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Reaction of 5-Aryloxytetrazoles with Dimethyl Sulfoxide and DMSO–Acetic Anhydride. Structure and Quantum-Chemical Calculations of 1-Methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole*

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Abstract—Decomposition of methyl 5-(4-nitrophenoxy)tetrazole-2-carboxylate in dimethyl sulfoxide at room temperature yields a mixture of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole, 1- and 2-methyl-5-(4-nitrophenoxy)tetrazoles, and 5-(4-nitrophenoxy)tetrazole. Methyl 5-aryloxytetrazole-2-carboxylates containing electron-donor substituents in the aryloxy group do not give rise to the corresponding products under analogous conditions. The reactions of 5-aryloxytetrazoles [Ar = 4-$O_2NC_6H_4$, C_6H_5, 2,6-$(MeO)_2C_6H_3$] with dimethyl sulfoxide in the presence of acetic anhydride lead to mixtures of 1- and 2-methylsulfanylmethyl-5-aryloxytetrazoles whose yield and ratio depend on the substituent in the aryloxy group. The structure of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole was studied by X-ray analysis, two-dimensional NMR spectroscopy (HSQC, HMBC, NOESY), and quantum-chemical methods (*ab initio*, AM1, PM3). A highly selective procedure was developed for the synthesis of 5-(4-nitrophenoxy)tetrazole.

Numerous tetrazole derivatives exhibit versatile biological activity due to the fact that the tetrazole ring is a metabolically stable replacement of carboxylic functionality [1]. Tetrazoles undergo various reactions such as alkylation and acylation, complex formation with metals, thermolysis, photolysis, decomposition with formation of nitrenes, etc. [2–11]. We previously studied interconversions of 1,5- and 2,5-substituted tetrazoles [2–4, 12–14] and showed that 1- and 2-alkoxycarbonyltetrazoles occur in equilibrium with the corresponding imidoyl azides. The state of the equilibrium depends on the solvent, temperature, and electron-acceptor power of functional group attached to the tetrazole ring.

It is known that dimethyl sulfoxide–*N*,*N*′-dicyclohexylcarbodiimide (DMSO–DCC) in the presence of a source of protons is a mild and efficient reagent for oxidation of alcohols to the corresponding carbonyl compounds (Pfitzner–Moffatt reaction) [15] and introduction of a methylsulfanylmethyl group into the *ortho* position of phenols [16–18]. Subsequently, a number of other reagents based on DMSO and sulfides have been proposed for methylsulfanylmethylation of phenols and anilines, e.g., DMSO–acetic anhydride [19], DMSO–trifluoroacetic anhydride [20], DMSO–oxalyl chloride (Swern reaction) [21], methyl sulfide–*tert*-butyl hypochlorite [22, 23], etc.

In the present work we examined reactions of 5-aryloxytetrazoles [Ar = 4-$O_2NC_6H_4$, Ph, 2,6-$(MeO)_2$-C_6H_3] with DMSO and DMSO–acetic anhydride with a view to introduce a methylsulfanylmethyl group into position *1* or *2* of the tetrazole ring. We previously showed [4, 14] that methyl 5-aryloxytetrazole-2-carboxylates readily undergo isomerization to produce an equilibrium mixture of methyl 5-aryloxytetrazole-1- and -2-carboxylates and that decarboxylation of the latter in the solid phase or in a polar solvent (DMSO, DMF, MeCN) yields 1- and 2-methyl-5-aryloxytetrazoles, respectively (Scheme 1). Surprisingly, in the reaction of methyl 5-(4-nitrophenoxy)tetrazole-2-carboxylate (**Ia**) with DMSO we isolated 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**) in 20–30%

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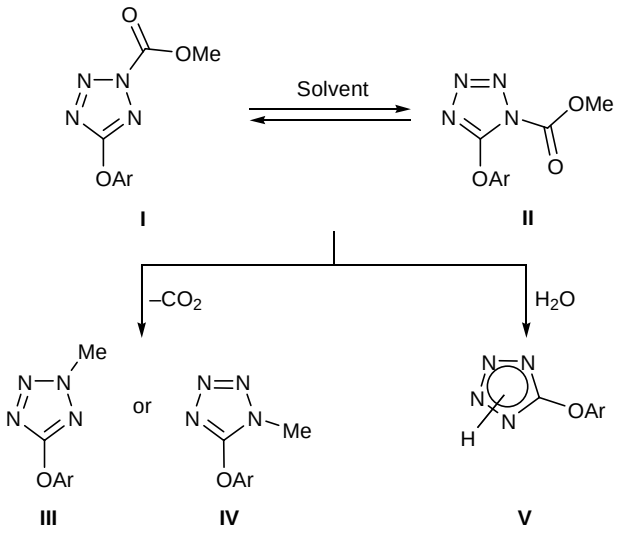
Scheme 1.



