On Triazoles. XXI [1].
Synthesis of 1,2,4-Triazolyldithiocarbonates

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The reaction of 5-amino-1,2,4-triazoles **1** with carbon disulfide and alkylating agents in basic condition to yield alkyl, aralkyl and aryl (5-amino-3-Q-1,2,4-triazol-1-yl)dithiocarbonates **2** and alkyl (3-Q-1,2,4-triazol-5-yl-amino)dithiocarbonates **3** was studied. The isomeric and tautomeric structure of derivatives obtained was proved with the help of their uv, pmr and cmr spectra using model compounds prepared for this purpose. The results obtained enabled us to correct some confusion in the literature.

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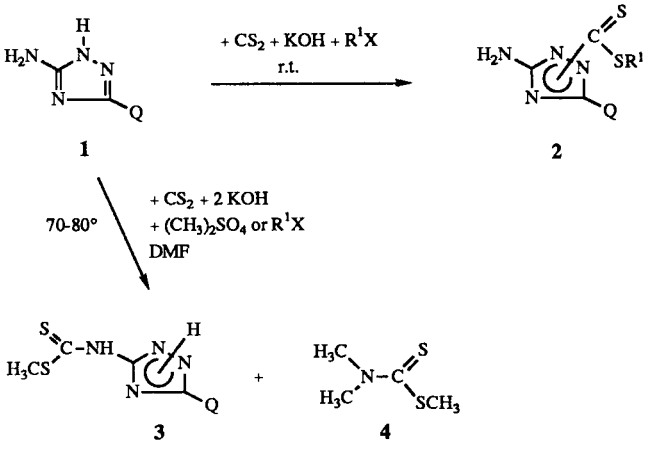
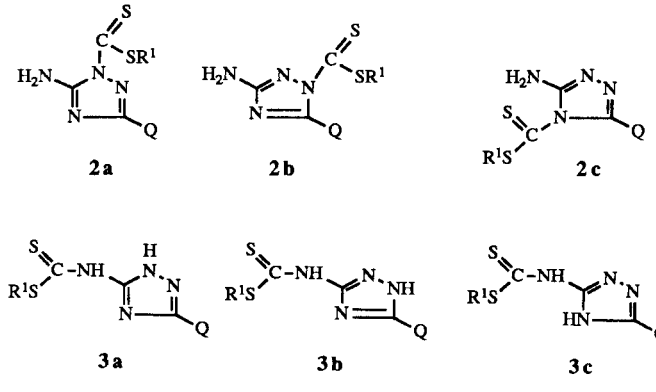
Recently we have described the synthesis and structure elucidation of different 5-amino-3-R-thio- [2] and 5-amino-3-R,R'-amino- [3] -1,2,4-triazole derivatives **1**. Reacting them at room temperature with carbon disulfide and potassium hydroxide the corresponding potassium 1,2,4-triazolyl dithiocarbonates were formed which were alkylated with alkyl, aralkyl and activated aryl halides to yield **2** type "ring dithiocarboxylated" alkyl, aralkyl or aryl (5-amino-3-Q-1,2,4-triazol-1-yl)dithiocarbonates (Scheme 1) (Table 1). If the potassium 1,2,4-triazolyldithiocarbonates were formed in dimethylformamide at 70-80° and the alkylation was provided with dimethyl sulfate according to the method described for amitrole (**1**, Q = H) [4] or with the corresponding alkyl halides the isomeric "exo dithiocarboxylated" methyl (3-Q-1,2,4-triazol-5-yl)aminodithiocarbonates **3** were obtained besides the unexpected **4** formed from dimethylamine, the decomposition product of dimethylformamide used as solvent and the hot base, with the reactants present.

Scheme 1



The "ring dithiocarboxylated" derivatives **2** may have any of the isomeric structures **2a-2c** (that could principally appear in different tautomeric forms), while - if excluding the possibility of the 5-imino tautomers - the "exo dithiocarboxylated" derivatives **3** may appear in the tautomeric forms **3a-3c**, respectively (Scheme 2).

Scheme 2



The ir spectra of derivatives **2** (Table II) were in accordance with any of the structures **2a-2c** but it was not possible to differentiate among them. The same was the situation with the uv spectra of derivatives **2** taken in ethanol that were characterised with two rather strong absorption maxima appearing between 336-374 and 280-308 nm, respectively, the lower one having greater intensity, that did not change significantly in acidic or alkaline media (Table II). However, without having in hand the spectra of all isomers, no information about the structure was available.

The amino groups of derivatives **2** appeared in the pmr spectra as singlets shifted except of derivative **2b/1** upfield as compared with those of the starting materials **1** analogously to those of the acylated 5-amino-3-Q-1,2,4-triazoles the structure of which was proved recently [5] that excluded the possibility of the 5-imino-tautomeric forms.

