2-R-7-Methyl[1,2,4]triazolo[2,3-*a*]pyrimidines: synthesis and structures

Kh. S. Shikhaliev,[a] D. V. Krylski,[a] A. Yu. Potapov,[a] S. E. Nefedov,[b] and O. E. Sidorenko[a]*

[a]*Voronezh State University,*
1 Universitetskaya pl., 394006 Voronezh, Russian Federation.
E-mail: chocd261@chem.vsu.ru
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation

Reactions of 5-R-3-amino-1,2,4-triazoles with ethoxymethylideneacetylacetone and ethyl ethoxymethylideneacetoacetate proceeded regioselectively, giving 2-R-7-methyl[1,2,4]triazolo[2,3-*a*]-pyrimidines in good yields. The compounds obtained were characterized by elemental analysis, ^{1}H NMR spectroscopy, and X-ray diffraction analysis (for ethyl 2-ethylthio-7-methyl-[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate). The frontier orbitals, the molecular electrostatic potential, and the geometries of the reagent molecules were calculated by the DFT method (B3LYP/6-31G**).

Key words: 5-R-3-amino-1,2,4-triazole, ethoxymethylideneacetylacetone, ethyl ethoxymethylideneacetoacetate, 2-R-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidines, synthesis, structures.

Condensation of aminoazoles (*e.g.*, 3-amino-1,2,4-triazole and its derivative **1**) with bielectrophiles provides a general route to fused heterocyclic systems. With unsymmetrical binucleophiles such as aminoazoles, a regioselectivity problem arises in their reactions with unsymmetrical electrophiles.[1—5] Structures, reactivity, and regioselectivity in reactions of 3-amino-1,2,4-triazole have been extensively studied by physicochemical, spectroscopic, X-ray diffraction, and quantum-chemical methods.[1—3,6—13]

Condensation of 3-amino-1,2,4-triazole with ethyl acetoacetate and its homologs proceeds regioselectively to give triazolopyrimidinones **2**,[1,3,14,15] while cyclization with unsymmetrical diketones leads to a mixture of regioisomeric triazolopyrimidines **3** and **3´** (Scheme 1). Their relative yields depend on the steric factor.[16]

A reaction of aminotriazole and its derivatives with β-ethoxymethylidenecarbonyl compounds, which is usually carried out in acetic acid, starts with nucleophilic substitution of the ethoxy group[17—19] with participation of the *exo*-amino group of the azole. This is followed by intramolecular cyclization involving the "pyrrole-type" ring N atom and ketone carbonyl, ester, or cyano groups (compounds **4**—**6**). In the case of ethyl ethoxymethylidenecyanoacetate, chemoselectivity takes place.[20—22] Use of ethoxymethylidenecyanamide for the synthesis of 5-amino[1,2,4]triazolo[2,3-*a*][1,3,5]triazines (5-azaadenines) **7** is described in Ref. 23.

Aminotriazoles can also be involved in three-component condensations with aldehydes and active methylene dicarbonyl compounds (dimedone, ethyl acetoacetate, and acetoacetanilides).[2,24—26] These reactions proceed through the formation of an ylidene derivative of the active methylene component, which was proved by an independent synthesis.

An attempt to extend the earlier[27] discovered three-component condensation with hetarylguanidines, linear β-dicarbonyl compounds, and triethyl orthoformate to 3-amino-1,2,4-triazole was unsuccessful. Instead of the expected triazolopyrimidines **8**, we isolated products of condensation of compound **1** with the orthoester. Compounds **8** were obtained through the use of ethoxymethylidene derivatives **9** (Scheme 2).