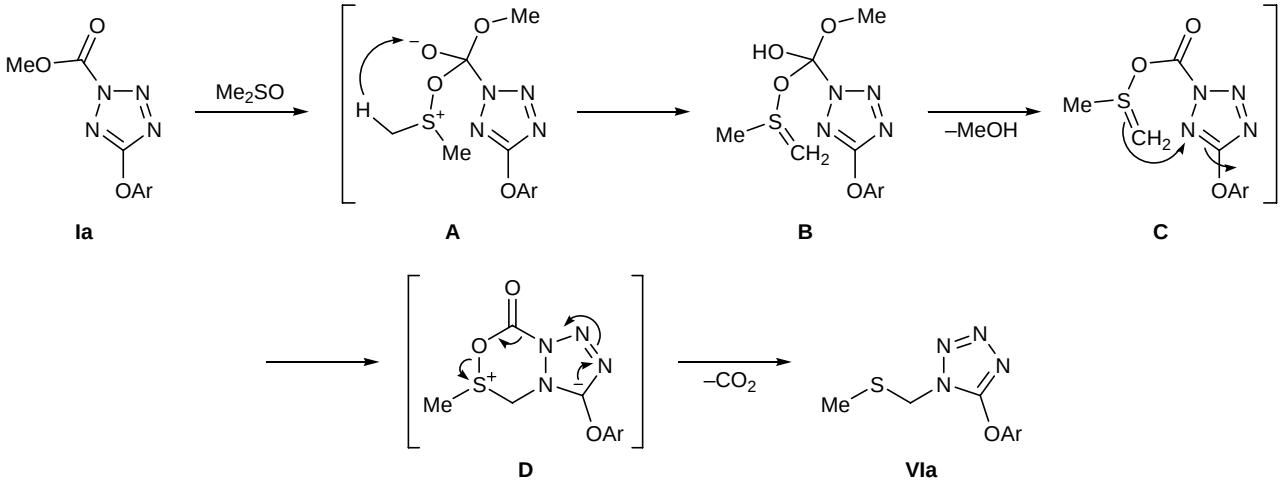
Solvent = DMSO, DMFA, CH_3CN; Ar = 4-$O_2NC_6H_4$ (**a**), Ph (**b**), 4-MeC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 2,6-$Me_2C_6H_3$ (**e**), 2,6-$(MeO)_2C_6H_3$ (**f**).

yield (Scheme 2). In addition, 25% of 1-methyl-5-(4-nitrophenoxy)tetrazole (**IVa**), 40% of 2-methyl-5-(4-nitrophenoxy)tetrazole (**IIIa**), and 5–15% of 5-(4-nitrophenoxy)tetrazole (**Va**) were isolated. Other 5-aryloxytetrazoles **Ib**–**If** containing donor substituents in the aryloxy group failed to produce the corresponding methylsulfanylmethyl derivatives **VIb**–**VIf**.

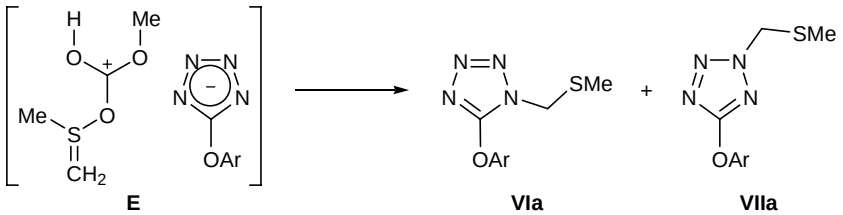
The reaction mechanism resembles that typical of Swern oxidation. There are three evidences in support of a concerted addition–elimination path shown in Scheme 2. First, no 2-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIIa**) is formed in the reaction; second, methanol is released; and third, carbonyl absorption band disappears from the IR spectrum. Ionic intermediates like **E** can be ruled out; otherwise, a mixture of **VIa** and **VIIa** would be obtained (Scheme 3).

Methylsulfanylmethylation of 5-aryloxytetrazoles **Va**, **Vb**, and **Vf** in the system dimethyl sulfoxide–acetic anhydride at 55–60°C (reaction time 24 h) afforded mixtures of 1- and 2-methylsulfanylmethyl derivatives **VIa**, **VIb**, **VIf** and **VIIa**, **VIIb**, **VIIf** (Scheme 4). Here, two very important observations should be noted. In all cases, methylsulfanylmethylation at position *1* of the tetrazole ring predominates over 2-methylsulfanylmethylation: the ratios of the 1- and 2-substituted isomers are 1.5, 1.63, and 1.75 for Ar = 4-$O_2NC_6H_4$, C_6H_5, and 2,6-$(MeO)_2C_6H_3$, respectively. Electron-withdrawing substituent in the 5-aryloxy group favors the methylsulfanylmethylation process: the overall yields of the products are 50, 42, and

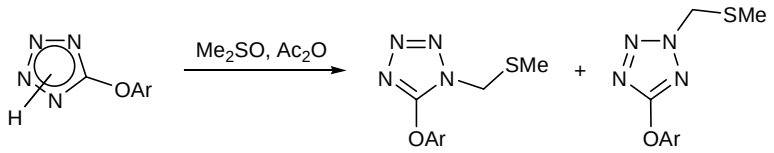
Scheme 2.



Scheme 3.

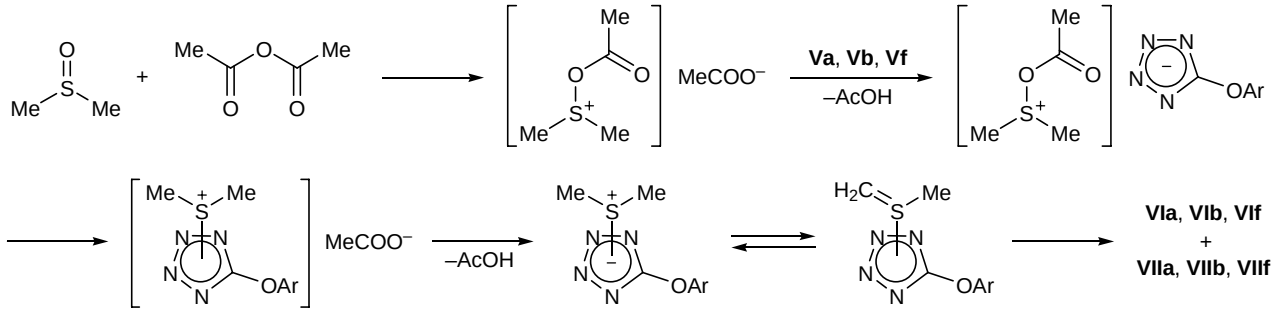


Scheme 4.