Table I

Compound No./Structure	Q	R^1	Conditions of Preparation X	Method	Yield (%)	mp (°C) (Crystallized from)	Molecular formula (MW)	Analysis Calcd./Found C	H	N	S
2b/1	H	Methyl	I	A	67	203-205 (EtOH)	$C_4H_6N_4S_2$ (174.25)	27.57 27.63	3.48 3.65	32.15 32.01	36.80 36.61
2a/2	Methylthio	Methyl	I	A	71	218-219 (2-PrOH) Lit [8] 189	$C_5H_8N_4S_3$ (220.34)	27.25 27.32	3.66 3.81	25.43 25.35	43.66 43.64
2a/3	Methylthio	Ethyl	I	A	58	182-184 (CH_3CN) Lit [8] 138	$C_6H_{10}N_4S_3$ (234.37)	30.75 30.89	4.30 4.52	23.91 23.81	41.05 40.83
2a/4	Methylthio	Benzyl	Br	A	57	197-198 (CH_3CN) Lit [8] 189	$C_{11}H_{12}N_4S_3$ (296.44)	44.56 44.71	4.08 4.11	18.70 18.90	32.45 32.28
2a/5	Dimethylamino	Methyl	I	A	69	228-229 (EtOH)	$C_6H_{11}N_5S_2$ (217.31)	33.16 33.11	5.10 5.11	32.22 31.92	29.51 29.23
2a/6	Diethylamino	Methyl	I	A		185-186 (EtOH)	$C_8H_{15}N_5S_2$ (245.37)	39.16 39.07	6.16 6.10	28.54 28.62	26.14 26.11
2a/7	Diallylamino	Methyl	I	A	51	105-107 (CH_3CN)	$C_{10}H_{15}N_5S_2$ (269.38)	44.59 44.32	5.61 5.67	26.00 25.82	23.80 24.04
2a/8	Piperidino	Methyl	I	A	65	171-173 (EtOH)	$C_9H_{15}N_5S_2$ (257.37)	42.00 42.24	5.87 6.02	27.21 27.42	24.91 24.79
2a/9	Piperidino	2-Ethoxycarbonylethyl	Br	A	52	110-113 (MeOH)	$C_{13}H_{21}N_5O_2S_3$ (343.46)	45.46 45.53	6.16 6.31	20.39 20.41	18.67 18.53
2a/10	Morpholino	Methyl	I	A	69	173-175 (MeOH)	$C_8H_{13}N_5OS_2$ (259.35)	37.04 37.13	5.05 5.11	27.00 27.09	24.73 24.75
2a/11	Morpholino	Ethoxycarbonylmethyl	Br	A	54	172-175 (EtOH)	$C_{11}H_{17}N_5O_3S_2$ (331.42)	39.86 40.05	5.17 5.16	21.13 21.12	19.35 19.29
2a/12	Morpholino	1-Ethoxycarbonylethyl	Br	A	53	158-160 (EtOH)	$C_{12}H_{19}N_5O_3S_2$ (345.44)	41.72 41.60	5.54 5.47	20.28 20.11	18.56 18.37
2a/13	Morpholino	2-Ethoxycarbonylethyl	Br	A	63	137-139 (EtOH)	$C_{12}H_{19}N_5O_3S_2$ (345.44)	41.72 41.85	5.54 5.70	20.28 20.12	18.56 18.44
2a/14	Morpholino	2,4-Dinitrophenyl	Cl	A	52	178-180 (CH_3CN)	$C_{13}H_{13}N_7O_5S_2$ (411.41)	37.95 37.87	3.18 3.21	23.83 23.69	15.59 15.47
2a/15	4-Methyl-piperazino	Methyl	I	A	62	183-185 (EtOH)	$C_9H_{16}N_6S_2$ (272.39)	39.69 39.84	5.92 6.04	30.85 30.65	23.54 23.63
2a/16	Amino	Methyl	I	A	58	215-217 (MeOH)	$C_4H_7N_5S_2$ (189.27)	25.38 25.44	3.73 3.80	37.01 36.91	33.88 33.90
3b/1	H	Methyl	I		48	>360 (*n*-BuOH) Lit [4] >360	$C_4H_6N_4S_2$ (174.25)	27.57 27.60	3.48 3.55	32.15 32.04	36.80 36.72
3b/2	Methylthio	Amyl	Br	B	35	157-159 (MeOH)	$C_9H_{16}N_4S_3$ (276.44)	39.10 38.87	5.82 5.65	20.26 20.04	34.79 34.57
3b/3	Ethylthio	Methyl	I	B	34	177-179 (DMF + CH_3CN)	$C_6H_{10}N_4S_3$ (234.37)	30.75 30.70	4.30 4.27	23.91 24.00	41.05 41.20
3b/4	2-Methyl-ethylthio	Methyl	I	B	14	159-161 (DMF + CH_3CN)	$C_7H_{12}N_4S_3$ (248.40)	33.85 33.90	4.87 4.97	22.56 22.44	38.73 38.60
3b/5	Dimethyl-amino	Methyl	-	C	23	184-186 (DMF)	$C_6H_{11}N_5S_2$ (217.31)	33.16 33.05	5.10 5.01	32.22 32.34	29.51 29.44
3b/6	Diethyl-amino	Methyl	-	C	18	146-148 (2-PrOH)	$C_8H_{15}N_5S_2$ (245.37)	39.16 38.98	6.16 6.02	28.54 28.40	26.14 25.99
3b/7	Morpholino	Methyl	-	D	38	181-183 (2-PrOH)	$C_8H_{13}N_5OS_2$ (259.35)	37.04 37.21	5.05 5.19	27.00 26.88	24.73 24.86
3b/8	Methylthio	2-Ethoxycarbonylethyl	Br	A	58	120-123 (MeOH)	$C_9H_{14}N_4O_2S_3$ (306.42)	35.28 35.32	4.61 4.68	18.28 18.11	31.39 31.23