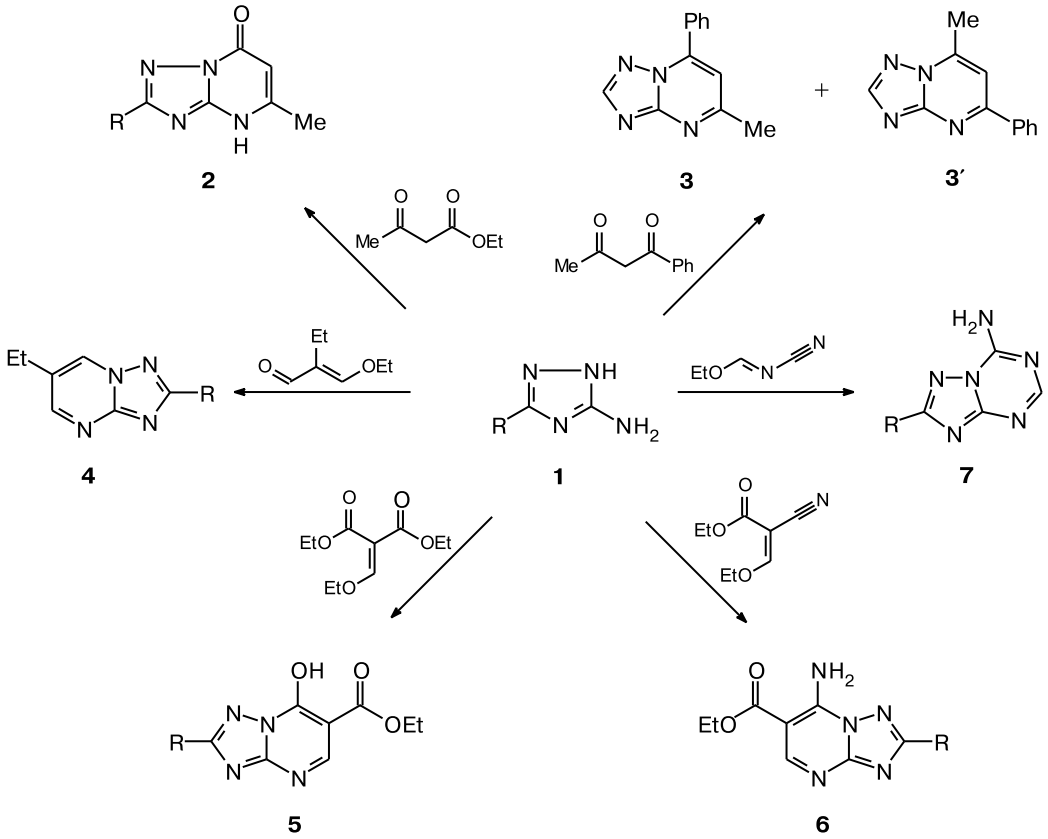
In the present work, we studied reactions of 5-R-3-amino-1,2,4-triazoles with ethoxymethylideneacetylacetone and ethyl ethoxymethylideneacetoacetate by using quantum-chemical molecular calculations, preparatively isolated the resulting compounds, and examined their structures.

Results and Discussion

We found that reflux of compounds **1a**—**f** with ethoxymethylideneacetylacetone or ethyl ethoxymethylideneacetoacetate in acetic acid for 40—60 min gives, regardless of the substituent R, the corresponding 2-R-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidines **8** in high yields rather than regioisomeric compounds **8´**. The plausible reaction scheme involves a nucleophilic attack of the *exo*-amino group of the aminoazole on the C atom of the ethoxymethylidene fragment with elimi-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1244—1248, June, 2008.