Va, **Vb**, **Vf** **VIa**, **VIb**, **VIf** **VIIa**, **VIIb**, **VIIf**

Scheme 5.



22% for Ar = 4-$O_2NC_6H_4$, C_6H_5, and 2,6-$(MeO)_2C_6H_3$, respectively. These data support our previous prediction that the reaction with DMSO of **Ia** containing an electron-withdrawing yields only isomer **VIa** and that no analogous product is formed from **Ib**–**If**. The formation of 2-substituted isomers may be regarded as an additional support for the mechanism shown in Scheme 2. An alternative mechanism (Scheme 5) is operative in the system DMSO–acetic anhydride; in this case, a mixture of **VI** and **VII** is obtained.

The structure of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**) was elucidated by the ^1H and ^{13}C (including two-dimensional HSQC, HMBC, NOESY techniques), IR, and mass spectra and elemental analysis. The HSQC spectrum shows correlations between the CH_3S protons (H^1, δ 2.326 ppm) and C^1 (δ_C 15.53 ppm), SCH_2 protons (H^2, δ 5.32 ppm) and C^2 (δ_C 49.21 ppm), H^3 (δ 7.70 ppm) and C^9, and H^4 (δ 8.36 ppm) and C^8. In the HMBC spectrum (Fig. 1a–1c), a long-range correlation between H^1 (δ 2.326 ppm) and C^2 (δ_C 49.21 ppm) was observed, while no correlations between the same proton and the other carbon atoms in molecule **VIa** were found. The SCH_2 protons correlate with both C^1 (δ_C 15.53 ppm) and C^3 (δ_C 158.56 ppm). The NOESY spectra revealed couplings between H^1 and H^2 in the methylsulfanylmethyl group and between H^3 and H^4 in the benzene ring. Thus, the ^1H–^{13}C HMBC correlation spectra indicate that the methylsulfanylmethyl group is attached to the N^1 atom of the tetrazole ring. The IR, ^1H and ^{13}C NMR, and mass spectral data of compounds **VIa**, **VIb**, **VIf**, **VIIa**, **VIIb**, and **VIIf** are given in Experimental.

The structure of **VIa** was also analyzed by X-ray crystallography (Fig. 2). The bond lengths, bond angles, and torsion angles in molecule **VIa** are given in Tables 1–3. The tetrazole ring in **VIa** is planar, and the *p*-nitrophenoxy group deviates from the tetrazole ring plane so that the torsion angles $C^5C^4O^1C^3$ and $C^4O^1C^3N^4$ are 68.6(3)° and 8.1(4)°, respectively. The torsion angle $O^1C^4C^5C^6$ equal to 173.6(2)° implies steric interaction between the benzene and tetrazole rings. The N^1–C^2 and C^5–O^1 bonds (in the methylsulfanylmethyl and *p*-nitrophenoxy groups) are not coplanar: the dihedral angle $C^2N^1C^3O^1$ is 5.1(4)°. Surprisingly, a weak resonance is observed between the O^1 atom and electron-withdrawing nitro group in the *para* position of the benzene ring (structure **VIa_2** in

Table 1. Bond lengths (*d*) in the molecule of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**)[a]

Bond	*d*, Å	Bond	*d*, Å
N^5–O^2	1.189(4)	O^1–C^3	1.324(3)
N^5–O^3	1.198(4)	C^3–N^1	1.326(3)
N^5–C^7	1.474(3)	N^1–N^2	1.348(3)
C^7–C^8	1.371(4)	N^2–N^3	1.287(3)
C^8–C^9	1.375(4)	N^3–N^4	1.364(3)
C^9–C^4	1.361(3)	N^4–C^3	1.304(3)
C^4–C^5	1.369(3)	N^1–C^2	1.453(3)
C^5–C^6	1.375(4)	C^2–S^1	1.788(3)
C^6–C^7	1.368(4)	S^1–C^1	1.790(3)
C^4–O^1	1.403(3)		

[a] Hereinafter, for atom numbering, see Fig. 2.

