1-(1,2,3-Triazol-4-yl)-Benzimidazolones, a New Series of Heterocyclic Derivatives

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New 1-(1,2,3-triazol-4-yl)-benzimidazolone derivatives were obtained on pursuing research about new tricyclic derivatives of medicinal interest, bearing a 1,2,3-triazole ring fused with another heterocyclic ring. 1-[(5-Carboxamido)-1,2,3-triazol-4-yl]-benzimidazolone was prepared by four different chemical routes and it was unequivocally confirmed by spectroscopic methods. Its chemical behaviour, was evaluated by some common chemical reactions such as hydrolysis, esterification, decarboxylation, nitration and N-methylation.

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On pursuing research about nitrogen heterocyclic derivatives of medicinal interest, bearing a 1,2,3-triazole ring fused to a benzodiazepine ring [1,2], we planned to synthesize the new tricyclic structure 1,2,3-triazolo[1,5-*a*]-[1,3,5]benzotriazepine **A** (Figure 1).

But, similarly to the new triazolylbenzotriazole structure **B** [3], which we had obtained rather than a triazolobenzotetrazepine structure **C**, this synthetic route unexpectedly gave the new triazolylbenzimidazolone derivatives **D** (Figure 1).

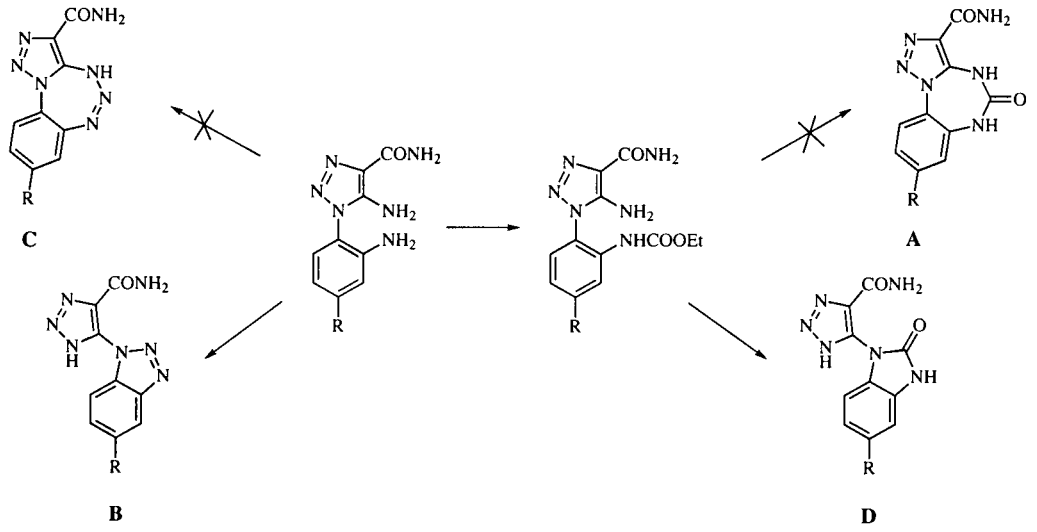


Figure 1. Formation of triazolyl-benzotrialzoles and triazolyl-benzimidazolones.

Thus, as illustrated in Scheme 1, the 1,3-dipolar cycloaddition reaction of 2-nitrophenylazide [4] with cyanoacetamide, carried out at room temperature for one night, provided the expected 1-(2-nitrophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole (**1**) [3] which precipitated and was isolated by filtration in 30-40% yield. Upon acidification of the alkaline mother-liquors of the reaction, the Dimroth isomer **2** [3] precipitated in 10-20% yield. On the contrary, when the reaction mixture, before isolation of **1**, was heated on a water bath in alkaline aqueous conditions, a complete Dimroth isomerization occurred so that only the isomer **2** was isolated by acidification.

