Synthesis and Tautomerization of 6,7-Dihydro-(1,2,3)-triazolo[1,5-*a*]pyrimidines

Sergey M. Desenko*, Evgeny S. Gladkov, Svetlana V. Shishkina and Oleg V. Shishkin

The Institute of Single Crystals,
UA-61001 Kharkov, Ukraine

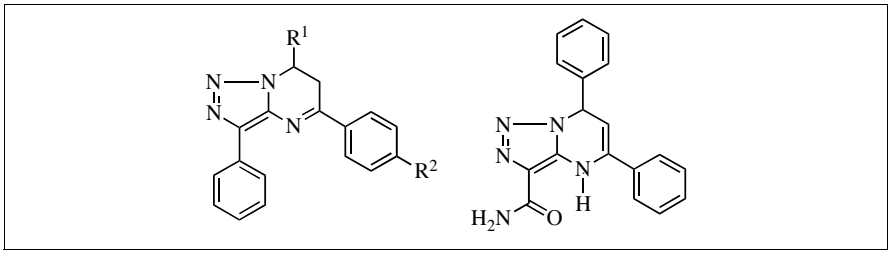
Sergey A. Komykhov and Valery D. Orlov

Kharkov National University, Department of Organic Chemistry,
UA-61077 Kharkov, Ukraine,

Herbert Meier

University of Mainz, Institute of Organic Chemistry,
D-55099 Mainz, Germany

Received February 7, 2006



The condensation of 5-amino-4-phenyl-1,2,3-triazole (**1**) with chalcones **2a-e** or 3-dimethylamino-propiophenone (**4f**) leads to the 6,7-dihydro-(1,2,3)-triazolo[1,5-*a*]pyrimidines **3a-f**. The equilibrium of **3** and the tautomeric 4,7-dihydro-(1,2,3)-triazolo[1,5-*a*]pyrimidines **3'** is described.

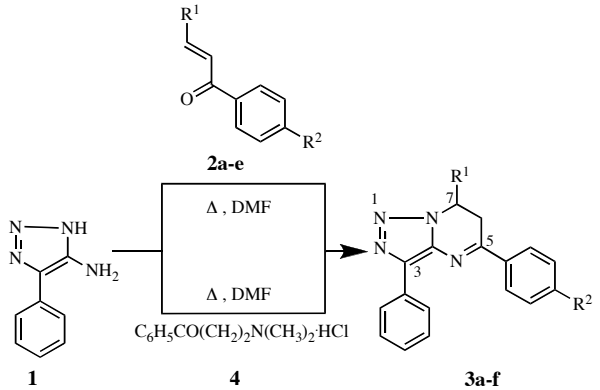
J. Heterocyclic Chem., **43**, 1563 (2006).

In continuation of our study of the synthesis and tautomerism of dihydroazolopyrimidines [1] with a nodal nitrogen atom we investigated some 6,7-dihydro-(1,2,3)-triazolo[1,5-*a*]pyrimidines. The formation of derivatives of this heterocyclic ring system in the cyclocondensation reaction of 4-amino-1,2,3-triazoles and arylideneacetoacetic esters was reported [2]. Although these compounds have interesting properties as calcium antagonists/agonists [2], the number of known heterocycles of this type is very low [2,3]. That is even more surprising, since many examples of the corresponding benzo condensed ring systems, the (1,2,3)triazolo[1,5-*a*]quinazolines, are known [4].

The most common method for the synthesis of dihydro-azolopyrimidines is the cyclocondensation of aminoazoles with α,β-unsaturated carbonyl compounds or Mannich bases [1]. We used now the cyclization reaction of 5-amino-4-phenyl-1,2,3-triazol (4-amino-5-phenyl-1,2,3-triazol) **1** with the chalcones **2a-e** to yield the 3,5,7-triaryl-6,7-dihydro-(1,2,3)-triazolo[1,5-*a*]pyrimidines **3a-e**. Compound **3f** was obtained in a corresponding reaction of **1** and the hydrochloride of the Mannich base **4** which can be regarded as an enone precursor. All cyclization processes were performed in boiling DMF.

