d**

Compound	**1b**	**6d**
Empirical formula	$C_{17}H_{17}N_3OS$	$C_{26}H_{25}N_5O_3S$
Formula weight	311.40	487.57
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	triclinic, *P-1*	triclinic, *P-1*
Unit cell dimensions	a = 7.4017(15) Å,	a = 10.060(2) Å,
	b = 7.4516(15) Å,	b = 11.077(2) Å,
	c = 16.587(3) Å	c = 21.546(4) Å
	α = 77.08(3)°,	α = 90.00(3)°,
	β = 88.40(3)°,	β = 90.04(3)°,
	γ = 62.17(3)°	γ = 90.00(3)°
Volume	785.5(3) Å^3	2401.0(8) Å^3
Z, Calculated density	2, 1.317 Mg/m^3	4, 1.349 Mg/m^3
Absorption coefficient	0.211 mm^{-1}	0.174 mm^{-1}
F(000)	328	1024
Crystal size	0.79 × 0.54 × 0.18 mm	0.241 × 0.188 × 0.034 mm
Theta range for data collection	3.12 to 30.69 deg	3.32 to 27.47 deg
Limiting indices	-8 ≤ h ≤ 9, -9 ≤ k ≤9, -21 ≤ l ≤ 21	-12 ≤ h ≤ 11, -14 ≤ k ≤ 14, -27 ≤ l ≤ 27
Reflections collected / unique	7751 / 3568 [R(int) = 0.0208]	20485 / 10214 [R(int) = 0.0839]
Completeness to theta = 27.47	73.3%	92.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3568 / 0 / 225	10214 / 0 / 772
Goodness-of-fit on F^2	1.079	0.901
Final R indices [I > 2sigma(I)]	*R1 = 0.0447, wR2 = 0.1296*	*R1 = 0.0707, wR2 = 0.0839*
R indices (all data)	*R1 = 0.0483, wR2 = 0.1330*	*R1 = 0.2032, wR2 = 0.1092*
Extinction coefficient	0.086(8)	0.0035(3)
Largest diff. peak and hole	0.393 and -0.446 e.Å^{-3}	0.215 and -0.189 e.Å^{-3}

Table 4. Selected bond lengths (Å) for the compound **1b** and **6d**

		1b			
S(1)-C(10)	1.6988(18)	N(3)-C(9)	1.481(2)	O(1)-C(8)	1.518(2)
N(1)-N(2)	1.3375(19)	N(3)-C(10)	1.342(2)	C(3)-C(4)	1.382(3)
N(1)-C(9)	1.409(2)	N(3)-C(17)	1.608(2)	C(8)-C(9)	1.430(2)
N(2)-C(10)	1.515(2)	O(1)-C(7)	1.2630(19)	C(14)-C(13)	1.684(3)
		6d			
S(1)-C(17)	1.740(3)	N(4)-N(5)	1.382(3)	N(5)-C(20)	1.269(4)
S(1)-C(18)	1.797(4)	N(1)-C(9)	1.367(4)	C(3)-C(4)	1.516(6)
O(1)-C(7)	1.383(5)	N(1)-C(10)	1.442(4)	C(8)-C(9)	1.499(5)
O(1)-C(8)	1.424(5)	N(1)-C(17)	1.372(4)	C(13)-C(14)	1.509(5)
O(2)-C(19)	1.218(3)	N(2)-C(9)	1.299(4)	C(18)-C(19)	1.502(5)
O(3)-C(26)	1.374(4)	N(3)-C(17)	1.305(4)	C(20)-C(21)	1.459(4)
N(2)-N(3)	1.409(3)	N(4)-C(19)	1.351(4)		

the crystal **6d** belongs to triclinic system with space group *P-1*, Atoms in triazole rings [N(1), C(9), N(2), N(3), C(17)] are quite planar, the deviation from the least squares plane through the ring atom is 0.0032 Å, the plane equation is 0.794 x – 1.940 y + 15.425 z = 6.5830. And atoms in benzene ring [C(10), C(11), C(12), C(14), C(15), C(16)] are also quite planar, the deviation from the least squares plane through the ring atom is 0.0039 Å, the plane equation is -6.662 x – 2.480 y + 15.419 z = 3.3448. The dihedral angle between the plane of triazole group and the plane of the