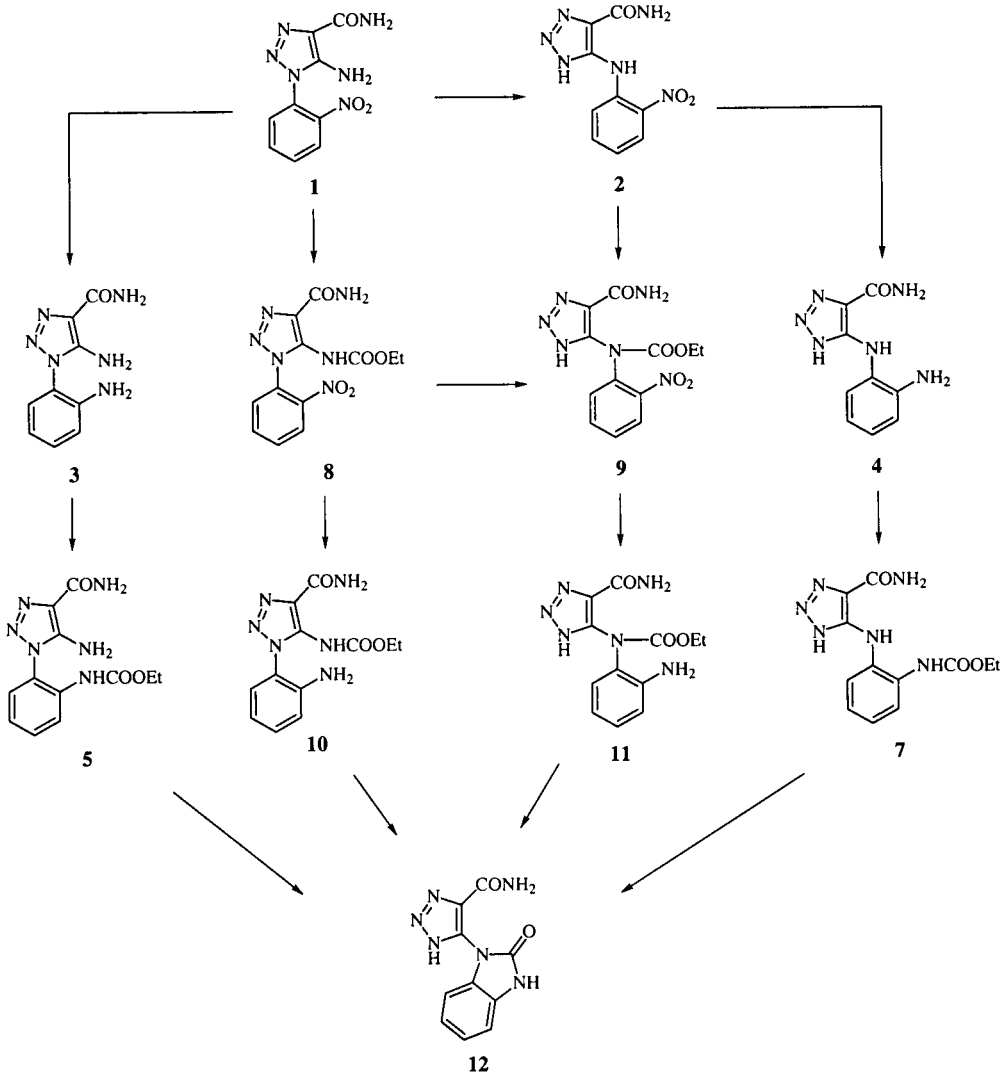
Both the triazole nitro derivatives **1** and **2** were reduced by catalytic hydrogenation to the corresponding amino derivatives **3** and **4**, described in the literature [3]. The 1-substituted triazole amino derivative **3** was then reacted with ethyl chloroformate in pyridine and the mixture heated at 50° for 4 hours. When a 1.2-1.3 molar ratio of

ethyl chloroformate was employed, **3** provided 80-90% of 1-(2-ethoxycarbonylaminophenyl)-4-carboxamido-5-amino-1*H*-1,2,3-triazole **5** together with a small amount (4-5%) of the disubstituted compound 1-(2-ethoxycarbonylaminophenyl)-4-carboxamido-5-ethoxycarbonylamino-1*H*-1,2,3-triazole **6**. When the reaction was carried out with excess of ethyl chloroformate (molar ratio 8:1) the fractionation of the reaction mixture by flash chromatography gave 40-50% of the disubstituted compound **6** and 40% of the monosubstituted compound **5**. Similarly the amino derivative **4**, the Dimroth isomer of **3**, by treatment with ethyl chloroformate (molar ratio 1:1.3) under the same experimental conditions provided the ethoxycarbonylamino derivative **7** in 67% yield.

A chemical validation of the structures **5** and **7** was obtained by the preparation of **10** and **11** (Scheme 1). Thus compound **2**, by the usual reaction with ethyl chloroformate, was converted to the ethoxycarbonylamino derivative **9** which was in its turn reduced to the corresponding amino derivative **11**. Similarly the reaction of **1** with ethyl chloroformate, carried out at room temperature for one night, provided the 5-ethoxycarbonylamino derivative **8** together with little unreacted compound **1** and a small amount of its isomer **2**. It is worth noting that **8** easily isomerized to **9** upon heating in methanol. Compound **8**, although impure with **2**, was isolated by flash chromatography then underwent catalytic hydrogenation to give the corresponding amino derivative **10**, impure with **4**. Upon heating in boiling dimethylformamide for 4-5 hours, the four mono ethoxycarbonylamino derivatives **5**, **7**, **10** and **11** underwent intramolecular cyclization to give in all the cases the same product identified as the 1-(5-carboxamido-1,2,3-triazol-4-yl)-benzimidazolone **12**; this structure was confirmed by analytical and spectroscopic data (see structure discussion).