Table II

Compound No./ Structure	*ir* [cm^{-1}]			*pmr* [ppm] (DMSO-d$_6$)				*cmr* [ppm] (DMSO-d$_6$)			*uv* λ max [nm] (ε.10^{-3})		
	ν NH_2 or ν NH	ν C=N	ν C=S	δ SCH_3(3)	δ SCH_3[1]	δ NH_2	other bands	δ C-3	δ C-4	δ C=S	EtOH	10% EtOH + 90% 0.1 *N* HCl	10% EtOH + 90% 0.1 *N* NaOH
2b/1	3280	1700	1270		2.66s	6.55	9.10	142.2	163.5	195.6	351 (10.7) 308 (12.9) 246 (3.2)	338 (9.6) 307 (12.7) 240 (3.3)	338 (4.3) 288 (10.5) 224 (9.9)
2a/2	3320	1657	1279	2.55 s	2.60 s	8.60 s		164.2	158.8	199.7	336 (9.9) 298 (13.4) 274 (9.8) 220 sh (3.2)	324 (10.3) 300 (13.7) 268 (6.5)	338 (6.6) 294 (12.3) 276 sh (9.2)
2a/3	3305 3060	1655 1546	1273	2.55 s		8.65s	3.18 qa 1.34 t	164.1	159.0	198.7	337(10.0) 302 (13.3) 284 (9.5)	326(5.8) 304 (6.8) 267 (3.7)	340(2.5) 302 (5.2) 270 sh (3.2)
2a/4	3330	1650	1280	2.49 s		8.65 s	4.43 s	164.4	159.0	197.5	340 (10.7) 300 (15.1) 278 (10.6)	335 (8.7) 302 (9.2)	342 (3.1) 298 (5.8)
2a/5	3300 3070	1651 1609	1263		2.51 s	8.65 s	2.94 s	164.2	158.7	195.9	368 (10.5) 293 (11.4) 228 sh (5.0)	354 (9.1) 299 (10.5)	372 (8.8) 288 (12.0)
2a/6	3290	1665 1595 1560			2.51 s	8.65 s	1.13 t 3.38 qa	162.9	158.8	195.7	370 (10.8) 288 (11.8) 228 sh (5.6)	356 (8.2) 276 (9.2)	
2a/7	3290 3060	1660	1275		2.57 s	8.0 s	4.00 d 5.25 dd 5.90 m	161.1	157.2	196.1	364 (11.8) 290 (12.5) 228 sh (4.5)	354 (10.6) 294 (10.8)	361 (10.9) 292 (11.5)
2a/8	3280 3050	1660	1280		2.57 s	8.0 s	1.62 m 3.45 t	161.6	157.1	195.7	367 (11.7) 290 (12.4) 224 sh (5.6)	344 (10.8) 296 (11.0) 262 (7.4)	358 (10.2) 290 (12.0)
2a/9	3310	1660	1280			7.7 bs	2.79 m 3.60 t	161.6	157.1	194.4	374 (12.4) 294 (13.5) 228 sh (6.2)	360 (10.9) 296 (11.6)	360 (11.2) 294 (9.9)
2a/10	3320	1663 1570	1277		2.58 s	7.8 s	3.47 t 3.75 t	161.8	157.1	197.1	360 (11.3) 292 (12.8) 228 sh (4.8)	350 (10.7) 295 (11.7) 272 (6.0)	358 (10.4) 290 (12.7)
2a/11	3320 3140	1660	1290			8.6 s	1.21 t 3.38 t 3.66 t 4.08 s 4.13 qa	163.8	159.1	194.2	364 (11.3) 287 (12.8) 228 sh (5.4)	356 (11.3) 287 (11.2)	358 (10.9) 290 (10.7)
2a/12	3310 3130	1660	1270			8.6 s	1.20 t 1.54 d 3.37 t 3.65 t 4.14 qa 4.37 qa	163.8	159.2	193.0	364 (12.0) 288 (13.7) 228 sh (6.4)	356 (11.6) 288 (11.7)	358 (10.9) 292 (11.6) 272 sh (8.1)

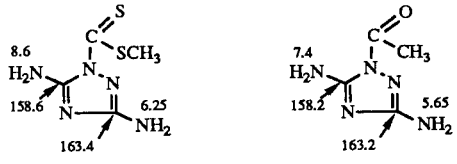
Table II [continued]

Compound No./ Structure	*ir* [cm^{-1}]			*pmr* [ppm] (DMSO-d$_6$)				*cmr* [ppm] (DMSO-d$_6$)			*uv* λ max [nm] (ε.10^{-3})		
	ν NH$_2$ or ν NH	ν C=N	ν C=S	δ SCH$_3$(3)	δ SCH$_3$[1]	δNH$_2$	other bands	δ C-3	δ C-4	δ C=S	EtOH	10% EtOH + 90% 0.1 *N* HCl	10% EtOH + 90% 0.1 *N* NaOH
2a/13	3285 3120	1650	1280			8.7 s	1.20 t 2.76 t 3.35 t (6H) 3.65 t 4.08 qa	163.7	159.1	195.1	362 (11.3) 292 (12.8) 228 sh (5.1)	353 (11.1) 294 (11.7) 268 sh (6.2)	348 (10.1) 294 (9.7) 268 sh (6.2)
2a/14	3335 3160 3100	1663 1591	1281			8.6 s	3.43 t 3.68 t 8.1 dd 8.6 m 8.92 dd	163.7	159.1	189.2	368 (10.8) 280 (13.8) 228 sh (6.0)		372 (10.1) 296 (11.6) 260 sh (10.3)
2a/15	3300	1651	1277		2.58 s	7.9 s	2.35 s 2.50 t 3.54 t	161.9	157.2	196.8	360 (11.3) 292 (12.5) 228 sh (4.5)	344 (10.8) 294 (12.0) 262 (7.4)	358 (10.2) 290 (12.0) 266 (4.8)
2a/16	3300 3100	1506	1252		2.51 s	6.25 s 8.6 s		163.4	158.6	196.0	253 (15.4) 280 (13.4)	254 (15.9) 279 (14.8)	
3b/1 [2]					2.55 s	12.1 b 13.9 b	8.44 s	144.0	158.0	199.4	279 (13.7)	276 (14.1)	252 (8.4)
3b/2	3230	1600 1550	1280		2.57 s	12.1 b	0.87 t 1.32 m 1.63 qi 3.19 t	153.7	154.0	199.8	249 (7.9) 286 (15.6)	249 (7.9) 286 (15.6)	
3b/3	3190 3050	1600 1520	1250		2.56 s	12.1 b	1.31 t 3.11 qa	153.3	153.9	200.8	282 (13.5) 246 (7.1)	282 (14.1) 246 (7.2)	
3b/4	3070	1600 1530	1275		2.57 s	12.1 b	1.34 d 3.39 m	152.3	154.3	200.8	281 (13.9) 248 (7.2)	281 (14.4) 249 (7.3)	
3b/5	3350 3200	1629 1529			2.51 s	11.8 b 12.3 b	2.91 s	153.4	158.5	200.7	282 (13.0) 246 (6.3)	282 (10.7) 247 (8.2)	260 sh (7.7)
3b/6	3200	1631 1608 1533			2.52 s	11.8 b 12.2 b	1.10 t 3.33 qa	153.3	156.6	200.5	282 (13.2) 246 (6.8)	282 (10.2) 250 (8.2)	259 sh (8.5)
3b/7	3300 3100	1608 1579 1522	1277		2.54 s	11.9 b 12.7 b	3.34 t 3.71 t	152.8	158.6	200.6	282 (12.0) 256 (8.0)	282 (13.0) 252 (7.4)	252 sh (9.4)
3b/8	3230 3090	1610 1560	1280		2.60 s	10.3	2.81 t 3.58 t	151.9	158.8	197.9	281 (14.3) 247 (8.7)	281 (14.9) 244 (9.4)	284 sh (3.5) 229 (14.8)