Scheme 1

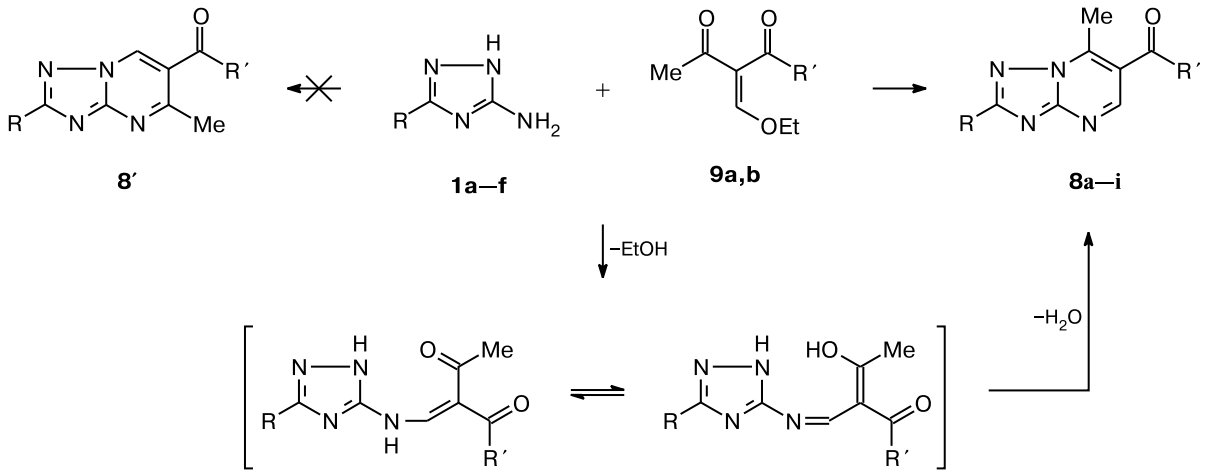


R = H, Me, MeS

nation of an ethanol molecule and subsequent cyclization through the endocyclic N atom and the carbonyl group.

The resulting 2-R-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidines were characterized by ^{1}H NMR spectra; the structure of ethyl 2-ethylthio-7-methyl[1,2,4]triazolo[2,3-

Scheme 2



1: R = H (**a**), Me (**b**), CF_3 (**c**), MeS (**d**), $PhCH_2S$ (**e**), EtS (**f**); **8:** R = H, R′ = Me (**a**), R = R′ = Me (**b**), R = CF_3, R′ = Me (**c**), R = H, R′ = OEt (**d**), R = Me, R′ = OEt (**e**), R = CF_3, R′ = OEt (**f**), R = MeS, R′ = Me (**g**), R = $PhCH_2S$, R′ = Me (**h**), R = EtS, R′ = OEt (**i**); **9:** R′ = Me (**a**), OEt (**b**)

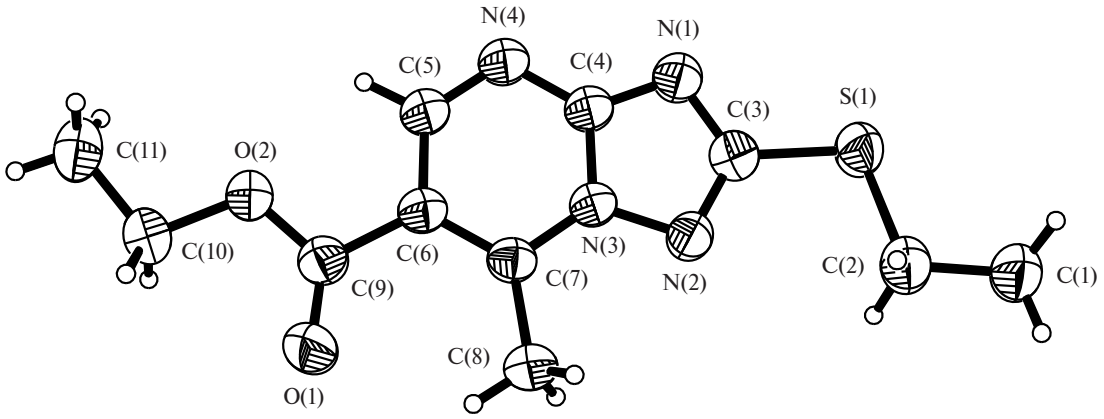


Fig. 1. Structure of ethyl 2-ethylthio-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate (**8i**).

a]pyrimidine-6-carboxylate (**8i**) was confirmed by X-ray diffraction data.