This result indicated that in boiling dimethylformamide the normal triazole derivative **5** did not cyclize directly to

Scheme 1



give the 3-carboxamido-1,2,3-triazolo [1,5-*a*][1,3,5] benzotriazepin-5-one (**A**) (Figure 2), but **5** isomerized to **7** then cyclized in a manner corresponding to that previously reported with the diazotization reaction, which provided an analogous triazolyl-benzotriazole derivative **B** [3] (Figure 1). It is worth noting that the monosubstituted compound **5**, upon heating to about 200° in a non polar solvent like toluene, cumene, or Dowtherm remained unchanged, without isomerization to **7** nor cyclization. Instead, the formation of the triazolyl-benzimidazolone **12** was obtained from four different compounds (**5**, **7**, **10** and **11**) upon heating in a polar solvent like dimethylformamide, so that **5** and **10** could isomerize to **7** and **11**, then cyclize.

Moreover the intramolecular cyclization of the 1-substituted triazoles **5** and **10**, without previous isomerization, would give the cyclic compound triazolo-benzotriazepine **A** (Figure 2). Compound **A** is different from compound **E**, which would come from the Dimroth isomer **7**, as well as from compound **12** obtained by different synthetic routes.

Further, the formation of **9** and **12**, starting from **8** and **10** respectively, could be explained as follows. First, the Dimroth isomerization [5] should produce the compounds **8i** and **10i** (Figure 3). A second isomerization follows, leading to tertiary amines **9** and **11** (Figure 4). The tentative mechanism, which takes care of the polar nature of the solvent, should involve a very unusual N(1) - N(5) shift of the ethoxycarbonyl function present on the Dimroth isomers **8i** and **10i**. In the case of the conversion of **10** into **12**, compound **11** was formed as a very unstable intermediate under the reaction conditions and was never isolated. The reaction conditions, like solvent and temperature, to convert **8** into **9** and **10** into **11** indicate a Dimroth isomerization as the first step and, consequently, the direct rearrangement through a

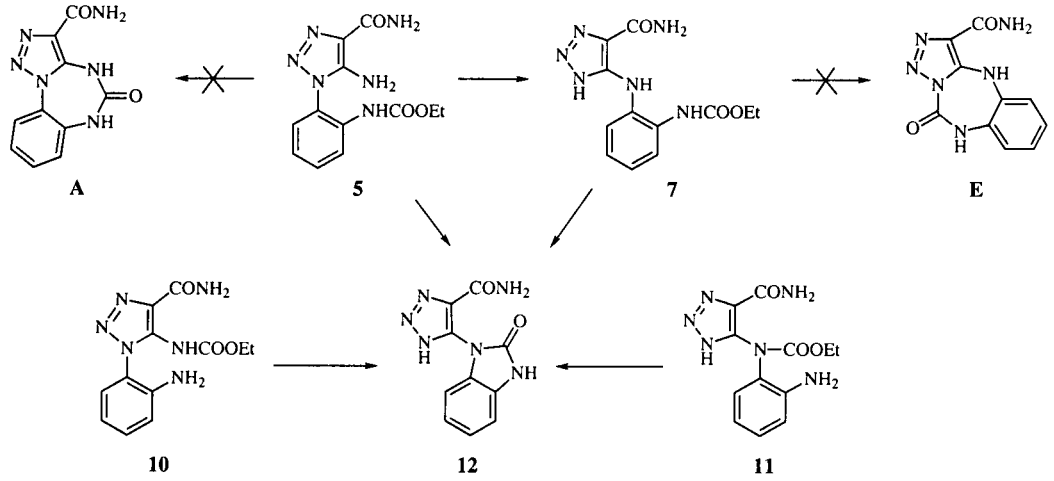


Figure 2. Formation of the triazolylbenzimidazolone **12**.

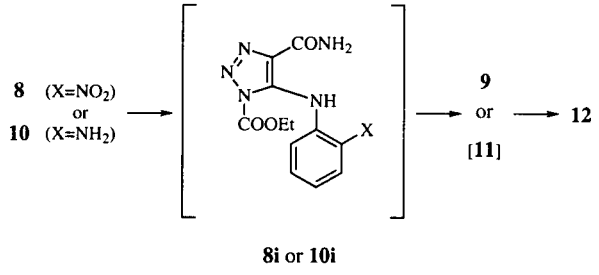


Figure 3. Formation of compounds **9** and **12**.

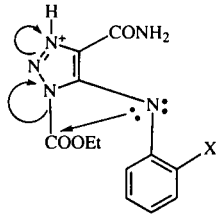


Figure 4. Tentative mechanism of isomerization in polar solvent of **8i** and **10i** into **9** and **11**.