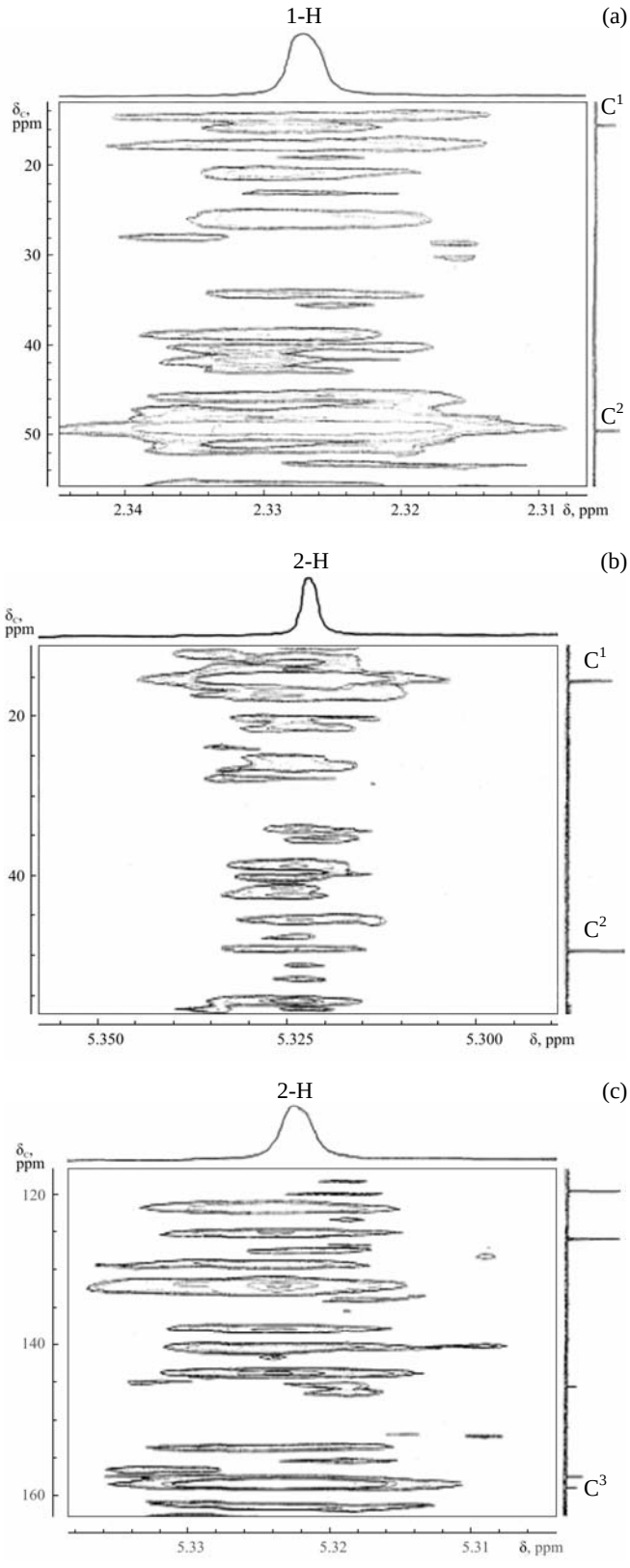
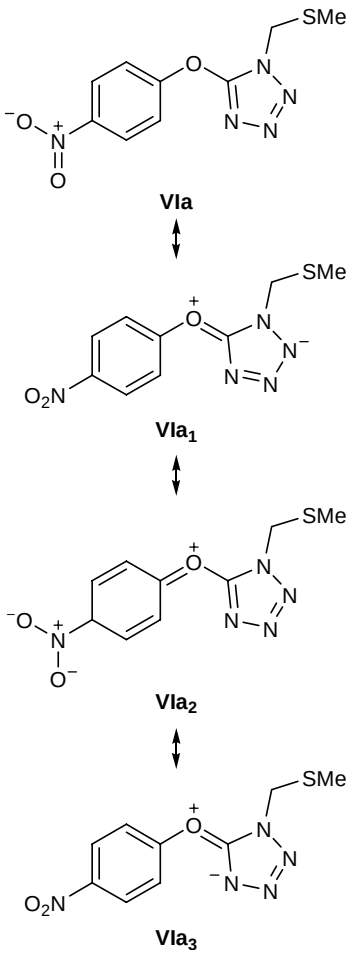


Fig 1. HMBC ^{1}H–^{13}C correlation spectra of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**) (expanded aliphatic region): (a) 1-H–C^2 correlation, (b) 2-H–C^1 correlation, and (c) 2-H–C^3 correlation.

Scheme 6). Instead, the O^1 atom is involved in conjugation with the tetrazole ring (**VIa$_1$**). The O^1–C^3 bond [1.324(3) Å] is shorter than C^4–O^1 [1.402(3) Å, Table 1]. These findings contradict our earlier conclusion that a strong electron-withdrawing substituent in position *5* should affect the electron density distribution over the tetrazole ring [13]. The results obtained by *ab initio*, AM1, and PM3 quantum-chemical calculations of molecules **VIa** and **VIIa** complement the experimental X-ray diffraction data (Tables 4–6).

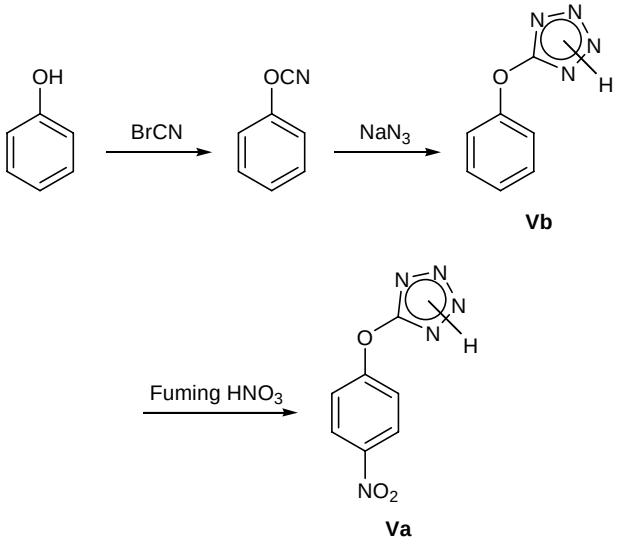
Scheme 6.



Compound **Va** was synthesized by Martin and Weise [24] in an overall yield of less than 10% by reaction of *p*-nitrophenol with cyanogen bromide, followed by treatment of *p*-nitrophenyl cyanate with sodium azide. We have developed a new highly selective procedure for the synthesis of 5-(4-nitrophenoxy)-tetrazole (**Va**) via direct nitration of 5-phenoxytetrazole **Vb** (Scheme 7). Tetrazole **Vb** was prepared in 70% yield by the procedure described previously [4, 13]. The nitration of **Vb** with fuming nitric acid

afforded 90% of **Va**, and the product contained no impurities of *meta* and *ortho* isomers. Obviously, the presence of a bulky tetrazolyl substituent prevents nitration of **Vb** at the *ortho* position.