According to X-ray diffraction data, the presence of the substituents 2-EtS (S(1)—C(3) 1.743(2) Å) and 6-EtOOC (C(6)—C(9) 1.496(3) Å, C(9)—O(1) 1.200(3) Å, and C(9)—O(2) 1.324(3) Å) in structure **8i** (Fig. 1) substantially changes the bond lengths in the planar triazolopyrimidine fragment (N(1)—C(3) 1.355(3) Å, N(2)—C(3) 1.331(3) Å, N(2)—N(3) 1.370(3) Å, N(1)—C(4) 1.322(3) Å, N(3)—C(4) 1.387(3) Å, N(4)—C(4) 1.345(3) Å, N(3)—C(7) 1.364(3) Å, N(4)—C(5) 1.312(3) Å, C(5)—C(6) 1.416(3) Å, C(6)—C(7) 1.378(3) Å, and C(7)—C(8) 1.494(3) Å) compared to the average distances in the known pyrimidine-containing molecules (C—N 1.333—1.342 Å, N—N 1.287—1.326 Å, and C—C 1.379—1.400 Å),[28] as well as compared to the sole structurally characterized[29] (1R,3R,4R)-1,7,7-trimethyl-3-(1,2,4-triazolo[2,3-*a*]pyrimidin-2-yl)bicyclo[2.2.1]heptan-2-one (N(1)—C(3) 1.362 Å, C(3)—N(2) 1.321 Å, N(2)—N(3) 1.363 Å, N(3)—C(7) 1.351 Å, N(3)—C(4) 1.350 Å, N(1)—C(4) 1.326 Å, N(4)—C(4) 1.356 Å, N(4)—C(5) 1.325 Å, C(5)—C(6) 1.396 Å, and C(6)—C(7) 1.352 Å), which shows a similar bond distribution in the heterocycle.[30]

To estimate the reactivities of the reagents, we performed quantum-chemical DFT calculations with the exchange-correlation functional B3LYP and the basis set 6-31G**.

According to our quantum-chemical calculations, the amplitude of the HOMO of aminotriazole **1a** is higher for the *exo*-amino group. In structures **9a,b**, the LUMO is most greatly contributed by the C_β atom at the double bond (Fig. 2).

The shapes of the frontier orbitals in the reactant molecules are consistent with the concept of the orbital control of the reaction in question. At the same time, the molecular electrostatic potential (MEP) map (Fig. 3) shows that the negative potential in 3-amino-1,2,4-triazole concentrates near the N(2) and N(4) atoms. This is an unfavorable factor in the context of the assumed reac-

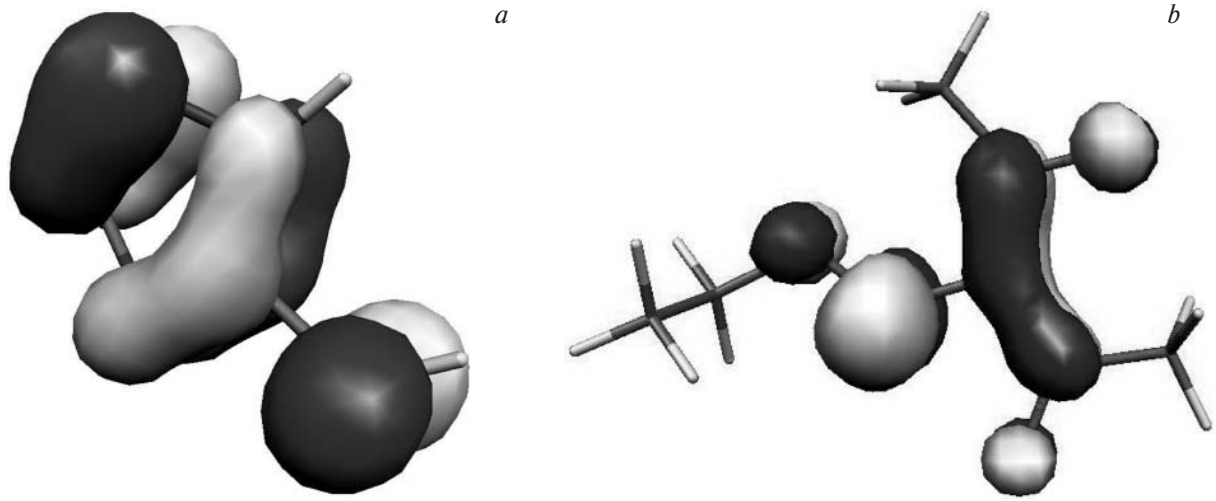


Fig. 2. B3LYP/6-31G**-calculated structure of the HOMO of 3-amino-1,2,4-triazole (*a*) and the LUMO of ethoxymethylideneacetylacetone (*b*).