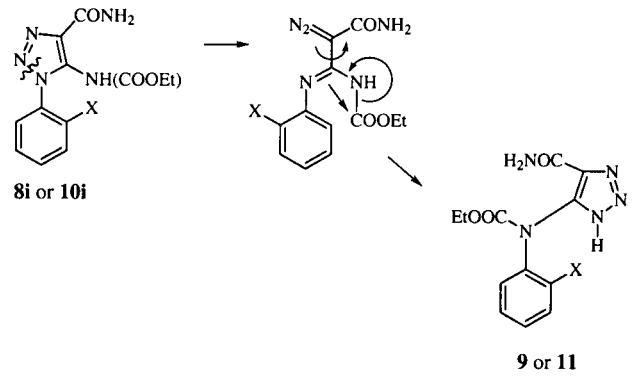


Figure 5. Alternative simultaneous mechanism of Dimroth isomerization and N(1) - $N^{(5)}$ shift of ethoxycarbonyl function.

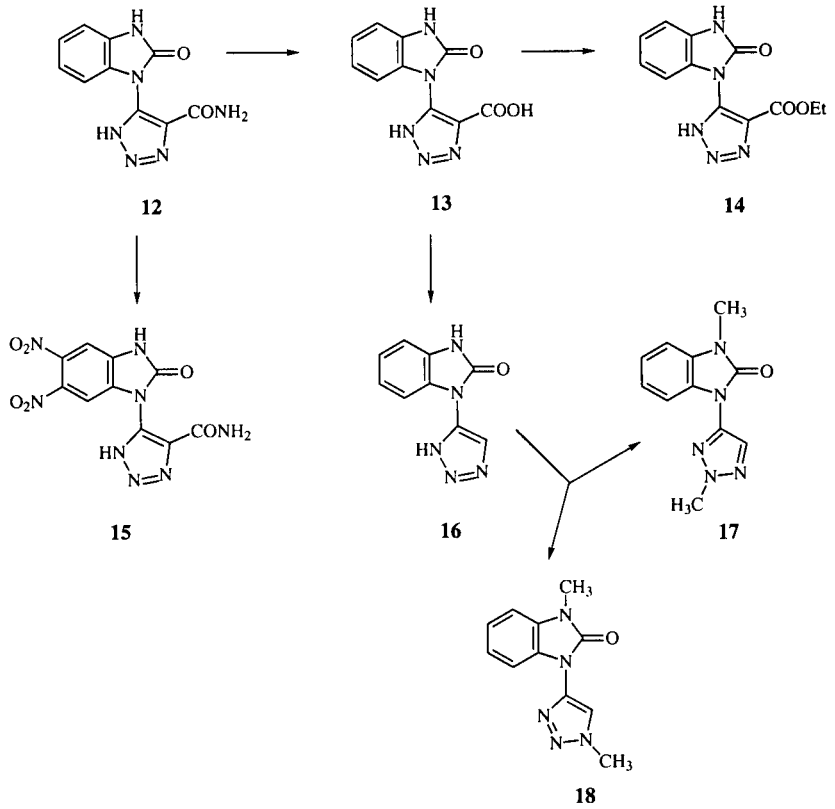
N(1) - N(5) shift of the phenyl ring cannot occur. Alternatively, since in these two conversions a Dimroth isomer (**8i** or **10i**) was never isolated, the simultaneous Dimroth isomerization and N(1) – N(5) shift of the ethoxycarbonyl function could happen as illustrated in Figure 5.

In order to evaluate the chemical behaviour and confirm the new triazolyl-benzimidazolone structure (Scheme 2), **12** underwent hydrolysis either under alkaline (12 hours refluxing in ethanolic 20% potassium hydroxide) or acid (24 hours refluxing in 50% sulfuric acid) conditions (Scheme 2).

pounds **17** and **18**, bearing one methyl group on the triazole ring and the other on the benzimidazolone ring.

The facile conversion of the compounds **1**, **5**, **8** and **10** to the corresponding Dimroth isomers and the formation of equilibrium mixtures made their purification difficult. Because the synthetic routes supported the structure of the

Scheme 2



The reaction product of both the hydrolyses was the same (**13**), corresponding to the hydrolysis of the carboxamide function keeping unchanged the benzimidazolone structure [6].

The acid **13** was isolated in 95% yield from the alkaline hydrolysis and in 45% yield from the acid hydrolysis; then it was converted by heating under reflux in excess of ethanol in the presence of 98% sulfuric acid for 24 hours, to the corresponding ethyl ester **14** in moderate yield (35%). The triazolyl-benzimidazolone **12**, upon nitration with 90% nitric acid (d = 1.48) in 98% sulfuric acid at room temperature for 3-5 hours gave the dinitro derivative **15** in 55% yield. The 5-carboxy-triazolyl-benzimidazolone **13** was easily decarboxylated by heating in dimethylformamide to give **16**, which was unchanged after hydrolysis under strong conditions, either acid (70% sulfuric acid) or alkaline (ethanolic 25% potassium hydroxide). The alkylation reaction of **16** with methyl iodide in dimethylformamide in the presence of anhydrous potassium carbonate at 60° for 4 hours provided a mixture of two di-*N*-methylated compounds obtained and all the routes provided the same compound **12**, only compounds **3**, **4**, **5** and **7** were analyzed and their ^{1}H- and ^{13}C-NMR spectral data are reported in Table II.

