SYNTHESIS AND REACTIONS OF 8-HYDRAZINOFURO[2′,3′:4,5]PYRROLO-[1,2-*d*][1,2,4]TRIAZINES

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5-Ethyl-8-hydrazinofuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine (**4a**) and its 2-methyl derivative **4b** were prepared from 4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazides **1a** and **1b,** respectively. Compounds **1a** and **1b** reacted with triethyl orthopropionate to give **2a** and **2b** which afforded with phosphorus(V) sulfide corresponding thiones **3a** and **3b**. The title compounds **4a** and **4b** were made by treatment of **3a** and **3b** with hydrazine hydrate. By reactions of triethyl orthoesters with the title compounds and similar derivatives furo[2′3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazolo[3,4-*f*][1,2,4]triazines **5a–5j** were prepared. Reactions of compounds **4** with some aldehydes and isocyanates led to hydrazones **6a–6c** and semicarbazones **7a** and **7b**, respectively.

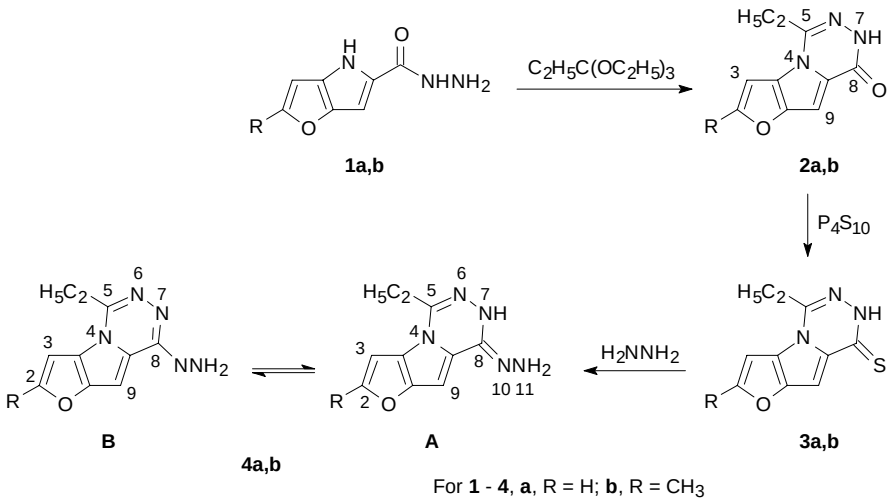
Key words: Furo[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine; Furo[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazolo[3,4-*f*][1,2,4]triazine; Cyclization; Hydrazones; Semicarbazones.

Compounds containing the 1,2,4-triazine moiety are used as pharmaceuticals, dyes, pesticides, herbicides *etc*., and a great number of reports have been directed to the synthesis of the condensed 1,2,4-triazines due to their potential biological properties[1,2]. A large number of 1,2,4-triazines fused with one or more heterocycles are well known and a wide variety of synthetic methods for their preparation are available[1,2]. We have been interested[3–8] in chemistry of the 1,2,4-triazine ring fused on its 4–5 bond with furo[3,2-*b*]pyrrole and on its 1–6 bond with 1,2,4-triazole ring. The present paper describes synthesis of some derivatives of the title ring system (Scheme 1) and their reactions (Scheme 2).

The synthesis of the 4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazide and its 2-methyl derivative as starting compounds for fusion with 1,2,4-triazine moiety was described in our previous papers[5,8]. Two reaction centres in the carbohydrazides **1** enable the formation of fused 1,2,4-triazine by reaction with triethyl orthopropionate (Scheme 1). Triazinones **2a** and **2b** prepared in such a way were converted to the corresponding thiones **3a** and **3b**, respectively, using phosphorus(V) sulfide in dry pyridine. Heating of

thiones **3a** and **3b** with hydrazine hydrate gave hydrazones **4a** and **4b** in moderate yields (Table I). The prolonged reaction time as well as the increased temperature did not influence the yield.