Table 5. Selected bond angles (°) for the compound **1b** and **6d**

1b					
S(1) -C(10)-N(2)	133.05(12)	N(1)-C(9)-N(3)	120.62(13)	C(10)-N(3)-C(9)	99.17(14)
S(1)-C(10)-N(3)	118.83(14)	N(2)-C(10)-N(3)	108.13(14)	C(9)-N(3)-C(17)	135.14(12)
O(1)-C(7)-C(1)	110.47(16)	N(1)-C(9)-C(8)	120.68(16)	C(10)-N(3)-C(17)	125.62(14)
O(1)-C(7)-C(6)	119.84(16)	N(3)-C(17)-(11)	129.28(13)	C(2)-C(4)-C(3)	114.4(2)
O(1)-C(8)-C(9)	108.81(14)	N(3)-C(17)-(16)	118.67(15)	C(12)-C(14)-C(13)	121.32(17)
N(1)-N(2)-C(10)	115.55(14)	N(3)-C(9)-C(8)	118.68(16)	C(13)-C(14)-C(15)	129.87(15)
N(2)-N(1)-C(9)	96.52(14)	C(7)-O(1)-C(8)	114.08(14)		
6d					
S(1)-C(17)-N(1)	121.1(3)	N(2)-N(3)-C(17)	106.4(3)	C(9)-N(1)-C(10)	130.6(3)
S(1)-C(17)-N(3)	127.6(3)	N(3)-N(2)-C(9)	107.1(3)	C(9)-N(1)-C(17)	104.0(3)
S(1)-C(18)-C(19)	109.0(3)	N(4)-N(5)-C(20)	119.0(3)	C(10-N(1)-C(17)	125.4(3)
O(1)-C(7)-C(1)	125.9(4)	N(5)-N(4)-C(19)	117.7(3)	C(7)-O(1)-C(8)	117.7(3)
O(1)-C(7)-C(6)	114.9(4)	N(1)-C(9)-C(8)	125.1(3)	C(2)-C(4)-C(3)	121.9(4)
O(1)-C(8)-C(9)	113.2(4)	N(1)-C(10)-C(11)	120.0(3)	C(3)-C(4)-C(5)	121.0(5)
O(2)-C(19)-N(4)	123.6(3)	N(1)-C(10)-C(16)	119.9(3)	C(12)-C(14)-C(13)	122.0(4)
O(2)-C(19)-C(18)	123.8(3)	N(2)-C(9)-C(8)	123.5(3)	C(13)-C(14)-C(15)	120.7(4)
O(3)-C(26)-C(21)	122.2(3)	N(4)-C(19)-C(18)	112.6(3)	C(20)-C(21)-C(22)	119.6(3)
O(3)-C(26)-C(25)	117.9(3)	N(5)-C(20)-C(21)	119.9(3)	C(20)-C(21)-C(26)	121.7(3)
N(1)-C(9)-N(2)	111.3(3)	C(17)-S(1)-C(18)	96.84(17)		
N(1)-C(17)-N(3)	111.2(3)	C(7)-O(1)-C(8)	117.7(3)		

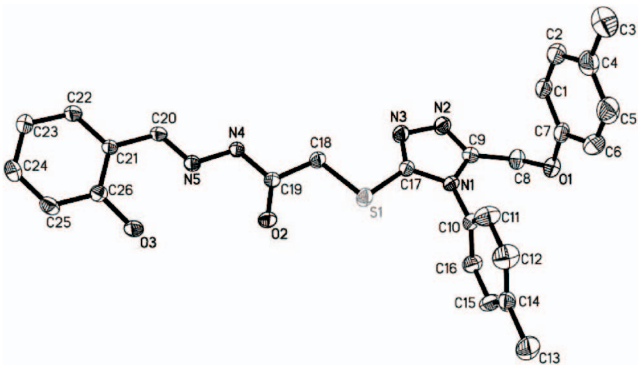


Fig. 3. Molecular structure of compound **6d**. The bonds length (Å): C(19)-O(2), 1.218(3); N(5)-C(20), 1.269(4): N(4)-C(19), 1.351(4); C(20)-C(21), 1.459(4); O(3)-C(26), 1.374(4).

benzene ring [C(10), C(11), C(12), C(14), C(15), C(16)] is 84°. In the crystal lattice, there exist some intermolecular hydrogen bonds (C-H···N, N-H···O and C-H···O hydrogen bonds) interactions, and the structure is stabilized by the hydrogen bond.[19-21] The bonds C(19)–O(2) of 1.218(3) Å and N(5)–C(20) Å of 1.269(4) have a double bond character, whereas bonds N(4)-C(19) of 1.351(4) Å, C(20)-C(21) of 1.459(4) Å and O(3)-C(26) of 1.374(4) Å are typical for a single bond. Bond lengths observed in the hydrazones fragment are in agreement with the values found in analogues compounds.[22]

EXPERIMENTAL

General Method

The ^{1}H NMR spectra were recorded on an Inova-400 (using TMS as internal standard, $CDCl_3$ as solvent). The IR spectra were recorded in KBr pellets on a Bruker FT-IR Equinox apparatus. Elemental analyses were performed on a Thermo Flash EA-1112 analyzer. Melting points were measured on a Büchi B-540 and were uncorrected. The boiling point range of petroleum ether was 60-90 °C. The TLC was performed by GF_{254} and 0.5% CMC. X-ray single-crystal diffraction datas for compounds **1b** and **6d** were collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K with Mo-$K\alpha$ radiation (λ = 0.71073 Å) by ω-φ scan mode. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL.