The position of the ethoxycarbonyl group in compounds like **5** and **7** was clearly indicated by the changes in chemical shift of the carbon in the 2' position as well as of the carbons in the *ortho* and *para* positions of the ethoxycarbonyl relative to that of compounds **3** and **4**. A similar consideration allowed the discrimination of **5** from its isomer **7**; the presence in this last compound of an amino substituent in the 1' position caused a shielding effect on the same position and a deshielding effect on its *ortho* and *para* positions.

In order to decrease the solvent viscosity, some spectra were recored at 50°. Under these experimental conditions, compounds like **5** showed clear evidence of isomerization; at higher temperature (80°) the mixtures appeared more complicated. Probably the migration of the ethoxycarbonyl group was also involved, as presumably occurred to

Table I

Chemical and Physical Properties of the prepared Compounds

Compound	Yield %	Crystallization Solvent	Mp°C	Mass m/z M+	Mass m/z Base	Elemental Analyses	Calcd./Found C	Calcd./Found H	Calcd./Found N
5	70	AcOEt	210-211	290	144	$C_{12}H_{14}N_6O_3$	49.64	4.86	28.96
							50.01	4.71	29.06
6	50	AcOEt	193-196	362	144	$C_{15}H_{18}N_6O_5$	49.71	5.01	23.20
							49.55	5.03	23.01
7	56	a	205-207	290	144	$C_{12}H_{14}N_6O_3$	49.64	4.86	28.96
							49.34	5.01	29.31
8	19	a	168-171						
9	93	MeOH	198-200	320	202	$C_{12}H_{12}N_6O_5$	44.99	3.78	26.25
							44.78	3.87	26.58
10	86	--------	70-75						
11	91	MeOH-H_2O	105-108	290	118	$C_{12}H_{14}N_6O_3$	49.64	4.86	28.96
							49.64	4.76	28.63
12	b	AcOEt	265-280dec	244	90	$C_{10}H_8N_6O_2$	49.17	3.30	34.42
							48.87	3.58	34.36
13	c	H_2O	218-220	245	201	$C_{10}H_7N_5O_3$	48.97	2.88	28.57
							48.68	2.67	28.34
14	35	EtOH	250-253	273	201	$C_{12}H_{11}N_5O_3$	52.73	4.06	25.64
							52.55	3.98	25.50
15	55	EtOH	320-325dec	291	90	$C_{10}H_6N_8O_6$	35.92	1.81	33.54
							36.23	1.70	33.28
16	73	AcOEt/Petr.Et.	238-240	201	118	$C_9H_7N_5O$	53.71	3.51	34.82
							53.41	3.71	35.01
17	45	a	118-122	229	229	$C_{11}H_{11}N_5O$	57.62	4.84	30.56
							57.69	5.03	30.87
18	20	a	178-180	229	200	$C_{11}H_{11}N_5O$	57.62	4.84	30.56
							57.48	4.95	30.76

a-Isolated by flash chromatography; b-procedure A = 71%; procedure B = 79%; procedure C = 61%; procedure D = 45%; c- procedure A = 71%; procedure B = 49%.

Table II

^{1}H-NMR Data (δ, ppm) for Compounds **3, 4, 5,** and **7** in DMSO-d_6

Compound	3'-H	4'-H	5'-H	6'-H	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	Et
3	6.93	7.24	6.71	7.09	8.18	1.36	7.24	1.57	7.85	
4	from	6.85	to	6.63						
5	7.37	7.30	7.54	7.86	7.96	2.30	6.74	1.28	8.14	4.05, 1.17
7	7.15	6.88	7.22	8.08	7.95	1.73	7.56	1.37	8.08	4.11, 1.23