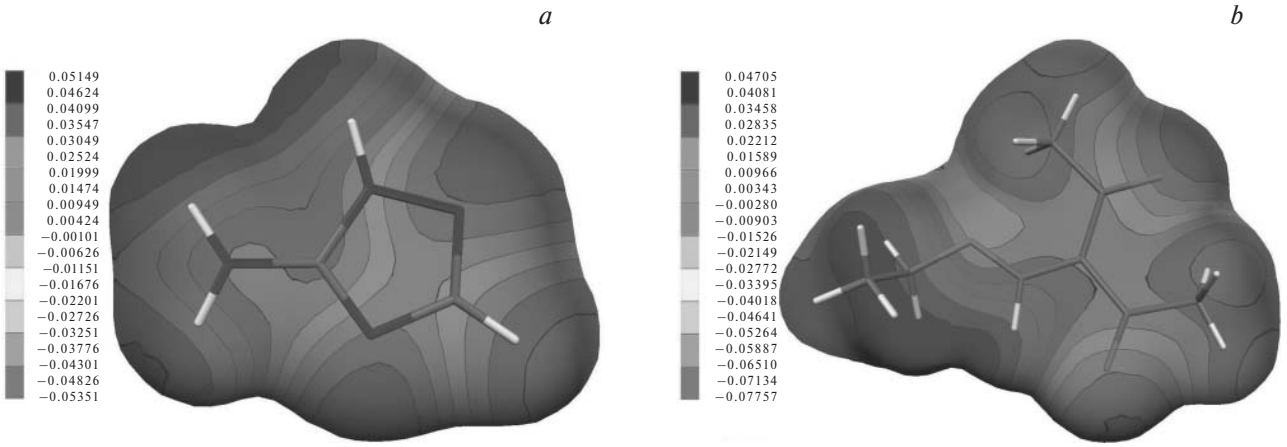


Fig. 3. B3LYP/6-31G**-calculated MEP map for 3-amino-1,2,4-triazole (*a*) and ethoxymethylideneacetylacetone (*b*).

tion mechanism. In ethoxymethylideneacetylacetone, the C_β atom of the ethoxymethylidene group is in the positive potential area, which favors this reaction scheme.

Therefore, the reaction is orbital-controlled.

Experimental

The course of the reactions was monitored and the purity of the compounds obtained was checked by TLC on Silufol UV-254 plates with chloroform—ethyl acetate (1 : 2) as an eluent. ^{1}H NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz) in DMSO-d_6 with Me_4Si as the internal standard.

Quantum-chemical calculations were performed with the GAUSSIAN-98 program package.[31] For graphical representation of the results obtained, the MOLEKEL program was used.[32,33]

1-(2-R-7-Methyl[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanones 8a—c,g,h and ethyl 2-R-7-methyl[1,2,4]triazolo[2,3-*a*]-pyrimidine-6-carboxylates 8d—f,i (general procedure). A mixture of an appropriate aminotriazole (0.01 mol) and ethoxymethylideneacetylacetone or ethyl ethoxymethylideneacetoacetate (0.011 mol) in glacial acetic acid (5 mL) was refluxed for 40—60 min. On cooling, the precipitate that formed was recrystallized from DMF.

1-(7-Methyl[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanone (8a). Yield 75%, m.p. 155—157 °C. Found (%): C, 54.65; H, 4.44; N, 31.86. $C_8H_8N_4O$. Calculated (%): C, 54.54; H, 4.58; N, 31.80. ^{1}H NMR, δ: 2.70, 3.08 (both s, 3 H each, Me); 7.86 (s, 1 H, CH, triazole); 9.55 (s, 1 H, CH, pyrimidine).

1-(2,7-Dimethyl[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanone (8b). Yield 67%, m.p. 126—128 °C. Found (%): C, 56.76; H, 5.47; N, 29.80. $C_9H_{10}N_4O$. Calculated (%): C, 56.83; H, 5.30; N, 29.46. ^{1}H NMR, δ: 2.59, 2.73, 3.08 (all s, 3 H each, Me); 9.20 (s, 1 H, pyrimidine).