[1] δ SCH$_3$ (ester); [2] In Lit [1] described as a thioketo-thioenol mixture of **3c/1**.

The comparison of the chemical shifts of the amino groups and the triazole carbon atoms of derivatives **2** (Table II) with those of the corresponding amino groups and triazole carbon atoms of the symmetrical 3,5-diaminotriazole derivative **2a/16** and that of its acetyl analogue **5** [5] (Scheme 3) made possible an easy decision among the isomeric structures **2a-2c** as the chemical surrounding of the carbon atoms 5 of all **2a** type derivatives is completely identical with that of the carbon atom 5 of **2a/16** and those of carbon atoms 5 of all **2b** type derivatives is identical with that of the carbon atom 3 of **2a/16** (Scheme 3, Table II). As it can be seen from the data of Table II except of derivative **2b/1** prepared from amitrole all **2** type derivatives appeared to be of type **2a** [compare *e.g.* δ NH_2 = 6.55 ppm of **2b/1** with δ NH_2 (3) = 6.25 ppm of **2a/16**, and δ NH_2 = 7.7-8.7 ppm of **2a/2-2a/15** with δ NH_2 (5) = 8.6 of **2a/16**; as well as δ C-5 = 163.5 ppm of **2b/1** with δ C-3 = 163.4 of **2a/16** and δ C-5 = 157.1-159.2 of **2a/2-2a/15** with δ C-5 = 158.6 of **2a/16** (Table II)]. The unexpected **2b/1** structure of derivative **2** (Q = H) is in accordance with the upfield shift of the triazole CH proton as compared with **1** (Q = H) {δ CH of **1** (Q = H) and **2b/1** (Q = H) = 7.6 ppm [6] and 9.10 ppm, respectively} as well as with the chemical shift of the corresponding triazole carbon atom 3 being practically identical with those of **3b/1** and **5b/1** (δ C-3 of **2b/1**, **3b/1** and **5b/1** = 142.2 ppm, 144.0 ppm and 143.0 ppm, respectively) in good agreement with our previous statement [7] that the chemical shift of the triazole carbon atoms depend mainly on its π-electron system.

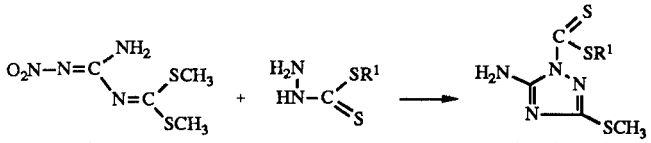
Scheme 3



2a/16 **5**

Three of these derivatives, **2a/2**, **2a/3** and **2a/4**, were described recently by Evers and Fischer [8] by the reaction of dimethyl *N*-nitroamidinodithiocarbamidate **6** and the corresponding alkyl or aralkyl dithiocarbazate **7** (Scheme 4). However their products melted very differently from those obtained by us (Table 1). In hope that the products obtained by the above authors were either the **2b**, or **2c** type isomers we repeated their experiments to obtain as crude products materials with the m.p.'s very similar to those described. However, after careful purification the melting points arose to our data and the products appeared to be identical with ours.

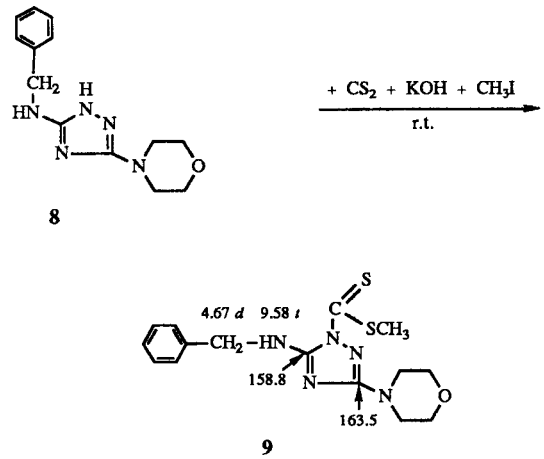
Scheme 4



6 **7** **2a**, Q = SCH_3

Compound **2a** type product **9** was also formed when instead of the **1** type 5-amino-1,2,4-triazole its 5-benzylamino-analogue, derivative **8** was reacted with carbon disulfide and methyl iodide in the presence of potassium hydroxide (Scheme 5). The position of the dithiocarbonic ester moiety on the triazole ring of **9** clearly shows the chemical shifts of the triazole carbon atoms 3 and 5 (163.5 and 158.8, respectively; compare with the corresponding data of derivatives **2a**, Table II), while the tautomeric structure shown is corroborated by the primary coupling between the exocyclic amino and the benzyl groups.