^{13}C-NMR Data (δ, ppm) for Compounds **3, 4, 5,** and **7** in DMSO-d_6

	4-C	5-C	1'-C	2'-C	3'-C	4'-C	5'-C	6'-C	N-C=O	C-C=O	Et
3	121.3	145.0	119.0	143.9	116.4	130.4	116.3	127.3	164.2		
4	128.9	149.0	124.7	137.5	116.4	118.0	121.8	117.4	164.1		
5	121.2	145.4	126.2	134.1	124.6	130.4	124.0	127.2	164.1	153.4	60.4, 14.1
7	121.1	149.0	137.2	125.1	127.3	119.9	126.7	116.3	163.9	154.8	61.0, 14.3

compounds **10** and **11**. On the contrary no changes were observed for the Dimroth isomers like **7**. In any case, the isolation of **12** as the only cyclization product was a reason to exclude the benzotriazepine structures **A** or **C** (Figure 1). Further evidence resulted from the examination of the ^{1}H- and ^{13}C-nmr spectra of **12** and its derivatives **13-18** reported in Table III. The proton spectra showed that three aromatic nuclei were so much alike in chemical shifts as to produce a single uninterpretable signal. In the spectra of **12, 13, 14** and **15**, the fourth proton, which was assigned to the 7'-H, appeared as a doublet shifted to upper fields of only 0.2 δ. This behaviour agreed with the triazolyl-benzimidazolone structure **12**, where the two substituents of the benzene ring have a similar nature, whereas the **A** or **C** structures should have a chemical shift distribution similar to that of **5**. The observation that the chemical

Table III

^{1}H-NMR Data (δ, ppm) for Compounds **12, 13, 14, 15, 16, 17**, and **18** in DMSO-d_6

Compound	5-H	4'-H, 5'-H, and 6'-H	7'-H	N-H	Other
12	----	7.04	6.79	11.0	7.7 and 7.4, NH_2
13	----	7.01	6.80	11.1	
14	----	7.02	6.88	11.3	4.16 and 1.06, Et
15	----	7.82	7.67	11.1	7.7 and 7.5, NH_2
16	8.23	7.11	7.73	11.2	
17	8.05	7.10	7.66	----	4.18 and 3.32, Me
18	8.44	7.16	7.81	----	4.15 and 3.39, Me

^{13}C-NMR Data (δ, ppm) for Compounds **12, 13, 14, 15, 16, 17**, and **18** in DMSO-d_6

	4-C	5-C	3a'-C	4'-C	5'-C	6'-C	7'-C	7a'-C	N-C=O	C-C=O	Other
12	138.1	135.4	128.7	109 .1	121.9	120.9	108.6	130.3	153.0	160.3	
13	139.6	132	128.7	109.1	122.0	120.9	108.5	130.1	152.8	160.0	
14	140.0	132	128.8	109.3	122.3	121.2	108.8	129.9	152.9	159.2	60.9, 13.6
15	136.7	135.6	132.6	105.8	137.2	131.7	105.5	138.1	152.2	160.0	
16	141.5	121.7	128.0	110.8	122.3	121.1	109.1	128.6	152.2	-----	
17	142.1	124.8	126.1	108.2	122.5	121.5	110.8	129.9	151.3	-----	41.8, 26.9
18	141.1	116.9	126.7	108.3	122.3	121.6	111.0	129.9	151.3	-----	37.0, 27.1

shifts of the carbon couples 4'-C, 7'-C and 5'-C, 6'-C of **12** and their derivatives were not much different, led to the same conclusion. In the spectrum of **16**, the 7'-H resonated about 1 ppm downfield with respect to the same proton in the 5-substituted triazole compounds. This marked effect could not be justified for the benzotriazepine structure, because the substitution site is very distant from the nucleus that shows the effect, both through space and through bonds.

On the contrary this shift could be easily justified for the structure **12** by hypothesizing a different behaviour in the rotameric equilibrium around the 1'-N, 4-C bond of the 5-substituted triazole compounds relative to that of the unsubstituted compound **16**. Finally the resonance lines of the triazole carbons 4-C and 5-C in the spectra of compounds **12-16**, appeared much broadened so that in some cases the frequency determination of the very enlarged 5-C line was inaccurate. This effect, lacking in the *N*-methyl derivatives **17** and **18**, could be attributed to a sufficiently slow tautomeric equilibrium of the triazole NH hydrogen. The proton spectrum of the dinitroderivative **15** showed two narrow singlets, characteristic of two *para* correlated protons; in addition the substitution of the 5' and 6' positions was confirmed, in the ^{13}C-nmr spectrum, by the good agreement between the experimental data and those calculated by the known additivity rules [7]. The position of the methyl group on the triazole ring of **17** and **18** was assigned by reference data [8] and by our previous results [9, 10]. In fact, substitution in the 2 position of a 1,2,3-triazole ring induced a moderate effect (≅2 ppm) on the chemical shift of the ring carbons, whilst the 1-substitution caused an upfield shift (≅6 ppm) of the C-5 carbon in the α position of the substituent. Furthermore, the carbon of a substituent in the 1 position resonated at a higher field (≅5 ppm).