Scheme 7.



EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Varian EM390 (90 MHz), Jeol JNMα-500 (500 MHz), and Bruker 500 Ultra Shield (500 MHz) spectrometers. The ^{13}C NMR spectra (125 MHz) were measured on Jeol JNMα-500 and Bruker 500 Ultra Shield instruments. The mass spectra were obtained using a Fision Trio 1000 GC–MS system. The IR spectra were recorded on Perkin–Elmer 1760X and Shimadzu IR-470 Fourier spectrometers. The elemental compositions were determined at the Research Institute of Petroleum Industry (Pazhouheshgah Bld., Qom Road, Tehran, Iran). The melting points were determined using a Gallenkamp apparatus and were not corrected. AM1, PM3, and *ab initio* (STO-3G) quantum-chemical calculations were performed using HyperChem Pro 6.0 software with optimization according to the Polak–Ribier algorithm.

2,6-Dimethoxyphenol, 4-methoxyphenol, 4-methylphenol, 2,6-dimethylphenol, phenol, bromine, sodium cyanide, dimethyl sulfoxide, sodium azide, and fuming nitric acid were commercial products and were used without additional purification. Cyanogen bromide [25] and phenyl cyanate [26] were synthesized by known methods. The solvents were purified by standard procedures prior to use.

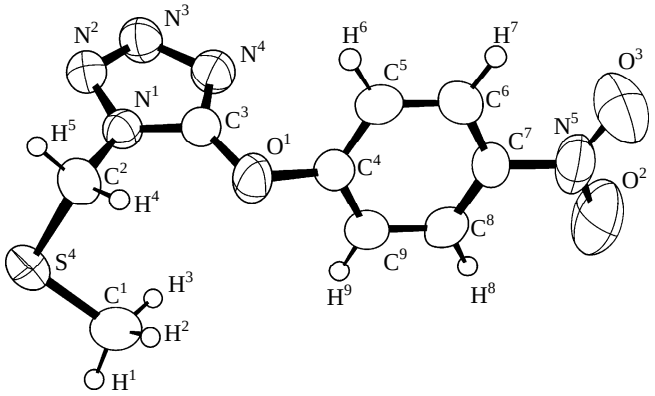


Fig. 2. Structure of the molecule of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**) according to the X-ray diffraction data.

X-Ray analysis of compound (VIa). Crystals of **VIa** were obtained by slow evaporation of a solution of **VIa** in a mixture of ethyl acetate and cyclohexane at room temperature. A suitable single crystal was sealed in a glass capillary. The data were acquired using a Rigaku RAXIS-Rapid diffractometer and were processed using Rigaku Rapid-auto program. Empirical corrections for absorption and Lorentz polarization were applied. Orthorhombic crystals, $C_9H_9N_5O_3S$, *M* 267.27. Unit cell parameters at 296(2) K: *a* = 12.2341(13), *b* = 7.6350(8), *c* = 25.428(3) Å; α = β = γ = 90°; *V* = 2375.2(5) Å^3; space group *Pbca* (no. 61); *Z* = 8; μ = 0.282 mm^{-1}. Total reflection number 19309 (λ = 0.71075 Å); number of independent reflections 2692 (R_{int} = 0.0630); final divergence factors [$I > 2\sigma(I)$]: R_1 = 0.0499, wR_2 = 0.1330. The structure was solved by the direct method using Crystal Structure

Table 2. Bond angles (ω) in the molecule of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**)

Angle	ω, deg	Angle	ω, deg
$C^2S^1C^1$	99.79(14)	$N^4C^3N^1$	111.3(2)
$C^3O^1C^4$	118.43(18)	$O^1C^3N^1$	118.9(2)
$C^3N^1N^2$	106.85(18)	$C^9C^4C^5$	122.6(2)
$C^3N^1C^2$	129.8(2)	$C^9C^4O^1$	116.8(2)
$N^2N^1C^2$	123.21(19)	$C^5C^4O^1$	120.3(2)
$N^3N^2N^1$	106.64(18)	$C^4C^5C^6$	118.9(2)
$N^2N^3N^4$	111.41(18)	$C^7C^6C^5$	118.3(2)
$C^3N^4N^3$	103.85(19)	$C^6C^7C^8$	122.8(2)
$O^3N^5O^2$	123.7(3)	$C^6C^7N^5$	118.9(2)
$O^3N^5C^7$	118.8(3)	$C^8C^7N^5$	118.3(2)
$O^2N^5C^7$	117.5(3)	$C^7C^8C^9$	118.5(2)
$N^1C^2S^1$	114.49(17)	$C^4C^9C^8$	118.9(2)
$N^4C^3O^1$	129.8(2)		

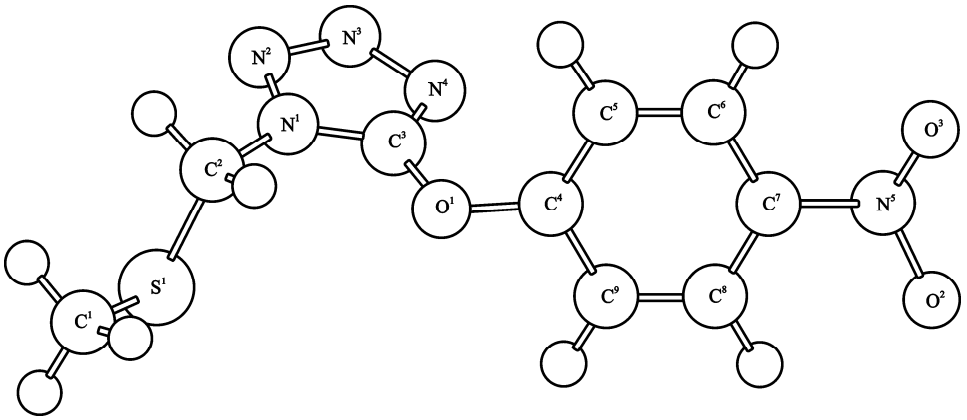
Table 3. Torsion angles (φ) in the molecule of 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**)