The broad utility of heterocyclic hydrazines as starting materials for preparation of



SCHEME 1

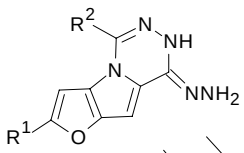
several fused systems containing triazole and tetrazole rings has received increasing attention[9–11]. The hydrazone tautomeric form of **4** enables the fusion of 1,2,4-triazole ring by the reaction with triethyl orthoformate, triethyl orthoacetate or triethyl orthopropionate giving compounds **5a–5j**. *N*,*N*-Dimethylformamide was found to be a good solvent for this reaction.

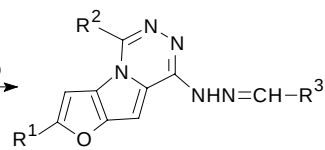
The IR spectra of **5a–5j** (Table II) showed absorption bands of C=N vibrations of triazole and triazine rings at *ca* 1 630 and 1 580 cm^{-1}, the band at the lower wavenumber being more intense. Bands of the same wavelengths were also found in the spectra of compounds **4a** and **4b**. These revealed ν(C–H) at 2 963–2 995 cm^{-1} and ν(C–H) at 2 963–2 995 cm^{-1} and ν(C–H)arom at 3 300–3 060 cm^{-1}. The wavenumbers of N–H bonds in the spectra of these compounds were 3 350–3 160 cm^{-1}.

The electronic spectra of compounds **2–4** were measured in methanol both in neutral (Table II) and acidic medium. The changes in λ_{max} and in band intensities evidence tautomerism of these compounds. The presence of ν(C=N) at 1 639 cm^{-1} in IR (Table II), very different chemical shift for NH_2 and NH, and the absence of the interaction between them in ^1H NMR spectrum give the evidence of the hydrazone form of the compounds **4a** and **4b**. Reactions of hydrazino derivative **4e** with furan-2-carbaldehyde, 5-phenylfuran-2-carbaldehyde and 4-nitrobenzaldehyde, respectively, yielded hydrazones **6a**–**6c**. Semicarbazides **7a** and **7b** were obtained by reaction of phenyl isocyanate with 8-hydrazino-2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine (**4e**) or 8-hydra-

zino-2,5-dimethylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine (**4f**) which were described in ref.[8].

Characteristic data of the synthesized compounds are summarized in Table I. The structure of the studied compounds has been confirmed by ^{1}H NMR spectra (Tables III and IV). ^{13}C NMR spectra were measured for selected compounds (Tables V and VI). The assignments of the carbon signals were based on the analysis of H,C-COSY spectra. The values of ^1J(C,H) coupling constants were read from ^{13}C satellites in ^{1}H NMR spectra. The ^{13}C NMR spectra of compounds **4c**–**4e**, **5k** and **5l** which were synthesized in our previous papers[5,8] are presented in order to compare their spectral data.