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage and are uncorrected. Infrared spectra in nujol mulls were recorded on a Mattson Genesis series FTIR spectrometer. ^{1}H-nmr spectra were recorded with a Bruker AC 200 spectrometer in DMSO-d_6 and are reported in δ units from tetramethylisilane as an internal standard. Mass spectra were performed with a Hewlett Packard MS/System 5988. Thin-layer chromatography data were obtained with Riedel de Haen, 37360 DC-Karten F_{254}, 0.2 mm, eluting with ethyl acetate/60-80°petroleum ether 1:2 mixture. Elemental analyses (C, H, N) were within ± 0.4% of the theoretical values and were performed on a Carlo Erba Elemental Analyzer Mod. 1106 apparatus. Petroleum ether corresponds to the fraction boiling at 40-60°. Physical and chemical data for the new compounds are reported in Table I.

1-(2-ethoxycarbonylamino-phenyl)-4-carboxamido-5-amino-1H-1,2,3-triazole (**5**) and 1-(2-ethoxycarbonylamino-phenyl)-4-carboxamido-5-ethoxycarbonylamino-1H-1,2,3-triazole (**6**).

To an ice-cooled and stirred solution of **3** [3] (1.00 g, 4.58 mmoles) in 10 mL of anhydrous pyridine, ethyl chloroformate (0.70 mL, 7.35 mmoles) was added dropwise. The ice bath was removed and the mixture was heated at 50° for 4hours, then stirred for one night at room temperature. The solution was acidified with 6*M* hydrochloric acid and extracted with chloroform. The chloroform layer was washed with 5% hydrochloric acid, then water, dried over magnesium sulfate and evaporated *in vacuo* to give a residue (0.900 g) consisting of a mixture of two compounds (tlc). This residue was fractionated by flash chromatography through a silica gel column (14.5 x 4.5 cm) eluting with ethyl acetate/petroleum ether 2:1. The disubstituted compound **6** was first obtained in 3% yield and the monosubstituted compound **5** followed as the main product of the reaction; **5** could be also isolated by crystallization from ethyl acetate. When the reaction was carried out with excess chloroformate (ratio 8:1) the disubstituted compound **6** was isolated in 50% yield.

4-Carboxamido-5-(2-ethoxycarbonylamino-anilino)-1,2,3-triazole (**7**).

To an ice-cooled and stirred solution of **4** [3] (1.50 g, 6.88 mmoles) in 10 mL of anhydrous pyridine, ethyl chloroformate (0.90 mL, 9.44 mmoles) was added. The reaction mixture was worked up as described for the preparation of **5**. Acidification of the reaction mixture caused the precipitation of a solid (1.34 g) which was collected and combined with the residue coming from the chloroform extraction of the mother liquors. The reaction product consisting of a mixture was fractionated by flash column chromatography through silica gel to give pure **7**.

1-(2-Nitrophenyl)-4-carboxamido-5-ethoxycarbonylamino-1H-1,2,3-triazole (**8**).

To an ice-cooled and stirred solution of **1** [3] (1.00 g, 4.23 mmoles) in 5 mL of anhydrous pyridine, ethyl chloroformate (2 mL, 21 mmoles) was added dropwise. The ice bath was removed and the mixture was stirred for one night at room temperature. The solution was again cooled (0-5°), then acidified with 5% hydrocloric acid to give a precipitate. After 2-3 hours of stirring the solid was collected by filtration and the tlc analysis indicated that it consisted of a mixture of **8** (Rf 0.76), **1** (Rf 0.15) and its Dimroth isomer **2** (Rf 0.55). This mixture was partitioned between 5% sodium hydroxide and chloroform. In the aqueous alkaline layer was the Dimroth isomer **2** as a sodium salt (soluble and/or insoluble). The chloroform layer was evaporated *in vacuo* (30°) to give a residue of **8** and **1** (0.460 g) which was adsorbed on 2-3 g of silica gel (by a chloroform solution evaporating in vacuo at a temperature (30°) and fractionated by flash chromatography through a silica gel column (14.5 x 4.5 cm) eluting with ethyl acetate/petroleum ether 2:1. Compound **8** was isolated mixed with a little of **2**.

4-Carboxamido-5-[*N*-(2-nitrophenyl)-N-ethoxycarbonyl]-1,2,3-triazole (**9**).

(A) A solution of 1.500 g (6.05 mmoles) of **2** [3] in 10 mL of ethylchlorofomate was heated under reflux for 15 hours. After cooling, water and solid sodium bicarbonate were added to the reaction mixture to decompose the reagent and to precipitate the solid, which was collected by filtration.

(B) Crystallization of **8** from methanol caused isomerization to **9.**

1-(2-Aminophenyl)-4-carboxamido-5-ethoxycarbonylamino-1H-1,2,3-triazole (**10**).

To a solution of **8** (contaminated by **2**) (0.230 g, 0.72 mmoles) in 70 mL of methanol, 10% Pd/C (0.020 g) was added and hydrogenation carried out at room temperature and pressure. The catalyst was filtered off and washed with hot methanol, and the filtrate was evaporated *in vacuo* to give **10** (contaminated by **4**).