The compounds **3a-f** were characterized by spectroscopic methods. The IR spectra in KBr contained typical bands of coupled stretching vibrations of CC and CN double bonds at 1590 - 1610 cm^{-1}. The ^1H NMR spectra of **3a-e** in $CDCl_3$ (Table 1) showed, besides the signals for the aromatic protons, an aliphatic ABX spin system; for **3f** an AA'MM' spin system was found.

Scheme 1



3	R^1	R^2	Yield [%]	m.p.[°C]
a	C_6H_5	H	76	168-170
b	C_6H_5	Cl	73	178-180
c	C_6H_5	OCH_3	55	238-239
d	4-H_3CO-C_6H_5	H	45	187-191
e	4-Cl-C_6H_5	H	30	221-223
f	H	H	57	168-170

Table 1

^{1}H NMR Data of **3a-f** in $CDCl_3$ (δ values, TMS as internal standard)

Compound	6-H A	B	7-H X	$^2J_{AB}$[Hz]	$^3J_{BX}$[Hz]	$^3J_{AX}$[Hz]	ArH	OCH_3
3a	3.60	3.52	5.99	-17.4	7.9	4.4	7.10-8.40	
3b	3.53	3.48	5.96	-14.0	6.5	5.8	7.05-8.35	
3c	3.58	3.47	5.97	-17.2	7.2	4.7	6.95-8.40	3.87
3d	3.58	3.50	5.93	-17.1	7.6	4.9	6.80-8.37	3.74
3e	3.58	3.52	5.97	-13.3	7.0	5.7	7.05-8.40	
3f	3.32 (AA`)		4.63 (MM`)				7.30-8.33	

Table 2

^{1}H NMR data of **3(')a-g** in CD_3SOCD_3
(δ values related to TMS as internal standard)

Compound	6-H		7-H	ArH	Other signals
3a	3.78	3.75	6.18	7.15-8.30	
3'a	5.29		6.56	-	
3b	3.79	3.71	6.15	7.16-8.29	
3'b	5.35		6.57	-	
3c	3.68	3.77	6.15	7.05-8.32	3.83 (OCH_3)
3d	3.73	3.71	6.09	6.90-8.28	3.70 (OCH_3)
3'd	5.25		6.49	-	3.70 (OCH_3)
3e	3.80	3.74	6.19	7.21-8.29	
3'e	5.28		6.61	-	
3f	3.44		4.64	7.32-8.25	
3'g	5.33		6.58	7.28-7.64	8.5 (NH), 7.2 (NH_2)

The measurement in CD_3SOCD_3 (Table 2) revealed for **3a,b,d,e** the presence of minor components **3'a,b,d,e**. The AB spin systems at 5.25 - 5.35 and 6.49 - 6.61 ppm indicated the enamine tautomers **3'** (Scheme 2). The noticeable population of tautomer **3'** in CD_3SOCD_3 in contrast to the solution in $CDCl_3$ illustrates the effect of the relative stabilization of the enamine form by a strong solvation. In particular, the formation of intermolecular N—H...O—S hydrogen bonds has to be examined. The ^{13}C NMR data of **3a-f** are summarized in Table 3. The signal assignment was based on DEPT measurements.

A comparison of the obtained results to literature data of related dihydro derivatives of (1,2,4)-triazolo[1,5-*a*]-pyrimidines **5** ⇄ **5'**, which exist predominantly or exclusively in the enamine form **5'** [1,11,12]), led to a conclusion about the essential influence of the nature of the azole ring on the ratio of tautomers (Scheme 2).

The shift of the tautomeric equilibrium to the enamine form **5'** (Table 4) is based, in our opinion, on the increase of the electron-acceptor effect of the π-system in the azole ring.