1-(7-Methyl-2-trifluoromethyl[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanone (8c). Yield 83%, m.p. 144—145 °C. Found (%): C, 44.49; H, 2.76; N, 23.06. $C_9H_7F_3N_4O$. Calculated (%): C, 44.27; H, 2.89; N, 22.95. ^{1}H NMR, δ: 2.78, 3.12 (both s, 3 H each, Me); 9.43 (s, 1 H, CH, pyrimidine).

Ethyl 7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate (8d). Yield 57%, m.p. 98—99 °C. Found (%): C, 52.44; H, 4.67; N, 27.35. $C_9H_{10}N_4O_2$. Calculated (%): C, 52.42; H, 4.89; N, 27.17. ^{1}H NMR, δ: 1.40 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 3.12 (s, 3 H, Me); 4.42 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1 Hz); 8.81 (s, 1 H, CH, triazole); 9.20 (s, 1 H, CH, pyrimidine).

Ethyl 2,7-dimethyl[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate (8e). Yield 62%, m.p. 114—116 °C. Found (%): C, 54.56; H, 5.41; N, 25.56. $C_{10}H_{12}N_4O_2$. Calculated (%): C, 54.54; H, 5.49; N, 25.44. ^{1}H NMR, δ: 1.34 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 2.62, 3.05 (both s, 3 H each, Me); 4.26 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1 Hz); 9.54 (s, 1 H, CH, pyrimidine).

Ethyl 7-methyl-2-trifluoromethyl[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate (8f). Yield 64%, m.p. 135—137 °C. Found (%): C, 43.69; H, 3.42; N, 20.46. $C_{10}H_9F_3N_4O_2$. Calculated (%): C, 43.80; H, 3.31; N, 20.43. ^{1}H NMR, δ: 1.45 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 3.20 (s, 3 H, Me); 4.32 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1 Hz); 9.66 (s, 1 H, CH, pyrimidine).

1-(7-Methyl-2-methylthio[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanone (8g). Yield 69%, m.p. 141—143 °C. Found (%): C, 48.58; H, 4.44; N, 25.36. $C_9H_{10}N_4OS$. Calculated (%): C, 48.63; H, 4.53; N, 25.21. ^{1}H NMR, δ: 2.66, 3.00 (both s, 3 H each, Me); 3.08 (s, 3 H, SMe); 9.21 (s, 1 H, CH, pyrimidine).

1-(2-Benzylthio-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidin-6-yl)ethanone (8h). Yield 60%, m.p. 130—131 °C. Found (%): C, 60.49; H, 4.92; N, 18.66. $C_{15}H_{14}N_4OS$. Calculated (%): C, 60.38; H, 4.73; N, 18.78. ^{1}H NMR, δ: 2.70, 2.98 (both s, 3 H each, Me); 4.50 (s, 2 H, SCH_2); 7.21—7.49 (m, 5 H, H arom.); 9.22 (s, 1 H, CH, pyrimidine).

Ethyl 2-ethylthio-7-methyl[1,2,4]triazolo[2,3-*a*]pyrimidine-6-carboxylate (8i). Yield 66%, m.p. 150—152 °C. Found (%): C, 49.59; H, 5.22; N, 21.16. $C_{11}H_{14}N_4O_2S$. Calculated (%): C, 49.61; H, 5.30; N, 21.04. ^{1}H NMR, δ: 1.45 (t, 3 H, $OCH_2C\underline{H}_3$, J = 7.1 Hz); 1.64 (t, 3 H, $SCH_2C\underline{H}_3$, J = 6.9 Hz); 3.22 (s, 3 H, Me); 3.11 (q, 2 H, $SC\underline{H}_2CH_3$, J = 6.9 Hz); 4.34 (q, 2 H, $OC\underline{H}_2CH_3$, J = 7.1 Hz); 9.72 (s, 1 H, CH, pyrimidine).