Angle	φ, deg	Angle	φ, deg
$C^3N^1N^2N^3$	0.8(2)	$C^3O^1C^4C^5$	68.6(3)
$C^2N^1N^2N^3$	177.4(2)	$C^9C^4C^5C^6$	–0.2(4)
$N^1N^2N^3N^4$	–0.4(3)	$O^1C^4C^5C^6$	173.6(2)
$N^2N^3N^4C^3$	–0.1(3)	$C^4C^5C^6C^7$	–0.2(4)
$C^3N^1C^2S^1$	–101.3(3)	$C^5C^6C^7C^8$	0.7(4)
$N^2N^1C^2S^1$	82.9(3)	$C^5C^6C^7N^5$	–179.3(3)
$C^1S^1C^2N^1$	73.1(2)	$O^3N^5C^7C^6$	0.3(4)
$N^3N^4C^3O^1$	177.9(3)	$O^2N^5C^7C^6$	–179.9(3)
$N^3N^4C^3N^1$	0.6(3)	$O^3N^5C^7C^8$	–179.6(3)
$C^4O^1C^3N^4$	8.1(4)	$O^2N^5C^7C^8$	0.1(4)
$C^4O^1C^3N^1$	–174.8(2)	$C^6C^7C^8C^9$	–0.8(4)
$N^2N^1C^3N^4$	–0.9(3)	$N^5C^7C^8C^9$	179.2(2)
$C^2N^1C^3N^4$	–177.2(2)	$C^5C^4C^9C^8$	0.1(4)
$N^2N^1C^3O^1$	–178.5(2)	$O^1C^4C^9C^8$	–173.9(2)
$C^2N^1C^3O^1$	5.1(4)	$C^7C^8C^9C^4$	0.4(4)
$C^3O^1C^4C^9$	–117.3(3)		

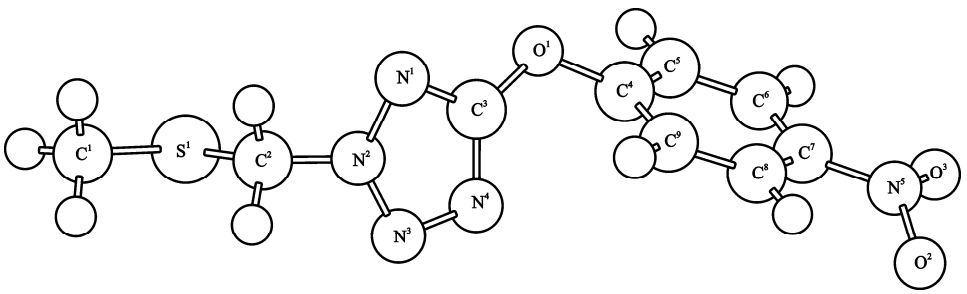
Version 2.0 program and was refined by the full-matrix least-squares procedure with respect to F^2 using SHELXL97 software [27]. Nonhydrogen atoms were refined with anisotropic temperature factors. The positions of hydrogen atoms were determined from the difference Fourier map and were refined isotropically. The crystallographic data for structure **VIa** were deposited to the Cambridge Crystallographic Data Center (entry no. CCDC-232963) and are available free of charge upon request to CCDC, 12 Union Road, Cambridge, UK (fax: +44-1223-336033, *e-mail*: *deposit@ccdc.cam.ac.uk*).

Methyl 5-aryloxytetrazole-2-carboxylates Ia–If were synthesized by the procedures reported in [13].

5-(4-Nitrophenoxy)tetrazole (Va). A 100-ml flask was charged with 10.0 g (62 mmol) of 5-phenoxytetrazole (**Vb**), and fuming nitric acid was added dropwise over a period of 20 min under stirring and cooling with an ice bath. The cooling bath was removed, and the mixture was allowed to warm up to 25–30°C over a period of 20 min and was transferred into a beaker containing crushed ice under stirring in a hood. The precipitate was filtered off and recrystallized from benzene. Yield 90%, mp 160–161°C; published data [24]: mp 162–163°C, yield <10%. IR spectrum (KBr), ν, cm^{-1}: 2500–3200 br, s, 1620, 1580, 1530, 1480, 1350, 1200, 1060, 870, 730, 670, 650. ^1H NMR spectrum (90 MHz, DMSO-d_6), δ, ppm: 14.60 br.s (1H), 8.60 d (2H, J = 9 Hz), 7.75 d (2H, J = 9 Hz).



VIa



VIIa

Fig. 3. Optimized structures of 1- and 2-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazoles **VIa** and **VIIa** (*ab initio* calculations).