1. Preparation of 4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazole-3-thione (1a, 1b)

A solution of corresponding thiosemicarbazide (10 mmol) in 2 N NaOH was refluxed for 5 h. The resulting solution was cooled to room temperature and acidified to pH 3-4 with 33% HCl. The precipitate formed was filtered,

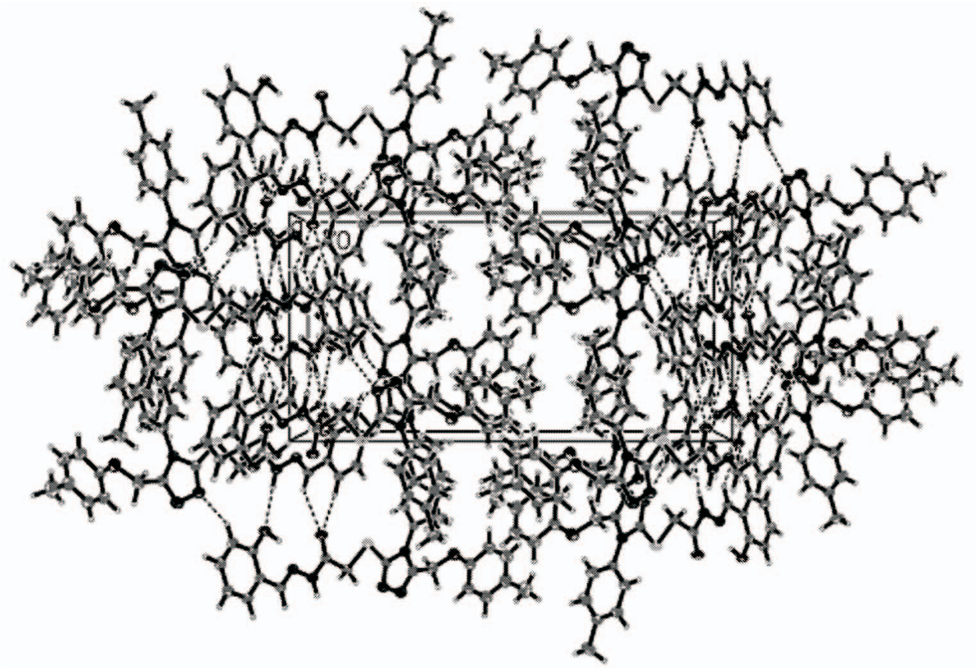


Fig. 4. Packing diagram of the unit cell of compound **6d**. Four intermolecular hydrogen bonds are shown.

washed with water and recrystallized from ethanol to afford the desired compounds.

2. Preparation of (4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazol-3-yl)-thiol ethyl acetate (2a, 2b)

To a mixture of **1** (2 mmol) and ethyl chloroacetate (2.5 mmol) in ethanol (30 mL), KOH (132 mg, in 10 mL H_2O) was added slowly. The mixture was stirred at room temperature overnight, H_2O was added and the separated solid was filtered off, washed with water and crystallized from ethanol to afford the desired compounds.

3. Preparation of (4-substituted phenoxy-5-substituted phenoxy-methyl-4*H*-1,2,4-triazol-3-yl)-thiol acetohydrazide (3a, 3b)

A solution of the corresponding compound **2** (10 mmol) in ethanol was refluxed with hydrazine hydrate (25 mmol) for 4 h. After cooling it to room temperature, a white solid appeared. The solid was recrystallized from ethanol to afford the desired products.

4. Preparation of Arylaldehyde (Arylketone)-(4-substituted phenyl-5-substituted phenoxy-methyl-4*H*-1,2,4-triazole-3-yl)-thiol acetyl hydrazones (5a-5g, 6a-6g)

A solution of the corresponding compound **3** (1 mmol) in absolute ethanol was refluxed with appropriate aldehyde (aryketone) (**4a-4g**) (1 mmol) for 5-20 h. After cooling the mixture to room temperature, a white solid appeared. This crude product was recrystallized from ethanol to afford the desired products.

The physical datas of new compounds are listed in Table 1. The datas of ^{1}H NMR and IR are listed in Table 2.

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