X-ray diffraction analysis was carried out on a Bruker P4 diffractometer (λ-Mo radiation, graphite monochromator, ω scan mode, $2\theta_{max}$ = 50°). For **8i**: molecular formula $C_{11}H_{14}N_4O_2S$, M = 266.32, space group $P2(1)/c$, a = 9.9130(10) Å, b = 11.1460(10) Å, c = 11.668(2) Å, α = 90°, β = 98.430(10)°, γ = 90° (295 K), V = 1275.3(3) Å^3, Z = 4, the number of measured reflections is 2213, the number of independent reflections with $F^2 > 2\sigma(I)$ is 1740, ρ_{calc} = 1.387 g cm^{-3}, μ = 0.254 cm^{-1}, R_1 = 0.0430, wR_2 = 0.1026. Calculations were performed with the

SHELXTL PLUS program package (PC version).[34,35] The structure was refined with the SHELXTL-97 program. Crystallographic parameters for compound **8i** have been deposited with the Cambridge Crystallographic Data Center (CCDC 641 944) and can be made available from www.ccdc.cam.ac.uk/data_request/cifwww.ccdc.cam.ac.uk/data_request/cif.

References

1. Ya. A. Levin, N. A. Gul´kina, V. A. Kukhtin, *Zh. Obshch. Khim.*, 1963, **33**, 2673 [*J. Gen. Chem. USSR*, 1963, **33** (Engl. Transl.)].
2. V. V. Lipson, S. M. Desenko, M. G. Shirobokova, V. V. Borodina, *Khim. Geterotsikl. Soedin.*, 2003, 1383 [*Chem. Heterocycl. Compd.*, 2003, **39** (Engl. Transl.)].
3. S. A. Yamashkin, N. Ya. Kucherenko, M. A. Yurovskaya, *Khim. Geterotsikl. Soedin.*, 1997, 579 [*Chem. Heterocycl. Compd.*, 1997, **33** (Engl. Transl.)].
4. V. D. Orlov, T. V. Berezkina, M. A. Kolosov, V. N. Kotlyar, A. Kh. Maruggo, *Tezisy dokladov Mezhdunarodnoi konferentsii po khimii geterotsiklicheskikh soedinenii, posvyashchennoi 90-letiyu prof. A. N. Kosta (Moskva, 17—21 oktyabrya 2005 g.)* [*Abstrs Int. Conf. on Heterocyclic Chemistry in Honor of the 90th Anniversary of A. N. Kost (Moscow, October 17—21, 2005)*], Moscow, 2005, 30 (in Russian).
5. O. V. Fedorova, M. S. Zhidovinova, I. G. Ovchinnikova, G. L. Rusinov, *Tezisy dokladov Mezhdunarodnoi konferentsii po khimii geterotsiklicheskikh soedinenii, posvyashchennoi 90-letiyu prof. A. N. Kosta (Moskva, 17—21 oktyabrya 2005 g.)* [*Abstrs Int. Conf. on Heterocyclic Chemistry in Honor of the 90th Anniversary of A. N. Kost (Moscow, October 17—21, 2005)*], Moscow, 2005, 333 (in Russian).
6. V. D. Orlov, S. M. Desenko, K. A. Potekhin, Yu. T. Struchkov, *Khim. Geterotsikl. Soedin.*, 1988, 229 [*Chem. Heterocycl. Compd.*, 1988, **24** (Engl. Transl.)].
7. D. V. Krylski, Kh. S. Shikhaliev, A. V. Falaleev, Yu. A. Kovygin, *Vestn. Voronezh. Gos. Univ., Ser. Khim. Biol. Farm.* [*Bulletin of the Voronezh State University, Ser. Chemistry, Biology, Pharmacy*], 2005, 58 (in Russian).
8. V. V. Makarskii, G. L. Starova, O. V. Frank-Kamenetskaya, V. A. Lopyrev, M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 1977, 1138 [*Chem. Heterocycl. Compd.*, 1977, **13** (Engl. Transl.)].
9. V. V. Makarskii, V. A. Zubkov, V. A. Lopyrev, M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 1977, 540 [*Chem. Heterocycl. Compd.*, 1977, **13** (Engl. Transl.)].
10. G. I. Chipen, V. Ya. Grinshtein, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.* [*Bulletin of the Academy of Sciences of the Latvian Soviet Socialist Republic, Ser. Chemistry*], 1962, 401 (in Russian).