Table 3

^{13}C NMR data of **3a**-**f** and **3'g** (δ values related to TMS as internal standard)

Compound	Solvent	C-3, C-3a	C-5	C-6	C-7	Aromat. CH	C_q	other
3a	$CDCl_3$	138.1, 140.0	164.4	33.4	56.2	126.0, 126.8, 127.4, 128. 1, 128.6, 128.8, 128.9, 129.4, 131.9	136.8 128.8 130.8	
3b	$(CD_3)_2SO$	138.1, 138.4	165.7	32.7	55.2	125.9, 126.3, 127.9, 128.3, 128.8, 128.9, 129.0, 129.3	136.9 135.1 130.6 137.1	
3c	$(CD_3)_2SO$	137.3, 138.6	165.9	32.4	55.5	114.2, 125.7, 126.2, 127.7, 128.3, 128.8, 128.8, 129.6	128.8 130.9 137.4 162.5	55.1 (OCH_3)
3d	$(CD_3)_2SO$	137.1, 137.9	166.7	32.7	55.0	114.2, 125.8, 127.4, 127.5, 127.7, 128.6, 128.7, 131.9	136.3 130.7 130.3 159.1	54.8 (OCH_3)
3e	$(CD_3)_2SO$	137.3, 138.0	166.7	32.6	54.6	125.9, 127.5, 127.9, 127.9, 128.4, 128.8, 128.9, 132.1	130.6 133.0 136.2 137.4	
3f	$(CD_3)_2SO$	136.7, 137.5	167.0	24.5	40.5	125.7, 127.3, 127.6, 128.6, 128.7, 131.7	130.8, 136.5	
3'g	$(CD_3)_2SO$	122.8, 138.0	141.4	97.1	58.6	125.4, 126.8, 126.9, 128.3, 128.7, 129.1	133.7, 133.8	163.7 ($CONH_2$)

Scheme 2

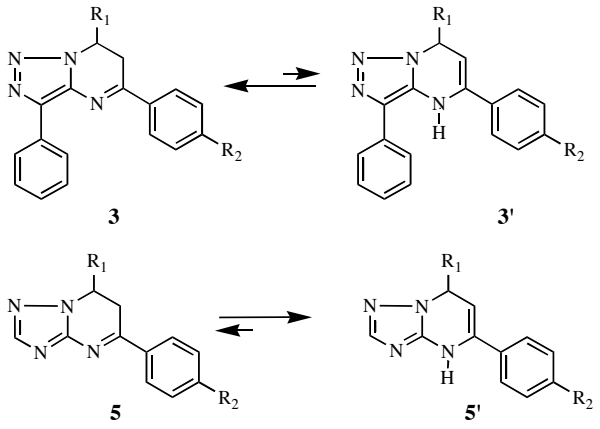


Table 4

Ratio of Tautomers **3a-3e** / **3'a-3'e** and **5a-c,f** / **5'a-c,f** in CD_3SOCD_3 Solution

	R^1	R^2	**3** : **3'**	**5** : **5'**
a	C_6H_5	H	85 : 15	- : 100
b	C_6H_5	Cl	100 : -	- : 100
c	C_6H_5	OCH_3	100 : -	- : 100
d	4-H_3CO-C_6H_5	H	90 : 10	
e	4-Cl-C_6H_5	H	90 : 10	
f	H	H	100 : -	15 : 85

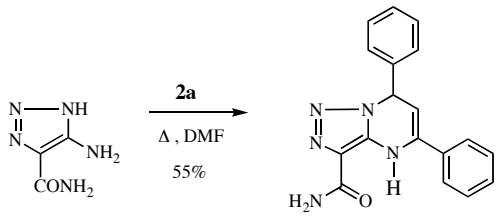
A relative stabilization of the enamine form **3'** may be expected for the introduction of substituents that permit the formation of intramolecular hydrogen bonds. We synthesized therefore 5,7-diphenyl-4,7-dihydro-1,2,3-triazolo[1,5-*a*]pyrimidine-3-carboxamide (**3'g**) (Scheme 3). The ^{1}H NMR spectrum of **3'g** in CD_3SOCD_3 (Table 2) showed - apart from the signals of aromatic rings and amide protons - an AX spin system of the dihydropyrimidine ring. Thus, the presence of the carboxamide group led to the total shift of the tautomeric equilibrium to the 4,7-dihydro form **3'**. (Scheme 3).