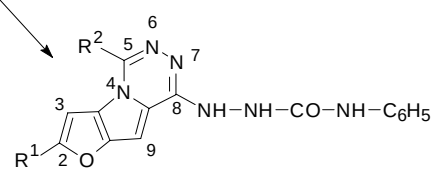


4	R^1	R^2
a	H	C_2H_5
b	CH_3	C_2H_5
c	H	H
d	H	CH_3
e	CH_3	H
f	CH_3	CH_3

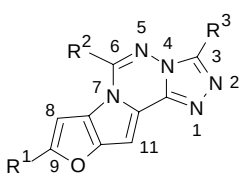
C_6H_5NCO

6	R^1	R^2	R^3
a	CH_3	H	2-furyl
b	CH_3	H	5-phenyl-2-furyl
c	CH_3	H	4-nitrophenyl

$R^3C(OC_2H_5)_3$



7	R^1	R^2
a	CH_3	H
b	CH_3	CH_3



5	R^1	R^2	R^3
a	H	H	C_2H_5
b	H	CH_3	C_2H_5
c	H	C_2H_5	H
d	H	C_2H_5	CH_3
e	H	C_2H_5	C_2H_5
f	CH_3	H	C_2H_5

5	R^1	R^2	R^3
g	CH_3	CH_3	C_2H_5
h	CH_3	C_2H_5	H
i	CH_3	C_2H_5	CH_3
j	CH_3	C_2H_5	C_2H_5
k	CH_3	H	H
l	CH_3	CH_3	H

SCHEME 2

TABLE I
Yields and physical properties of compounds **2a–7b**

Compound	Yield, %	M.p., °C (solvent)	Formula M.w.	Calculated/Found		
				% C	% H	% N
2a	73	286–287 (DMF)	$C_{10}H_9N_3O_2$ 203.2	59.11 59.20	4.46 4.52	20.68 20.56
2b	80	220–222 (DMF)	$C_{11}H_{11}N_3O_2$ 217.2	60.82 60.76	5.10 4.94	19.34 19.44
3a[a]	73	241–242 (ethanol)	$C_{10}H_9N_3OS$ 219.3	54.78 54.82	4.14 4.30	19.16 19.23
3b[b]	73	256–258 (ethanol)	$C_{11}H_{11}N_3OS$ 233.3	56.63 56.58	4.75 4.76	18.01 18.11
4a	66	263–265 (DMF)	$C_{10}H_{11}N_5O$ 217.2	55.29 55.36	5.10 4.94	32.24 32.18
4b	58	268–271 (DMF)	$C_{11}H_{13}N_5O$ 231.3	57.13 57.02	5.67 5.58	30.28 30.18
5a	67	265–266 (DMF)	$C_{11}H_9N_5O$ 227.2	58.15 58.28	3.99 3.86	30.82 30.78
5b	75	272–273 (DMF)	$C_{12}H_{11}N_5O$ 241.3	59.74 59.58	4.60 4.66	29.03 28.99
5c	59	250–253 (DMF)	$C_{11}H_9N_5O$ 227.2	58.15 58.99	3.99 4.02	30.82 30.78
5d	60	246–248 (ethanol)	$C_{12}H_{11}N_5O$ 241.3	59.74 59.78	4.60 4.56	29.03 29.10
5e	47	250–251 (DMF)	$C_{13}H_{13}N_5O$ 255.3	61.17 61.15	5.13 5.31	27.43 27.49
5f	55	272–273 (DMF)	$C_{12}H_{11}N_5O$ 241.3	59.74 59.68	4.60 4.72	29.03 29.12
5g	49	288–289 (DMF)	$C_{13}H_{13}N_5O$ 255.3	61.17 61.22	5.13 5.21	27.43 27.50
5h	58	242–244 (DMF)	$C_{12}H_{11}N_5O$ 243.7	59.74 59.55	4.60 4.69	29.03 28.99
5i	40	265–268 (DMF)	$C_{13}H_{13}N_5O$ 255.3	61.17 61.04	5.13 5.35	27.43 27.45

TABLE I
(*Continued*)

Compound	Yield, %	M.p., °C (solvent)	Formula M.w.	Calculated/Found		
				% C	% H	% N
5j	40	255–256 (DMF)	$C_{14}H_{15}N_5O$ 269.3	62.44 62.36	5.61 5.75	26.01 26.14
6a	45	248–249 (ethanol)	$C_{14}H_{11}N_5O_2$ 281.3	59.78 59.62	3.94 4.02	24.90 25.01
6b	50	248–249 (ethanol)	$C_{20}H_{15}N_5O_2$ 357.4	67.22 67.24	4.23 4.02	19.60 19.48
6c	52	319–321 (AcOH)	$C_{16}H_{12}N_6O_3$ 336.3	57.14 57.24	3.60 3.72	24.99 24.89
7a	50	273–276 (ethanol)	$C_{16}H_{14}N_6O_2$ 322.3	59.62 59.44	4.38 4.52	26.07 26.09
7b	85	252–254 (ethanol)	$C_{17}H_{16}N_6O_2$ 336.3	60.71 60.84	4.79 4.68	24.99 24.89

[a] % S calculated: 14.62, found: 14.58. [b] % S calculated: 13.74, found: 13.70.