11. V. V. Mel´nikov, M. S. Pevzner, V. V. Stolpakova, L. F. Khor´kova, *Khim. Geterotsikl. Soedin.*, 1971, 409 [*Chem. Heterocycl. Compd.*, 1971, **7** (Engl. Transl.)].
12. Zh. N. Fidler, E. F. Shibanova, P. V. Makerov, I. D. Kalikhman, A. M. Shulunova, G. I. Sarapulova, L. V. Klyba, V. Yu. Vitkovskii, I. N. Chipanina, V. A. Lopyrev, M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 1980, 1414 [*Chem. Heterocycl. Compd.*, 1980, **16** (Engl. Transl.)].
13. M. H. Palmer, D. Christen, *J. Mol. Struct.*, 2004, 177.
14. L. M. Werbel, E. F. Elslager, V. P. Chu, *J. Heterocycl. Chem.*, 1973, **10**, 631.
15. W. T. Monte, W. A. Kleschick, R. W. Meikle, S. W. Snider, J. Bordner, *J. Heterocycl. Chem.*, 1989, **26**, 1393.
16. J. Reiter, L. Pongo, I. Kovesdi, I. Pallagi, *J. Heterocycl. Chem.*, 1995, **32**, 407.
17. F. V. Bagrov, *Zh. Org. Khim.*, 2000, **36**, 214 [*Russ. J. Org. Chem.*, 2000, **36** (Engl. Transl.)].
18. R. S. Vartanyan, Zh. V. Kazaryan, *Khim. Geterotsikl. Soedin.*, 1983, 1318 [*Chem. Heterocycl. Compd.*, 1983, **19** (Engl. Transl.)].
19. C. Romano, E. Cuesta, C. Avendano, *Heterocycles*, 1990, **31**, 267.
20. M. Kunstlinger, E. Breitmaier, *Synthesis*, 1983, 44.
21. J. P. Clayton, N. H. Rogers, V. J. Smith, R. Stevenson, T. J. King, *J. Chem. Soc., Perkin Trans.*, 1980, **1**, 1347.
22. J. Reiter, L. Pongo, P. Dvortsak, *J. Heterocycl. Chem.*, 1987, **24**, 1149.
23. I. Lalezari, S. Nabahi, *J. Heterocycl. Chem.*, 1980, **17**, 1121.
24. O. V. Fedorova, M. S. Zhidovinova, G. L. Rusinov, I. G. Ovchinnikova, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 1677 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1768].
25. K. M. Dawood, A. M. Farag, Z. E. Kandeel, *J. Chem. Res. (S)*, 1999, 88.
26. E. A. Muravyova, V. A. Chebanov, S. M. Desenko, L. M. Afanasiadi, V. I. Musatov, *Abstrs Int. Conf. "Chemistry of Nitrogen Containing Heterocycles" (Kharkiv, September 30—October 03, 2003)*, Kharkiv, 2003, 99.
27. D. V. Krylski, Kh. S. Shikhaliev, A. Yu. Potapov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* [*Bulletin of High Schools, Chemistry and Chemical Technology*], 2005, **48**, 72 (in Russian).
28. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Qrpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.
29. *Cambridge Structural Database*, CSD version 5.28, November 2006, update 1 (Jan 2007).
30. U. Groðelj, S. Reènik, J. Svete, A. Meden, B. Stanovnik, *Tetrahedron: Asymm.*, 2002, **13**, 821.
31. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Menucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, *GAUSSIAN 98*, *Revision A. 3*, Gaussian, Inc., Pittsburgh (PA), 1998.
32. P. Flukiger, H. P. Luthi, S. Portmann, J. Weber, *MOLEKEL 4.3*, Swiss Center for Scientific Computing, Manno (Switzerland), 2000—2002.
33. S. Portmann, H. P. Luthi, *Chimia*, 2000, **54**, 766.
34. *SMART (control) and SAINT (integration) Software, Version 5.0*, Bruker AXS Inc., Madison, WI, 1997.
35. G. M. Sheldrick, *SADABS. Program for Scaling and Correction of Area Detector Data*, University of Göttingen, Göttingen, 1997.

Received July 14, 2006;
in revised form July 27, 2007