In principle, the structure of the compound **3'g** was confirmed by an X-ray diffraction study (Figure 1, Tables 5-7). In the crystalline state however, an intramolecular hydrogen bond is not present. The comparably long O(1) – C(18) bond of 1.232 Å results from a corresponding intermolecular hydrogen bond [H···O' 2.08 Å, N(1) – H···O' 161°].

The triazolopyrimidine fragment and the atoms C(18), O(1) and N(5) are co-planar within a deviation of 0.02 Å. The planarity of the dihydropyrimidine ring does not conform with the general principles of conformational analysis of six-membered dihydroheteroaromatic rings [14,15]. Earlier studies revealed, that 4,7-dihydro-(1,2,4)-triazolo[1,5-*a*]pyrimidines, which bear a substituent in 7-position, have a boat conformation in the crystalline state [16-18]; a fairly planar structure was only found for 4,7-dihydro-5-phenyl-(1,2,4)-triazolo[1,5-*a*]pyrimidine [19]. The planar structure of **3'g** in the crystal may be caused by two reasons: either significant strengthening of the conjugation between enamine fragment and 1,2,3-triazole ring as compared to the 1,2,4-triazole ring system or the influence of intermolecular interactions in the crystal. The bond length N(1)-C(1) in **3'g** does not indicate a conjugation interaction between the π-system of the triazole ring and the enamine fragment. Therefore, intermolecular interactions in the crystal are the most probable reason of the flattening of the dihydropyrimidine ring in molecule **3'g**.

The phenyl substituent on C(3) is turned relative to the plane of the bicyclic fragment (the N(4)-C(3)-C(12)-C(13) torsion angle amounts to 43.9(2)°). The phenyl substituent on C(5) is not in conjugation with the C(4)-C(5) double bond; the C(4)-C(5)-C(6)-C(11) torsion angle is 107.5(2)° and the C(5)-C(6) bond length amounts to 1.492(2) Å as compared to 1.488 Å, the mean value for such bond lengths in non-conjugated systems [20]). Tables 5-7 summarize the atomic coordinates, bond lengths and selected bond angles of the obtained crystal structure.

Scheme 3



1g **3'g** (mp 235-237 °C)

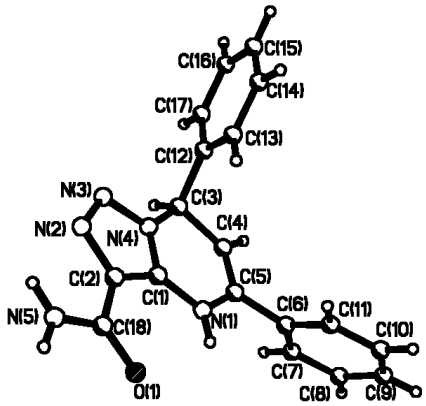


Figure 1. Molecular structure of 3'g in crystal.

Table 5

Atomic coordinates [10^4 Å] and equivalent isotropic thermal parameters for non-hydrogen atoms in the structure **3'g**.