Protons H-3 of the furopyrrole moiety in compounds **2–4**, **6** and **7** have a little lower chemical shift values with 2-methyl substitution (compounds indicated **b**) than those unsubstituted (compounds indicated **a**) due to methyl electron-donating character. The same effect can be observed on the H-8 shift of compounds **5**. In the ^{13}C NMR spectra, the marked upfield shift of the furan carbon C-3 (compounds **2–4**, **6** and **7**) or C-8 (compounds **5**) due to the effect of CH_3 group was observed. Formation of 1,2,4-triazine derivatives **2a** and **2b** from **1a** and **1b** was backed by the C-6-C_2H_5 proton signals. The replacement of oxygen in **2a** and **2b** by sulfur leading to compounds **3a** and **3b** results in a downfiled shift of furopyrrole H-3, H-9 and N-H proton signals (Table III).

In order to confirm the preferred tautomeric form of compounds **4**, ^{15}N NMR spectra of two selected compounds were measured (Table VII). We have compared the ^{15}N NMR chemical shifts and coupling constant values with those in phenylhydrazine[12]. The proton noise-decoupled ^{15}N NMR spectrum of neat phenylhydrazine exhibits two resonances at –288.6 (NH) (–288.3 in $(CD_3)_2SO$) and at –313.8 (NH_2) (–314.4 in $(CD_3)_2SO$) upfield from the external nitric acid standard. The coupling constant for the ^{15}NH-signal is $^1J(^{15}N\text{-}H)$ = 88 Hz. It is evident that the chemical shifts and coupling constant values (Table VII) differ from those of phenylhydrazine[12] and therefore we can state that the hydrazo form (A) is preferred. The NH_2 groups gave appropriate

triplets in proton-coupled ^{15}N NMR spectra while no splitting was found for signals of nitrogen N-10 originating from the hydrazine form (B) under the same experimental conditions (Scheme 1).

EXPERIMENTAL

The starting carbohydrazide **1a** was prepared according to the procedure described in ref.[5]. Melting points were determined on a Kofler hot plate apparatus and are uncorrected. UV spectra were measured on a M-40 (Zeiss, Jena) spectrophotometer in methanol (λ_{max}, nm; ε, $m^2\ mol^{-1}$). The IR spectra were taken on a FTIR PU 9802/25 (Philips) spectrophotometer using KBr technique (0.5 mg in 300 mg KBr, wavenumbers in cm^{-1}).

TABLE II
IR and UV spectral data of compounds **2a–7b**

Compound	IR spectrum ν	UV spectrum λ_{max} (log ε)
2a	1 651 (C=O), 3 114 (NH)	336 (3.37), 291 (3.21)
2b	1 653 (C=O), 3 189 (NH)	238 (3.37), 306 (3.27)
3a	1 557 (C=S), 3 202 (NH)	356 (3.32), 279 (3.20)
3b	1 557 (C=S), 3 212 (NH)	364 (3.34), 278 (3.18)
4a	3 324, 3 179 (NH), 1 632 (C=N)	300 (3.61)
4b	3 343, 3 176 (NH), 1 630 (C=N)	306 (3.53)
5a	1 593, 1 643 (C=N)	243 (3.59), 301 (3.28)
5b	1 590, 1 638 (C=N)	244 (3.56), 302 (3.24)
5c	1 590, 1 638 (C=N)	247 (3.60), 302 (3.25)
5d	1 588, 1 636 (C=N)	246 (3.54), 300 (3.22)
5e	1 586, 1 642 (C=N)	244 (3.58), 302 (3.27)
5f	1 593, 1 638 (C=N)	244 (3.54), 309 (3.29)
5g	1 590, 1 642 (C=N)	253 (3.50), 296 (3.19)
5h	1 597, 1 640 (C=N)	253 (3.63), 311 (3.32)
5i	1 592, 1 642 (C=N)	254 (3.52), 296 (3.22)
5j	1 590, 1 642 (C=N)	246 (3.57), 309 (3.30)
6a	1 626 (C=N), 3 112 (NH)	289 (3.65)
6b	1 617 (C=N), 3 366 (NH)	301 (3.59), 348 (3.50)
6c	1 522 (NO_2)as, 1 345 (NO_2)s, 1 591 (C=N)	307 (3.58)
7a	1 680 (C=O), 3 360 (NH), 1 597 (C=N)	309 (3.52), 237 (3.41)
7b	1 717 (C=O), 3 322 (NH), 1 595 (C=N)	309 (3.53), 238 (3.43)