Table 4. Selected bond lengths (*d*, Å) in molecules **VIa** and **VIIa** according to AM1, PM3, and *ab initio* calculations and experimental data for **VIa**

Bond	Experiment (X-ray diffraction)	AM1		PM3		*Ab initio*	
		VIa	**VIIa**	**VIa**	**VIIa**	**VIa**	**VIIa**
C^4–O^1	1.403(3)	1.404	1.395	1.399	1.388	1.412	1.414
O^1–C^3	1.324(3)	1.376	1.379	1.358	1.357	1.373	1.384
C^3–N^1	1.326(3)	1.419	1.372	1.392	1.353	1.399	1.386
N^1–N^2	1.348(3)	1.358	1.348	1.392	1.367	1.399	1.408
N^2–N^3	1.287(3)	1.280	1.369	1.266	1.350	1.379	1.419
N^3–N^4	1.364(3)	1.332	1.262	1.337	1.277	1.420	1.382
N^4–C^3	1.304(3)	1.377	1.441	1.361	1.406	1.342	1.409
N^1–C^2	1.453(3)	1.441	–	1.474	–	1.472	–
C^2–S^1	1.788(3)	1.773	1.769	1.824	1.824	1.815	1.815
S^1–C^1	1.790(3)	1.752	1.750	1.801	1.799	1.796	1.796

Table 5. Selected bond angles (ω, deg) in molecules **VIa** and **VIIa** according to AM1, PM3, and *ab initio* calculations and experimental data for **VIa**

Angle	Experiment (X-ray diffraction)	AM1		PM3		*Ab inilio*	
		VIa	**VIIa**	**VIa**	**VIIa**	**VIa**	**VIIa**
$C^2S^1C^1$	99.79(14)	104.18	104.20	104.01	103.83	98.74	97.18
$C^3O^1C^4$	118.43(18)	115.14	115.40	116.63	120.31	114.81	114.39
$C^3N^1C^2$	129.8(2)	127.15	–	130.08	–	129.60	–
$N^2N^1C^2$	123.21(19)	126.95	123.30	123.36	123.76	122.14	119.40
$N^1C^2S^1$	114.49(17)	115.75	–	116.33	–	111.58	–
$O^1C^3N^1$	118.9(2)	120.21	126.05	121.79	132.56	116.96	120.12

Table 6. Selected torsion angles (φ, deg) in molecules **VIa** and **VIIa** according to AM1, PM3, and *ab initio* calculations and experimental data for **VIa**

Angle	Experiment (X-ray diffraction)	AM1		PM3		*Ab initio*	
		VIa	**VIIa**	**VIa**	**VIIa**	**VIa**	**VIIa**
$C^2N^1N^2N^3$	177.4(2)	179.0	–	178.5	–	174.8	–
$C^4O^1C^3N^4$	8.1(4)	8.2	83.5	3.4	144.3	–3.2	109.6
$N^2N^1C^3O^1$	–178.5(2)	–179.5	–172.6	–180.0	–172.0	–178.9	–173.25
$C^2N^1C^3O^1$	5.1(4)	1.6	–	2.2	–	5.1	–
$C^3O^1C^4C^5$	68.6(3)	125.3	44.7	126.9	22.8	129.5	–47.73
$O^1C^4C^5C^6$	173.6(2)	173.5	174.5	173.9	176.9	175.8	175.99

Reaction of methyl 5-(4-nitrophenoxy)tetrazole-2-carboxylate (Ia) with dimethyl sulfoxide. A mixture of methyl 5-(4-nitrophenoxy)tetrazole-2-carboxylate (**Ia**) and DMSO (taken as solvent) was stirred for 12 h at room temperature using a magnetic stirrer. The progress of the reaction was monitored by TLC (cyclohexane–ethyl acetate, 80:20). Excess DMSO was removed, and the residue was passed through a column charged with silica gel using cyclohexane–ethyl acetate (90:10) as eluent. We isolated 1-methylsulfanylmethyl-5-(4-nitrophenoxy)tetrazole (**VIa**), mp 67–68°C, 2-methyl-5-(4-nitrophenoxy)tetrazole (**IIIa**), mp 89°C, and 1-methyl-5-(4-nitrophenoxy)tetrazole (**IVa**), mp 109°C (108– 109°C [4]).

Reaction of 5-(4-nitrophenoxy)tetrazole (Va) with DMSO in the presence of acetic anhydride. Compound **Va**, 0.5 g, was dissolved in 5 ml of acetic anhydride, and 20 ml of dry DMSO was added drop-

wise over a period of 30 min. The mixture was stirred for 24 h at 55–60°C, excess DMSO and acetic anhydride were removed under reduced pressure, and the residue was washed with several 2–3-ml portions of water. The precipitate was dissolved in 20 ml of methylene chloride, the solution was dried over calcium chloride and evaporated, and the residue was separated by column chromatography on silica gel using ethyl acetate–cyclohexane (80:20) as eluent to isolate compounds **VIa** and **VIIa**.

1-Methylsulfanylmethyl-5-(4-nitrophenoxy)-tetrazole (VIa). Yield 30%, mp 67–68°C. IR spectrum (KBr), ν, cm^{-1}: 3020, 1640, 1610, 1520, 1410, 1350, 1240, 1180, 1160, 1120, 860, 710. ^{1}H NMR spectrum (500 MHz, $CDC1_3$), δ, ppm: 8.36 m (2H, J = 9.5 Hz), 7.70 d (2H, J = 9.0 Hz), 5.32 s (2H), 2.33 s (3H). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 158.56, 157.08, 145.44, 125.89, 119.63, 49.21, 15.53. Mass spectrum (EI), m/z (I_{rel}, %): 269 (10) $[M + 2]^+$, 267 (47) $[M]^+$, 192 (75), 150 (8), 122 (28), 101 (90), 76 (33), 61 (100). Found, %: C 40.5; H 3.5; N 26.8. $C_9H_9N_5O_3S$. Calculated, %: C 40.5; H 3.4; N 26.2.