Atom	X/a	Y/b	Z/c	U(eq)
O(1)	507(1)	6518(2)	4888(1)	42(1)
N(1)	919(1)	2420(3)	5619(1)	35(1)
N(2)	2276(1)	5127(3)	5323(1)	37(1)
N(3)	2572(1)	3426(3)	5618(1)	40(1)
N(4)	2083(1)	2266(3)	5744(1)	32(1)
N(5)	1358(1)	8414(3)	4724(1)	46(1)
C(1)	1477(1)	3257(3)	5527(1)	29(1)
C(2)	1599(1)	5090(3)	5252(1)	28(1)
C(3)	2241(1)	227(3)	6071(1)	31(1)
C(4)	1585(1)	-561(3)	6132(1)	35(1)
C(5)	993(1)	492(3)	5937(1)	32(1)
C(6)	397(1)	-129(3)	6097(1)	30(1)
C(7)	63(1)	-2165(4)	5962(1)	41(1)
C(8)	-455(1)	-2727(4)	6156(1)	49(1)
C(9)	-634(1)	-1290(5)	6488(1)	53(1)
C(10)	-306(1)	753(5)	6620(1)	58(1)
C(11)	201(1)	1334(4)	6421(1)	45(1)
C(12)	2758(1)	701(3)	6610(1)	32(1)
C(13)	2715(1)	2595(4)	6896(1)	47(1)
C(14)	3172(1)	2966(5)	7396(1)	60(1)
C(15)	3678(1)	1422(5)	7611(1)	64(1)
C(16)	3720(1)	-491(5)	7334(1)	69(1)
C(17)	3262(1)	-845(4)	6834(1)	49(1)
C(18)	1111(1)	6738(3)	4939(1)	31(1)

Table 6

Bond Lengths [Å] in the structure **3'g**.

O(1)-C(18)	1.232(2)	N(1)-C(1)	1.363(2)
N(1)-C(5)	1.398(2)	N(2)-N(3)	1.301(2)
N(2)-C(2)	1.365(2)	N(3)-N(4)	1.362(2)
N(4)-C(1)	1.342(2)	N(4)-C(3)	1.462(2)
N(5)-C(18)	1.331(2)	C(1)-C(2)	1.379(3)
C(2)-C(18)	1.459(3)	C(3)-C(4)	1.505(2)
C(3)-C(12)	1.518(3)	C(4)-C(5)	1.329(3)
C(5)-C(6)	1.492(2)	C(6)-C(11)	1.377(3)
C(6)-C(7)	1.378(3)	C(7)-C(8)	1.384(3)
C(8)-C(9)	1.366(3)	C(9)-C(10)	1.375(3)
C(10)-C(11)	1.378(3)	C(12)-C(17)	1.374(3)
C(12)-C(13)	1.375(3)	C(13)-C(14)	1.383(3)
C(14)-C(15)	1.371(3)	C(15)-C(16)	1.370(4)
C(16)-C(17)	1.383(3)		

Table 7

Selected Bond Angles [°] of **3'g**

C(1)-N(1)-C(5)	118.2(2)	N(3)-N(2)-C(2)	109.8(2)
N(2)-N(3)-N(4)	107.0(1)	C(1)-N(4)-N(3)	110.6(2)
C(1)-N(4)-C(3)	127.9(2)	N(3)-N(4)-C(3)	121.5(1)
N(4)-C(1)-N(1)	120.4(2)	N(4)-C(1)-C(2)	105.1(1)
N(1)-C(1)-C(2)	134.4(2)	N(2)-C(2)-C(1)	107.6(2)
N(2)-C(2)-C(18)	124.6(2)	C(1)-C(2)-C(18)	127.8(2)
N(4)-C(3)-C(4)	106.6(1)	N(4)-C(3)-C(12)	111.6(2)
C(4)-C(3)-C(12)	110.2(2)	C(5)-C(4)-C(3)	125.1(2)
C(4)-C(5)-N(1)	121.6(2)	C(4)-C(5)-C(6)	122.0(2)
N(1)-C(5)-C(6)	115.9(2)	C(11)-C(6)-C(7)	118.8(2)
C(11)-C(6)-C(5)	118.4(2)	C(7)-C(6)-C(5)	122.6(2)
C(6)-C(7)-C(8)	120.1(2)	C(9)-C(8)-C(7)	120.6(2)
C(8)-C(9)-C(10)	119.5(2)	C(9)-C(10)-C(11)	120.0(2)
C(6)-C(11)-C(10)	120.8(2)	C(17)-C(12)-C(13)	118.6(2)
C(17)-C(12)-C(3)	119.8(2)	C(13)-C(12)-C(3)	121.5(2)
C(12)-C(13)-C(14)	121.1(2)	C(15)-C(14)-C(13)	119.6(2)
C(16)-C(15)-C(14)	119.9(2)	C(15)-C(16)-C(17)	120.1(2)
C(12)-C(17)-C(16)	120.7(2)	O(1)-C(18)-N(5)	124.0(2)
O(1)-C(18)-C(2)	119.5(2)	N(5)-C(18)-C(2)	116.6(2)