4-Carboxamido-5-[N-(2-aminophenyl)-N-ethoxycarbonyl]-1,2,3-triazole (**11**).

To a solution of **9** (1.0 g, 3.10 mmoles) in 500 mL of methanol, Nickel-Raney suspension (0.2 g) was added and hydrogenation carried out at room temperature and pressure. The catalyst was filtered off and washed with hot methanol, and the filtrate was evaporated *in vacuo* to give **11**.

1-[(5-Carboxamido)-1,2,3-triazol-4-yl]-benzimidazolone (**12**).

Method A.

A solution of 2.88 g (9.91 mmoles) of **5** in 100 mL of dimethylformamide was refluxed for 5 hours. The solution was evaporated *in vacuo* to 1/3 of the initial volume and water was added to precipitate the title compound, which was collected by filtration.

Method B.

A solution of 0.300 g (1.03 mmoles) of **7** in 10 mL of dimethylformamide was worked up as described above.

Method C.

A solution of 0.250 g (0.86 mmoles) of **11** in 3 mL of dimethylformamide was refluxed for 4 hours. The solution was diluted with water and the crude brown suspension obtained was extracted repeatedly with ethyl acetate. The combined extracts were concentrated and upon addition of 40-60° petroleum ether the title compound precipitated.

Method D.

A solution of 0.170 g (0.58 mmoles) of **10** (contaminated by **4**) in 5 mL of dimethylformamide was refluxed for 4 hours. Water was added to the solution, the precipitated solid was treated with 5% sodium hydroxide to dissolve **4** and the residue crystallized.

1-[(5-Carboxy)-1,2,3-triazol-4-yl]-benzimidazolone (**13**).

(A) A solution of **12** (0.704 g, 2.88 mmoles) in 15 mL of ethanolic 20% potassium hydroxide was heated under reflux for 12 hours. The reaction mixture was evaporated *in vacuo*, the residue acidified (pH 1-2) to precipitate **13** as a colourless crystalline solid.

(B) A suspension of **12** (0.587 g, 2.40 mmoles) in 12 mL of 50% sulfuric acid was heated at 120° for 19 hours and then at 140° for 3 hours. After cooling, the precipitated solid, consisting of the starting material (0.120 g), was filtered off and the solution was diluted with water and extracted with chloroform. The chloroform layer was dried and evaporated to give **13**.

1-[(5-Carbethoxy)-1,2,3-triazol-4-yl]-benzimidazolone (**14**).

To a solution of 0.200 g (0.81 mmoles) of **13** in 30 mL of anhydrous ethanol 5-6 drops of 98% sulfuric acid were added and the mixture was heated under reflux for 24 hours. The reaction mixture was evaporated *in vacuo*, treated with 6% sodium bicarbonate and extracted with chloroform. Acidification of the aqueous layer precipitated the starting acid **13** (0.100 g). The chloroform layer, dried and evaporated, provided the title compound.

1-[(5-Carboxamido)-1,2,3-triazol-4-yl]-4,6-dinitro-benzimidazolone (**15**).

To an ice-cooled and stirred solution of **12** (0.244 g, 1.00 mmole) in 2 mL of 98% sulfuric acid, a solution of 0.1 mL of 90% nitric acid and 0.25 mL of 98% sulfuric acid was slowly added. After 30 minutes the ice bath was removed and the solution was stirred at room temperature for 3-4 hours. The reaction mixture was poured into crushed ice, and the precipitated solid, consisting of crude **15**, was collected, washed with water and crystallized.

1-(1,2,3-triazol-4-yl)- benzimidazolone (**16**).

A solution of 0.150 g (0.60 mmoles) of **13** in 1 mL of dimethylformamide was refluxed for 4 hours. The solution was diluted with water to precipitate **16** as a white solid.

1-[(2-Methyl)-1,2,3-triazol-4-yl]-3-methyl- benzimidazolone (**17**) and 1-[(1-Methyl)-1,2,3-triazol-4-yl]-3-methyl- benzimidazolone (**18**).

To a solution of **16** (0.254 g, 1.26 mmoles) in 5 mL of anhydrous dimethylformamide, anhydrous potassium carbonate (0.350 g, 2.53 mmoles) and methyl iodide (0.25 mL, 4.0 mmoles) were added and the mixture was stirred at room temperature for 30 minutes, then heated at 60° for 4 hours. After one night the solvent was evaporated *in vacuo*, the residue was treated with water and the insoluble material was collected by filtration: 0.200 g of a solid consisted of a mixture of **17** and **18** (by tlc). The mixture was fractionated by flash chromatography through a silica gel column (14x4 cm) eluting with ethyl acetate/ petroleum ether 1:1, to give **17** and **18**.

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