The ^{1}H NMR (80 MHz) spectra were recorded on a Tesla BS 587 spectrometer, ^{13}C (90.56 MHz) and ^{15}N NMR (36.50 MHz) spectra on a Bruker AMX 360 spectrometer equipped with a 5 mm broadband probe and X32 computer using the UXNMR software. The NMR spectra were recorded in $(CD_3)_2SO$. ^{1}H and ^{13}C chemical shifts were referred to internal TMS (δ = 0.00), ^{15}N chemical shifts to external nitromethane (δ = 0.0) placed in a coaxial capillary. Negative values of ^{15}N chemical shifts denote upfield shifts with respect to standards.

TABLE III
^{1}H NMR data (δ, ppm; *J*, Hz) of compounds **2a–4b** in $(CD_3)_2SO$

Compound	R	H-3	H-9	NH(bs)	NH_2(s)	C_2H_5	*J*(2,3)
2a	7.98 d[a]	7.11 d	7.09 s	11.64	–	3.00 q, 1.29 t	2.0
2b	2.45 s[b]	6.75 s	7.02 s	11.59	–	2.93 q, 1.26 t	–
3a	8.09 d[a]	7.21 dd[c]	7.24 d	13.23	–	3.09 q, 1.30 t	2.2
3b	2.47 s[b]	6.79 s	7.16 s	13.10	–	3.00 q, 1.28 t	–
4a	7.62 d[a]	6.58 dd[c]	6.93 d	11.43	6.01	2.69 q, 1.22 t	2.2
4b	2.30 s[b]	6.22 s	6.83 s	11.15	5.95	2.67 q, 1.20 t	–

[a] H-2. [b] CH_3. [c] ^5J(3,9) = 0.8.

TABLE IV
^{1}H NMR data (δ, ppm; *J*, Hz) of compounds **5a–5j** in $(CD_3)_2SO$

Compound	H-8	H-11	R^1	R^2	R^3
5a	7.24 d[a]	7.37 s	8.00 d	9.27 s	3.20 q, 1.36 t
5b	7.20 d[a]	7.28 s	7.95 d	2.58 s	3.19 q, 1.38 t
5c	7.17 d[a]	7.31 s	7.93 d	3.00 q, 1.35 t	9.23 s
5d	7.23 d[a]	7.30 s	7.96 d	2.98 q, 1.36 t	2.81 s
5e	7.22 d[a]	7.30 s	7.96 d	3.20 q, 1.38 t	3.20 q, 1.38 t
5f	6.90 s	7.32 s	2.52 s	9.23 s	3.17 q, 1.36 t
5g	6.88 s	7.25 s	2.49 s	2.57 s	3.15 q, 1.37 t
5h	6.84 s	7.25 s	2.53 s	3.03 q, 1.40 t	9.18 s
5i	6.84 s	7.20 s	2.47 s	2.97 q, 1.35 t	2.76 s
5j	6.90 s	7.27 s	2.53 s	3.03 q, 1.41 t	3.17 q, 1.41

[a] J(8,9) = 2.2.

2-Methyl-4*H*-furo[3,2-*b*]pyrrole-5-carbohydrazide (**1b**)

Hydrazine hydrate (94%, 5 ml) was added to a solution of methyl 2-methyl-4*H*-furo[3,2-*b*]pyrrole-5-carboxylate[13] (1.79 g, 10 mmol) in ethanol (40 ml), the mixture was refluxed for 20 h and separated crystals were filtered off after cooling. Yield 1.43 g (80%); m.p. 290–294 °C (ethanol). For $C_8H_9N_3O_2$ (179.2) calculated: 53.63% C, 5.06% H, 23.45% N; found: 53.46% C, 5.12% H, 23.35% N. IR spectrum: 1 698 (C=O). UV spectrum: 308 (3.50). ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.32 s, 3 H (CH_3); 4.28 bs, 2 H (NH_2); 6.17 s, 1 H (H-3); 6.67 s, 1 H (H-6); 9.17 bs, 1 H (NH); 11.03 bs, 1 H (H-4).