EXPERIMENTAL

The melting points, determined on a Kofler apparatus, are uncorrected. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 400 in $CDCl_3$ or CD_3SOCD_3 with TMS as internal standard. The IR spectra were obtained in KBr pellets with a Specord 75 IR spectrometer. The EI mass spectra (70 eV) and FD mass spectra were recorded on a Finnigan M 95 spectrometer.

6,7-Dihydro-3,5,7-triphenyl-(1,2,3)-triazolo[1,5-*a*]pyrimidine (**3a**).

A mixture of 0.32 g (2.0 mmoles) of 5-amino-4-phenyl-1,2,3-triazole (**1**, [22]) and 0.42 g (2.0 mmoles) of **2a** in 0.2 mL of DMF was refluxed for 0.5 h. The reaction mixture was cooled to 20 ºC, 5 mL of methanol was added and the precipitate formed was filtered and recrystallized from methanol. Compound **3a** (0.53 g, 76%) melted at 168 - 170 ºC. The EI MS spectrum showed peaks at *m/z* (%): 350 (37) [$M^{+\cdot}$], 219 (100), 115 (28), 103 (25).

Anal. Calcd. for $C_{23}H_{18}N_4$ (350.4): C, 78.83; H, 5.18; N, 15.99. Found: C, 78.62; H, 5.47; N, 15.86.

The compounds **3b-e** were prepared as described for **3a**.

5-(4-Chlorophenyl)-6,7-dihydro-3,7-diphenyl-(1,2,3)-triazolo-[1,5-*a*]pyrimidine (**3b**).

The compound was obtained in a yield of 73 % and melted at 178 - 180 ºC. The EI MS spectrum showed peaks at *m/z* (%): 384 (25)/ 386 (8) [$M^{+\cdot}$, Cl_1 isotope pattern], 253 (100), 218 (49), 191 (37), 140 (90), 137 (41), 116 (31), 115 (76).

Anal. Calcd. for $C_{23}H_{17}N_4Cl$ (384.9): C, 71.78; H, 4.45; N, 14.56. Found: C, 71.57; H, 4.62; N, 14.29.

6,7-Dihydro-5-(4-methoxyphenyl)-3,7-diphenyl-(1,2,3)-triazolo-[1,5-*a*]pyrimidine (**3c**).

The compound was obtained in a yield of 55 % and melted at 238 - 239 ºC. The FD MS spectrum showed the molecular ion at *m/z* (%): 380 (100) [$M^{+\cdot}$].

Anal. Calcd. for $C_{24}H_{20}N_4O$ (380.4): C, 75.77; H, 5.30; N, 14.73. Found: C, 75.85; H, 5.58; N, 14.45.

6,7-Dihydro-7-(4-methoxyphenyl)-3,5-diphenyl-(1,2,3)-triazolo-[1,5-*a*]pyrimidine (**3d**).

The compound was obtained in a yield of 45 % and melted at 187 - 191 ºC. The EI MS spectrum showed peaks at *m/z* (%): 380 (99) [$M^{+\cdot}$], 351 (100).

Anal. Calcd. for $C_{24}H_{20}N_4O$ (380.4): C, 75.77; H, 5.30; N, 14.73. Found: C, 75.54; H, 5.51; N, 14.52.

7-(4-Chlorophenyl)-6,7-dihydro-3,5-diphenyl-(1,2,3)-triazolo-[1,5-*a*]pyrimidine (**3e**).

The compound was obtained in a yield of 30 % and melted at 221-223 ºC. The FD MS spectrum showed the molecular ion at *m/z* (%): 384 (100)/ 386 (36) [$M^{+\cdot}$, Cl_1 isotope pattern].