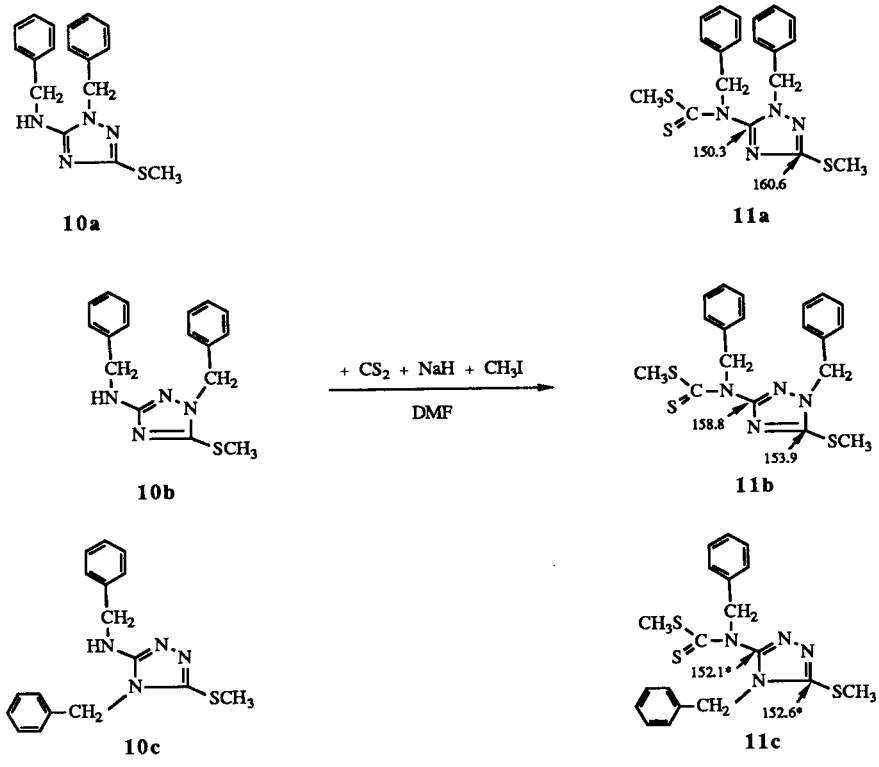
Scheme 5



8 **9**

In the case of derivatives **3** the ir spectra (Table II) were again not characteristic for any of the structures **3a-3c**. Their uv spectra taken in ethanol were characterised with the absorption maxima appearing between 279-282 and 246-256 nm, respectively, but now the higher one was the more intensive, that did not change again in acidic media enabeling their easy differentiation from those of derivatives **2** (Table II). However, to choose among the tautomeric structures **3a-c** derivatives with "fixed" tautomeric structures **a-c** as models were required. Thus the known [5] dibenzyl derivatives **10a-c** were converted to the corresponding potassium dithiocarbonates which were then alkylated with methyl iodide to yield derivatives **11a-c** representing the three possible tautomeric forms **a-c** of derivatives **3** (Scheme 6). The uv spectra of all three model compounds **11a-c** were characterised with two maxima appearing at about 280 and 250 nm, respectively.