TABLE V
^{13}C NMR data[a] (δ, ppm) of compounds **4a–4e**[b] in $(CD_3)_2SO$

Compound	C-2	C-3	C-3a	C-5	C-8	C-8a	C-9	C-9a
4a	146.41 (204.3)	100.08 (178.5)	128.51	156.54	148.58	121.03	91.72 (178.6)	147.03
4b	155.46	96.31	127.21	156.27	148.64	119.19	91.49	147.02
4c[c]	146.71 (204.5)	100.02 (178.5)	126.72	145.71 (212.3)	148.12	120.52	92.22 (181.3)	148.38
4d[c]	146.38 (204.3)	99.99 (178.4)	126.33	152.52	148.36	121.16	91.61 (178.9)	148.24
4e[d]	155.77	96.31	127.53	145.41	148.12	118.51	91.99	147.03

[a] $^1J(^{13}C,H)$ in Hz are given in parentheses. [b] **4a**: R^2: 17.35 (CH_2), 11.36 (CH_3); **4b**: R^1: 14.79 (CH_3), R^2: 17.28 (CH_2), 11.38 (CH_3); **4d**: R^2: 9.84 (CH_3); **4e**: R^1: 14.80 (CH_3). [c] ^{1}H NMR data in ref.[5]. [d] ^{1}H NMR data in ref.[8].

TABLE VI
^{13}C NMR data (δ, ppm) of compounds **5b**, **5k** and **5l** in $(CD_3)_2SO$[a]

Compound	C-3	C-6	C-7a	C-8	C-9	C-10a	C-11	C-11a	C-11b
5b[b]	[c]	[c]	122.11	101.83 (183.1)	147.77 (208.2)	[c]	89.67 (183.2)	120.88	139.01
5k[d]	135.58 (214.6)	139.55 (218.9)	124.05	96.31 (182.9)	157.85	147.81	90.37 (182.4)	118.32	132.54
5l[e]	144.07	138.54 (217.9)	123.67	97.94 (182.9)	157.44	147.66	90.16 (182.1)	118.73	139.03

[a] $^1J(^{13}C,H)$ in Hz are given in parentheses. [b] **5b**: R^2: 9.14 (CH_3); R^3: 24.65 (CH_2), 9.14 (CH_3). [c] 148.13 or 146.82 or 146.11. [d] **5k**: R^1: 14.41 (CH_3); ^{1}H NMR data in ref.[8]. [e] **5l**: R^1: 14.41 (CH_3); R^3: 18.17 (CH_3); ^{1}H NMR data in ref.[8].

5-Ethylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8(7*H*)-one (**2a**)

A mixture of **1a** (1.65 g, 10 mmol) and triethyl orthopropionate (2.11 g, 12 mmol) was refluxed in *N*,*N*-dimethylformamide (5 ml) for 7 h. After cooling, the precipitate was filtered off.

5-Ethyl-2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8(7*H*)-one (**2b**) was prepared analogously from **1b**.

5-Ethylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8(7*H*)-thione (**3a**)

A mixture of compound **2a** (2.03 g, 10 mmol) and phosphorus(V) sulfide (2.3 g, 10 mmol) was refluxed in dry pyridine (10 ml) with stirring for 4 h. The mixture was poured into hot water (70 ml) and the precipitate was filtered off.

5-Ethyl-2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8(7*H*)-thione (**3b**) was prepared analogously from **2b**.

5-Ethyl-8-hydrazinofuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine (**4a**)

A mixture of compound **3a** (2.19 g, 0.01 mol) and hydrazine hydrate (95%, 10 ml) was stirred at 110 °C for 6 h. The precipitate was filtered off after cooling and washed with water.

5-Ethyl-8-hydrazino-2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazine (**4b**) was prepared analogously from **3b**.

General Procedure for Preparation of Furo[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazolo[3,4-*f*][1,2,4]-triazines **5a–5j**

A mixture of the corresponding compound **4** (5 mmol) and the corresponding triethyl orthoester (7 mmol) in dry *N*,*N*-dimethylformamide (5 ml) was refluxed for 3 h. After cooling, the crystals were filtered off and washed with ethanol. The characteristic data are given in Table I.