Anal. Calcd. for $C_{23}H_{17}N_4Cl$ (384.9): C, 71.78; H, 4.45; N, 14.56. Found: C, 71.66; H, 4.35; N, 14.21.

6,7-Dihydro-3,5-diphenyl-(1,2,3)-triazolo[1,5-*a*]pyrimidine (**3f**).

The compound was prepared in an analogous procedure; 0.32 g (2.0 mmoles) of **1** and 0.43 g (2.0 mmoles) of **4** yielded 0.31 g (57 %) of product that melted at 168-170 ºC. The EI MS spectrum showed peaks at *m/z* (%): 274 (100) [$M^{+}\cdot$], 243 (68).

Anal. Calcd. for $C_{17}H_{14}N_4$ (274.3): C, 74.43; H, 5.14; N, 20.42. Found: C, 74.18; H, 5.31; N, 20.12.

The compounds **3a-f** exhibit in KBr an IR band at 1600±10 cm^{-1} which is typical for the coupled stretching vibrations of CC and CN double bonds.

4,7-Dihydro-5,7-diphenyl-(1,2,3)-triazolo[1,5-*a*]pyrimidine-3-carboxamide (**3'g**).

A mixture of 0.25 g (2.0 mmoles) of 5-amino-1,2,3-triazole-4-carboxamide (**1b**, [14]) and 0.42 g (2.0 mmoles) of **2a** in 0.2 mL of DMF was refluxed for 15 min. The reaction mixture was cooled to 20 ºC, 5 mL of methanol was added and the precipitate formed was filtered and recrystallized from methanol. Compound **3'g** (0.35 g, 55%) melted at 235-237 ºC. The EI MS spectrum showed peaks at *m/z* (%): 317 (40) [$M^{+}\cdot$], 289 (18), 271 (12), 260 (25), 240 (40), 184 (85), 157 (35), 103 (60), 77 (100).

Anal. Calcd. for $C_{18}H_{15}N_5O$ (317.3): C, 68.13; H, 4.76; N, 22.07. Found: C, 68.41; H, 7.92; N, 22.21.

Crystal structure analysis of **3'g**.

The crystals of $C_{18}H_{15}N_5O$ are monoclinic. At 293 K: a = 20.905(4), b = 5.905(1), c = 26.758(6) Å, β = 109.13(2) °, V = 3121(1) $Å^3$, space group *C*2/c, Z = 8, d_{calc} = 1.351gcm^{-3}, μ = 0.089 mm^{-1}, F(000) = 1328. Intensity of 2795 reflections (2718 independent, R_{int} = 0.178) was measured on an automatic four-circle Siemens P3/PC diffractometer (graphite monochromated MoK_α radiation, Θ/2Θ scanning, $2\Theta_{max}$ = 50°). The structure was solved by direct method using SHELX 97 package [23]. Positions of hydrogen atoms were located from electron density difference maps and refined by the "riding" model with U_{iso}= 1.2U_{eq}. Full-matrix least-squares refinement against F2 in anisotropic approximation using 2718 reflections was converged to R1 = 0.038 (for 1583 reflections with F>4σ(F)), wR2 = 0.104, S = 0.965.

Acknowledgement

We are grateful to DAAD for financial support.

REFERENCES AND NOTES

[*] Author to whom correspondence should be addressed

[1] S. M. Desenko, *Khim. Geterotsikl. Soedin*. 147 (1995); *Chem. of Heterocycl. Compd*. (Engl. Transl.) **31**, 125 (1995).

[2] Y. Tsuda, T. Mishina, M. Obata, K. Araki, J. Inui, T. Nakamura, Yoshitomi Pharmaceutical Industries, Ltd, *US Patent* 4,918,074 (1990); *Chem. Abstr*., **114**, 81873j (1991); *Jap. Patent* 63,107,983 (1988); *Chem. Abstr*., **109**, 129063w (1988).

[3] Z.-T. Huang, M.-X. Wang, *J. Org. Chem*., **57**, 184 (1992).