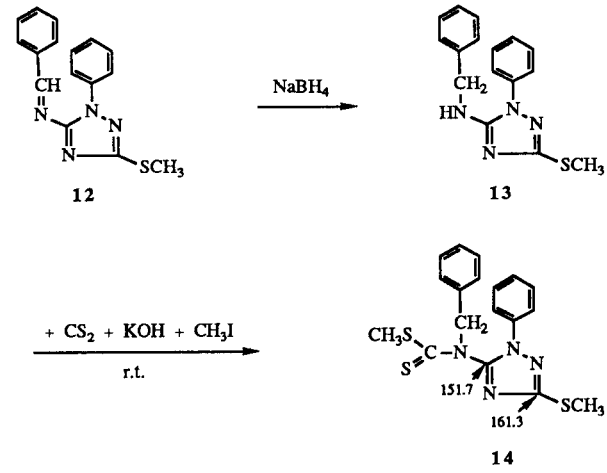
Scheme 6



However, while the intensity of the two maxima of derivatives **11a** and **11c** with the "linearily-conjugated" double bond systems proved to be approximately the same, in case of derivative **11b** having "cross-conjugated" double bond system the intensity of the maxima appearing at 280 nm was significantly higher then that of appearing at 250 nm. The analogy amoung the uv spectra of **11b** with those of derivatives **3** indicates that their dominant tautomeric structure in ethanolic solution is **3b**. In the pmr spectra of derivatives **3** the two NH groups appeared separately as broad singlets above 10 ppm unequivocally proving the exo position of the dithiocarbonic ester moiety but giving again no information about the dominant tautomeric structure of these derivatives. On the other hand the cmr spectra of derivatives **3** taken in DMSO-d_6 solution made possible again to prove their dominant tautomeric structure by the comparision of the chemical shifts of the triazole carbon atoms with those of the model compounds **11a-c**. The visible analogy between the chemical shifts of the triazole carbon atoms 3 and 5 of derivatives **3b/5-8** and those of derivative **11b** (δ C-3 of **3b/5-3b/8** and **11b** = 151.9-153.4 and 153.9 ppm, respectively, and δ C-5 of **3b/5-3b/8** and **10b** = 156.6 - 158.8 and 158.8 ppm, respectively, Table II, Scheme 5) gave again an unequivocal proof of the **3b** dominant tautomeric structure of all these compounds in DMSO-d_6 solution in accordance with the uv measurements in ethanolic solution. However, in the case of derivatives **3b/2-4** on the basis of the chemical shifts of the carbon atoms 5 being of the value of 153.9-154.7 ppm the presence of a little amount of the corresponding **3a** type tautomers have to be taken in account, too, in DMSO-d_6 solution. The chemical shift of the triazole carbon atom 3 of **3b/1** (Q = H) was just disscussed above.

These results made it possible to correct the tautomeric structure of **3** (Q = H) that was proposed by the Canadian authors [4] to be the mixture of the thio-keto and thio-enol

Scheme 7



tautomers both with a triazole ring in the 4*H*-tautomeric form. The dominant tautomeric form of this compound is either in ethanolic or in DMSO-d_6 solution the thio-keto- and 2*H*-, *i.e.* **3b** (Q = H) form. An exocyclic, *i.e.* a **3a** type product **14** was formed from the 5-benzylamino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole **13** prepared by reduction of the known [11] 5-benzalimino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole (**12**), too, when it was reacted with carbon disulfide and methyl iodide in basic conditions (Scheme 7). The chemical shifts of its triazole carbon atoms were very analogues to those of **11a** proving unequivocally its structure.

EXPERIMENTAL

Melting points were determined on a Koffler-Boëtius micro apparatus and are uncorrected. The infrared spectra were obtained as potassium bromide pellets using Perkin-Elmer 577 spectrophotometer. The ultraviolet spectra were obtained by a Pye Unicam SP 8-150 instrument. The ^{1}H-nmr and the ^{13}C-nmr measurements were performed using Brucker WM-250 and Brucker WP-80 SY instruments.

General Method for the Preparation of Alkyl(5-Amino-3-Q-1,2,4-triazol-1-yl)dithiocarbonates **2**.

Method A.

To a solution of 0.1 mole of the corresponding 5-amino-3-Q-1*H*-1,2,4-triazole (**1**) [2,3] in 30 ml of dimethylformamide 8.4 g (6.6 ml = 0.11 mole) of carbon disulfide was added dropwise with stirring, then the solution of 5.6 g (0.1 mole) of potassium hydroxide in 10 ml of water was added to the mixture dropwise it with stirring and cooling keeping the temperature of the reaction mixture below 15°. After stirring the reaction mixture at the above temperature for 30 minutes 0.1 mole of the corresponding alkyl halide (Table 1) was added keeping the temperature of the reaction mixture below 15°. The reaction was completed by stirring the mixture at room temperature for 2 hours, then 30 ml of water was added, the crystals precipitated were filtered off, washed with water and recrystallised from an appropriate solvent (Tables I and II).

General Methods for the Preparation of Alkyl(3-Q-1,2,4-Triazol-5-yl)aminodithiocarbonates **3**.

Method B.

To a solution of 0.1 mole of the corresponding 5-amino-3-Q-1,2,4-triazole **1** [2,3] and 6.6 ml (0.1 mole) of carbon disulfide in 50 ml of dimethylformamide and a solution of 11.2 g (0.02 mole) of potassium hydroxide in 20 ml of water was added by dropping it at room temperature. The thick slurry obtained was heated to 80° at which the precipitate dissolved. The solution obtained was kept with stirring at 80° for 4 hours. After cooling 0.2 mole of the corresponding Alkyl halide was dropped to the reaction mixture with stirring keeping its temperature below 25°. The stirring was continued for a further hour, then 30 ml of water was added to the reaction mixture, the crystals precipitated were collected, dissolved in a small amount of dimethylformamide and precipitated again with acetonitrile to yield the products (Table 1 and II).

Extracting the water containing mother liquor with ethyl acetate the corresponding dialkyl (3-Q-1,2,4-triazole-5-yl)-iminodithiocarbonates were obtained, see [9].

Method C.

To a solution of 0.1 mole of the corresponding 5-amino-3-Q-1,2,4-triazole **1** [2,3] and 6.6 ml (0.1 mole) of carbon disulfide in 50 ml of dimethylformamide and a solution of 11.2 g (0.02 mole) of potassium hydroxide in 20 ml of water was added dropwise at room temperature. The thick slurry obtained was heated to 80° at which the precipitate dissolved. The solution obtained was kept with stirring at 80° for 4 hours. After cooling 9.5 ml (0.1 mole) of dimethyl sulfate was added dropwise to the reaction mixture with cooling maintaining its temperature below 30°. After standing overnight 100 ml of water and 5 ml of acetic acid was added to the reaction mixture. If the product crystallised it was filtered off and recrystallised from an appropriate solvent (Table I). If the product did not crystallise it was extracted with three 150 ml portions of chloroform, the combined chloroform layers were washed with water dried and evaporated *in vacuo* to dryness. The residue obtained was chromatographed on a silica gel column (eluent a 1:2 mixture of benzene and ethyl acetate) to obtain 0.8-1.0 g (6-7%) of methyl *N,N*-dimethylaminodithioate **4**, mp 42-43° (petroleum ether); ir: ν C=S=1310 cm^{-1}; pmr (deuteriochloroform): δ, ppm 2.63 (s, 3H, SCH_3), 3.38 (s, 3H, NCH_3), 3.56 (s, 3H, NCH_3).