TABLE VII
^{15}N NMR data (δ, ppm; *J*, Hz) of compounds **4a** and **4e** in $(CD_3)_2SO$

Nitrogen atom	**4a**		**4e**	
	δ	$^{x}J(^{15}N,H)$	δ	$^{x}J(^{15}N,H)$
N-4	–208.8 s	–	–207.2 d	7.6[a]
N-6	–79.9	–	–72.0 d	11.1[a]
N-7	–257.4 dd	99.3[b] 3.7[c]	–257.1 dd	99.5[b] 3.8[c]
N-10	–84.9 s	–	–79.0 s	–
N-11	–318.1 t	73.5[b]	–315.3 t	72.3[b]

[a] $x = 2$. [b] $x = 1$. [c] $x = 3$.

Furan-2-carbaldehyde (2-Methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8-yl)hydrazone (**6a**)

A solution of furan-2-carbaldehyde (0.48 g, 5 mmol) in DMF (3 ml) was added to a solution of compound **4e** (0.8 g, 4 mmol) in DMF (7 ml) and the reaction mixture was stirred at 110 °C for 6 h. Then 4 ml DMF was distilled off *in vacuo*, diethyl ether added and the precipitate was collected. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.37 s, 3 H (CH_3); 6.26 s, 1 H (H-3); 6.80 dd, 1 H (H-4′); 6.82 s, 1 H (H-9); 7.29 d, 1 H, J(3′,4′) = 3.5 (H-3′); 8.09 d, 1 H (H-5′); 8.93 s, 1 H (CH); 9.19 s, 1 H (H-5); 11.34 bs, 1 H (NH).

Analogously the following compounds were prepared:

5-Phenylfuran-2-carbaldehyde (2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8-yl)hydrazone (**6b**). ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.38 s, 3 H (CH_3); 6.25 s, 1 H (H-3); 6.88 s, 1 H (H-9); 7.29–7.93 m, 7 H (5-phenyl-2-furyl); 8.93 d, 1 H (CH); 9.19 s, 1 H (H-5); 11.33 bs, 1 H (NH).

4-Nitrobenzaldehyde (2-methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8-yl)hydrazone (**6c**). ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.38 d, 3 H, J = 0.9 (CH_3); 6.26 m, 1 H (H-3); 6.83 d, 1 H, J(3,9) = 0.5 (H-9); 8.17 d, 2 H, J = 9 (H-2′,6′), 8.42 d, 2 H, J = 9 (H-3′,5′); 9.22 s, 1 H, 9.26 s, 1 H (CH, H-5); 11.30 bs, 1 H (NH).

The characteristic data of compounds **6a**–**6c** are given in Table I.

1-(2-Methylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8-yl)-4-phenylsemicarbazide (**7a**)

A solution of phenylisocyanate (0.15 ml, 1.5 mmol) in DMF (1 ml) was added to a solution of compound **4e** (0.2 g, 1 mmol) in DMF (4 ml) and the reaction mixture was stirred at 120 °C for 6 h. Then 4 ml DMF was distilled off *in vacuo*, ethanol and diethyl ether (1 : 1) added and the precipitate was collected. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.34 s, 3 H (CH_3); 6.25 s, 1 H (H-3); 6.57 s, 1 H (H-9); 6.90–7.52 m, 5 H (H-arom); 8.62 s, 1 H (H-5); 9.58 bs, 1 H, 9.91 bs, 1 H (NH); 11.42 bs, 1 H (NH).

1-(2,5-Dimethylfuro[2′,3′:4,5]pyrrolo[1,2-*d*][1,2,4]triazin-8-yl)-4-phenylsemicarbazide (**7b**) was prepared analogously from **4f**. ^{1}H NMR spectrum ($(CD_3)_2SO$): 2.27 s, 3 H (C-2-CH_3); 2.33 s, 3 H (C-5-CH_3); 6.22 s, 1 H (H-3); 6.53 s, 1 H (H-9); 6.98–7.51 m, 5 H (H-arom); 9.56 bs, 1 H, 9.75 bs, 1 H (NH); 11.37 bs, 1 H (NH).

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