2-Methylsulfanylmethyl-5-(4-nitrophenoxy)-tetrazole (VIIa). Yield 20%, mp 92–94°C. IR spectrum (KBr), ν, cm^{-1}: 3020, 2980, 1620, 1530, 1480, 1340, 1240, 1200, 1090, 1000, 870, 740. ^{1}H NMR spectrum (500 MHz, CCl_4, DMSO-d_6), δ: 8.40 d (2H, J = 9.0 Hz), 7.78 d (2H, J = 9.0 Hz), 5.57 s (2H), 2.26 s (3H). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 159.71, 158.25, 145.90, 126.86, 121.15, 49.62, 15.60. Mass spectrum (EI), m/z (I_{rel}, %): 269 (2.6) $[M + 2]^+$, 267 (65) $[M]^+$, 192 (36), 191 (40), 122 (30), 101 (32), 75 (28), 61 (100). Found, %: C 40.6; H 3.6; N 27.4. $C_9H_9N_5O_3S$. Calculated, %: C 40.5; H 3.4; N 26.2.

Reaction of 5-phenoxytetrazole (Vb) with DMSO in the presence of acetic anhydride. Dry DMSO, 20 ml, was added dropwise over a period of 30 min to a solution of 0.5 g of compound **Vb** in 5 ml of acetic anhydride. The mixture was stirred for 24 h at 45–50°C, excess DMSO and acetic anhydride were removed under reduced pressure, and the residue was washed with several small portions of water and dissolved in 20 ml of methylene chloride. The solution was dried over calcium chloride and evaporated, and the residue was separated by column chromatography on silica gel to isolate compounds **VIb** and **VIIb**.

1-Methylsulfanylmethyl-5-phenoxytetrazole (VIb). Yield 26%. IR spectrum (KBr), ν, cm^{-1}: 3020, 2993, 1510, 1490, 1410, 1200, 1020, 750, 680. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.31 m (5H), 5.49 s (2H), 2.34 s (3H). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 171.30, 154.73, 130.26, 125.87, 119.55, 56.86, 16.25. Mass spectrum (EI), m/z (I_{rel}, %) 224 (0.64) $[M + 2]^+$, 222 (14) $[M]^+$, 147 (70), 101 (79), 77 (100), 74 (23), 61 (58). Found, %: C 48.8; H 4.7; N 25.6. $C_9H_{10}N_4OS$. Calculated, %: C 48.63; H 4.53; N 25.2.

2-Methylsulfanylmethyl-5-phenoxytetrazole (VIIb). Yield 16%. IR spectrum (KBr), ν, cm^{-1}: 3060, 3000, 2920, 1550, 1490, 1310, 1250, 1190, 1160, 750, 680. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.40 m (5H), 5.32 s (2H), 2.35 s (3H). ^{13}C NMR spectrum (125 MHz, $CDC1_3$), δ_C, ppm: 160.18, 154.71, 130.45, 126.89, 119.60, 49.30, 15.96. Mass spectrum (EI), m/z (I_{rel}, %) 224 (0.64) $[M + 2]^+$, 222 (14) $[M]^+$, 176 (27), 147 (16), 101 (22), 77 (67), 61 (100).

Reaction of 5-(2,6-dimethoxyphenoxy)tetrazole (Vf) with DMSO in the presence of acetic anhydride. Dry DMSO, 10 ml, was added dropwise over a period of 30 min to a solution of 0.285 g of compound **Vf** in 4 ml of acetic anhydride. The mixture was stirred for 40 h at 45–50°C, excess DMSO and acetic anhydride were removed under reduced pressure, and the residue was washed with several 2–3-ml portions of water. The precipitate was dissolved in 20 ml of methylene chloride, the solution was dried over calcium chloride and evaporated, and the residue was separated by column chromatography on silica gel to isolate compounds **VIf** and **VIIf**.

1-Methylsulfanylmethyl-5-(2,6-dimethoxyphenoxy)tetrazole (VIf). Yield 14%. IR spectrum (KBr), ν, cm^{-1}: 3010, 3000, 2900, 2840, 1600, 1580, 1510, 1480, 1300, 1260, 1180, 1100, 750, 700. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.22 t (1H, J = 8.5 Hz), 6.70 d (2H, J =10 Hz), 5.46 s (2H), 3.85 s (6H), 2.33 s (3H). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 172.01, 152.84, 132.33, 126.92, 105.73, 56.67, 56.52, 16.17. Mass spectrum (EI), m/z (I_{rel}, %) 284 (1.7) $[M + 2]^+$, 282 (43) $[M]^+$, 207 (34), 179 (27), 165 (70), 122 (52), 107 (88), 101 (100), 77 (47), 61 (68). Found, %: C 48.2; H 5.3; N 17.6. $C_{11}H_{14}N_4O_3S$. Calculated, %: C 46.8; H 5.0; N 19.8.

2-Methylsulfanylmethyl-5-(2,6-dimethoxyphenoxy)tetrazole (VIIf). Yield 8%. IR spectrum (KBr), ν, cm^{-1}: 3000, 1590, 1530, 1390, 1370, 1300, 1260, 1180, 1110, 760. ^{1}H NMR spectrum (500 MHz, $CDCl_3$), δ, ppm: 7.21 t (1H, J = 10 Hz), 6.69 d (2H, J = 10 Hz), 5.46 s (2H), 3.87 s (6H), 2.56 s (3H). ^{13}C NMR spectrum (125 MHz, $CDCl_3$), δ_C, ppm: 178.05, 152.70,

131.81, 127.12, 105.64, 56.68, 13.58. Mass spectrum (EI), m/z (I_{rel}, %) 284 (0.6) $[M + 2]^+$, 282 (15) $[M]^+$, 281 (20), 236 (83), 151 (73), 140 (39), 107 (59), 43 (100).

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