Anal. Calcd. for $C_4H_9NS_2$ (MW 135.26): C, 35.52; H, 6.71; N, 10.36; S, 47.42. Found: C, 35.48; H, 6.76; N, 10.30; S, 47.34.

Continuing the chromatography the corresponding alkyl (3-Q-1,2,4-triazol-5-yl)aminodithiocarbonate **3** and in some cases a small amount of the corresponding dialkyl (3-Q-1,2,4-triazol-5-yl)-iminodithiocarbonate [9] was obtained (see Tables I and II).

Method D.

To a solution of 16.9 g (0.1 mmole) of 5-amino-3-morpholino-1*H*-1,2,4-triazole (**1**, Q = morpholino) [3] in 25 ml of dimethylformamide 6.6 ml (8.4 g, 0.11 mole) of carbon disulfide was added dropwise with stirring, followed by dropwise addition of a solution of 11.16 g (0.199 mole) of potassium hydroxide in 8 ml of water keeping the temperature of the reaction mixture between 20-25°. The mixture was then stirred at 80° for 6 hours. After cooling 100 ml of water and 9.5 ml (0.1 mole) of dimethyl sulfate was added to the reaction mixture and stirred for further 2 hours between 35-40°. After cooling the reaction mixture was acidified with 5 ml of acetic acid, the crystals precipitated were filtered off, washed with water, methanol and recrystallised from 2-propanol to yield 9.9 g (38%) of methyl (3-morpholino-1,2,4-triazole-5-yl)iminodithiocarbonate (**3b/2**) (Tables I and II).

Methyl (5-Amino-3-methylthio-1,2,4-triazol-1-yl)dithiocarbonate (**2a/2**).

This was synthesised from the corresponding **6** and **7** according to [8], yield 57%, mp 218-219° (2-propanol). For analytical and spectral data see Tables I and II.

Ethyl(5-Amino-3-methylthio-1,2,4-triazol-1-yl)dithiocarbonate (**2a/3**).

This was synthesised from the corresponding **6** and **7** according to [8], yield 54%, mp 282-284° (2-propanol). For analytical and spectral data see Tables I and II.

Benzyl(5-Amino-3-methylthio-1,2,4-triazol-1-yl)dithiocarbonate (**2a/4**).

This was synthesised from the corresponding **6** and **7** according to [8], yield 48%, mp 197-198° (2-propanol). For analytical and spectral data see Tables I and II.

Methyl(5-Benzylamino-3-morpholino-1,2,4-triazol-1-yl)dithiocarbonate (**9**).

To the solution of 12.3 g (0.05 mole) of 5-benzylamino-3-morpholino-1*H*-1,2,4-triazole (**8**) [10] in 65 ml of dimethylformamide 3.76 g (2.95 ml = 0.05 mole) of carbon disulfide was added dropwise with stirring and cooling keeping the temperature of the reaction mixture between 0-5°. Then the solution of 3.5 g (0.625 mole) of potassium hydroxide in 20 ml of water was dropped with stirring to the reaction mixture keeping its temperature between 5-10°. The stirring was continued for 3 hours, followed by adding of 4.4 ml (0.031 mole) of methyl iodide with stirring and cooling keeping the temperature of the reaction mixture below 10°. The temperature of the reaction mixture was let to raise with stirring to 25° and 200 ml of water was added to it. After continuing the stirring for further 10 minutes the crystals precipitated were filtered off and recrystallised from methanol to yield 15.2 g (87%) of the title product, mp 112-113°, ir: ν C = N = 1590 and 1520, ν C = S = 1290 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.52 (s, 3H, SCH_3), 3.40 (t, 4H, NCH_2), 3.64 (t, 4H, OCH_2), 4.67 [d(J = 6 Hz), 2H, $NHCH_2$], 7.4 (m, 5H, ArH), 9.58 [t(J = 6 Hz), 1H, NH]; cmr (DMSO-d_6): δ ppm 19.8 (SCH_3), 46.9 (NCH_2), 48.3 ($NHCH_2$), 67.2 (OCH_2), 128.9, 129.0 and 130.0 (o,m,p-Ph), 139.5 (s-Ph), 158.8 (triazole C_5), 163.5 (triazole C_3), 196.4 (C=S); uv (ethanol); λ max nm (ϵ 10^{-3}) 292 (15.5), 365 (10.1); uv (10% ethanol + 90% 0.1 *N* hydrochloric acid): λ max nm (ϵ 10^{-3}) 293 (15.1), 361 (10.2).

Anal. Calcd. for $C_{15}H_{19}N_5OS_2$ (MW 349.47): C, 51.55; H, 5.48; N, 20.04; S, 18.35. Found: C, 51.60; H, 5.55; N, 19.87; S, 18.30.

Methyl(1-Benzyl-3-methylthio-1*H*-1,2,4-triazole-5-yl)-*N*-benzyliminodithiocarbonate (**11a**).