[4] For the corresponding (1,2,3)-triazolo[1,5-*a*]quinazolines see references [5 - 10].

[5] P. Jones, M. Chambers, *Tetrahedron* **58**, 9973 (2002) and references therein.

[6] T. C. Porter, R. K. Smalley, M. Teguichi, B. Purwono, *Synthesis*, 773 (1997).

[7] G. Biagi, I. Giorgi, O. Livi, V. Scartoni, S. Velo, *Fármaco*, **51**, 131 (1996).

[8] D. L. Hooper, W. H. Manning, R. J. Lafrance, K. Vaughan, *Can. J. Chem*., **64**, 250 (1986).

[9] D. R. Sutherland, G. Tennant, *J. Chem. Soc. Perkin Trans. 1*, 534 (1974).

[10] G. Tennant, *J. Chem. Soc*., *C* 2290 (1960).

[11] V. D. Orlov, S. M. Desenko, K. A. Potekhin, Y. T. Struchkov, *Khim. Geterotsikl. Soedin*., 229 (1988); *Chem. of Heterocycl. Compd*. (Engl. Transl.), **24**, 192 (1988).

[12] S. M. Desenko, V. D. Orlov, V. V. Lipson, O. V. Shishkin, S. V. Lindeman, Y. T. Struchkov, *Khim. Geterotsikl. Soedin*., 1539 (1991); *Chem. of Heterocycl. Compd*. (Engl. Transl.), **27**, 1242 (1991).

[13] D. R. Sutherland, G. Tennant, *J. Chem. Soc. C*, 2156 (1971).

[14] O. V. Shishkin, A. S. Polyakova, S. M. Desenko, V. D. Orlov, S. V. Lindeman, Y. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim*., 1009 (1994); *Chem. Abstr.,* **122**, 105024b (1995).

[15] O. V. Shishkin, S. M. Desenko, V. D. Orlov, S. V. Lindeman, Y. T. Struchkov, A. S. Polyakova, E.I.Mikhedkina, *Izv. Akad. Nauk, Ser. Khim*., 1418 (1994); *Chem. Abstr*., **122**, 105027e (1995).

[16] O. V. Shishkin, N. V. Getmansky, S. M. Desenko, V. D. Orlov, S. V. Lindeman, Y. T. Struchkov, *Izv. Akad. Nauk, Ser. Khim*., **42**, 1912 (1993); *Russ. Chem. Bull.*, **42**, 1827 (1993).

[17] S. M. Desenko, V. D. Orlov, O. V. Shishkin, K. E. Barykin, S. V. Lindeman, Y. T. Struchkov, *Khim. Geterotsikl. Soedin*., 1357 (1993); *Chem. Heterocycl. Compd*. (Engl. Transl.), **29**, 1163 (1993).

[18] V. D. Orlov, S. M. Desenko, K. A. Potekhin, Y. T. Struchkov, *Khim. Geterotsikl. Soedin*., 229 (1988,); *Chem. Heterocycl. Compd*. (Engl. Transl.), **24**, 192 (1988).

[19] S. M. Desenko, V. D. Orlov, V. V. Lipson, O. V. Shishkin, S. V. Lindeman, Y. T. Struchkov, *Khim. Geterotsikl. Soedin*., 1539 (1991); *Chem. Heterocycl. Compd*. (Engl. Transl.), **27**, 1242-1246 (1991).

[20] H.-B. Burgi, J. D. Dunitz *Structure Correlation*, Vol. 2, p.741 VCH, Weinheim, 1994.

[21] Y. V. Zeforov, P. M. Zorky, *Uspekhi Khimii* 713 (1989); *Russ. Chem. Rev*., **58**, 421 (1989).

[22] J. R. E. Hoover, A. R. Day, *J. Am. Chem. Soc*., **78**, 5832 (1956).

[23] G.M. Sheldrick SHELX97. PC Version. A system of computer programs for the crystal structure solution and refinement. Rev 2. (1998).