To a mixture of 0.4 g (0.015 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 15 ml of absolute dimethylformamide 3.1 g (0.01 mole) of 1-benzyl-5-benzylamino-3-methylthio-1*H*-1,2,4-triazole (**10a**) [5] was added with stirring in small portions keeping the temperature of the reaction mixture below 15°. The reaction mixture was stirred at 15° for 15 minutes, then 0.9 g (0.7 ml = 0.012 mole) of carbon disulfide was added dropwise, stirred for further 15 minutes and finally 1.4 g (0.65 ml = 0.01 mole) of methyl iodide was added to it. The reaction was completed by stirring the mixture at room temperature for a further 30 minutes then 20 ml of water was added, the crystals which precipitated were filtered off, washed with water and recrystallised from ethanol to yield 3.4 g (85%) of **11a**, mp 90-92°; ir: ν C = N = 1570 and 1500, ν C = S = 1280 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.54 and 2.57 (two s, 2 x 3H, SCH_3), 4.71 and 5.25 (two s, 2 x 2H, NCH_2), 7.35 (m, 10H, ArH); cmr (deuteriochloroform): δ ppm 14.2 (SCH_3), 20.3 (SCH_3 ester), 52.4 (NCH_2), 58.5 (NCH_2), 150.9 (triazole C_5), 160.6 (triazole C_3), 203.5 (C = S); uv (ethanol): λ max nm (ϵ 10^{-3}) 203 (30.0), 249 (11.0), 281 (10.9).

Anal. Calcd. for $C_{19}H_{20}N_4S_3$ (MW 400.57): C, 56.97, H, 5.03, N, 13.99, S, 24.01. Found: C, 57.15, H, 4.92, N, 14.11, S, 23.89.

Methyl(2-Benzyl-3-methylthio-2*H*-1,2,4-triazole-5-yl)-*N*-benzyliminodithiocarbonate (**11b**).

The compound was prepared as **11a** starting from 2-benzyl-5-benzylamino-3-methylthio-2*H*-1,2,4-triazole (**10b**) [5], yield 2.8 g (70%) of **11b**, mp 76-77° (ethanol); ir: ν C = N = 1595 and 1500, ν C = S = 1290 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.60 and 2.61 (two s, 2 x 3H, SCH_3), 5.17 and 5.61 (two s, 2 x 2H, NCH_2), 7.1-7.4 (m, 10H, ArH); cmr (deuteriochloroform): δ ppm 15.8 (SCH_3), 20.7 (SCH_3 ester), 52.6 and 58.5 (NCH_2), 153.9 (triazole C_3), 158.8 (triazole C_5), 203.0 (C=S); uv (ethanol): λ max nm (ϵ 10^{-3}) 203 (27.0), 256 (11.1), 279 (13.2).

Anal. Calcd. for $C_{19}N_{20}N_4S_3$ (MW 400.57): C, 56.97; H, 5.03; N, 13.99; S, 24.01. Found: C, 56.77; H, 4.92; N, 14.11; S, 23.87.

Methyl(4-Benzyl-3-methylthio-4*H*-1,2,4-triazole-5-yl)-*N*-benzyliminodithiocarbonate (**11c**).

This compound was prepared as **11a** starting from 4-benzyl-5-benzylamino-3-methylthio-4*H*-1,2,4-triazole (**10c**) [5], yield 3.2 g (80%) of **11c**, mp 144-146° (ethanol); ir: ν C=N= 1590 and 1500, ν C=S = 1260 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.54 and 2.70 (two s, 2 x 3H, SCH_3), 4.64 and 5.10 (two s, 2 x 2H, NCH_2), 6.95-7.4 (m, 10H, ArH); cmr (deuteriochloroform): δ ppm 14.8 (SCH_3), 20.4 (SCH_3 ester), 47.9 and 58.8 (NCH_2), 152.1* (triazole C_5), 152.6* (triazole C_3), 204.1 (C=S); uv (ethanol): λ max nm (ϵ 10^{-3}) 203 (26.1), 253 (11.0), 281 (10.9).

Anal. Calcd. for $C_{19}H_{20}N_4S_3$ (MW 400.57): C, 56.97; H, 5.03; N, 13.99; S, 24.01. Found: C, 56.78; H, 5.04; N, 13.91; S, 23.82.

1-Phenyl-5-benzylamino-3-methylthio-1*H*-1,2,4-triazole (**13**).

To a solution of 19.0 g (0.065 mole) of 5-benzalimino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole (**12**) [11] in 100 ml of methanol the solution of 5.0 g (0.13 mole) of sodium borohydride in 35 ml of water was dropped while stirring keeping the temperature of the reaction mixture between 30-35°. The reaction was completed by heating the mixture to 40° for an hour, then it was decomposed with 1% hydrochloric acid (*p*H = 3), made alkaline with sodium hydrocarbonate (*p*H = 9) and extracted twice with 100 ml portions of ethyl acetate. The combined extracts were washed twice with 50 ml of water, dried over anhydrous sodium sulfate and evaporated *in vacuo* to dryness to yield 13.0 g (68%) of the title product, mp 103-105° (ethanol); ir: ν NH = 3300, ν C=N = 1600 and 1570 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.46 (s, 3H, SCH_3), 4.46 (d, 2H, CH_2), 7.1-7.4 (m, 10H, ArH), 7.5 (b, 1H, NH), cmr (DMSO-d_6): δ ppm 15.1 (SCH_3), 48.6 (CH_2), 157.3 (triazole C_5), 159.8 (triazole C_3).

Anal. Calcd. for $C_{16}H_{16}N_4S$ (MW 296.39): C, 64.84; H, 5.44; N, 18.90; S, 10.82. Found: C, 65.03; H, 5.61; N, 18.74; S, 10.66.

Methyl(3-Methylthio-1-phenyl-1*H*-1,2,4-triazole-5-yl)-*N*-benzyliminodithiocarbonate (**14**).

This compound was prepared as **11a** starting from 1-phenyl-5-benzylamino-3-methylthio-1*H*-1,2,4-triazole (**13**), yield 3.4 g (88%) of **14**, mp 78-80° (ethanol); ir: ν C=N = 1590 and 1500, ν C=S = 1290 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.49 and 2.58 (two s, 2 x 3H, SCH_3), 5.33 (s, 2H, NCH_2), 7.2-7.6 (m, 10H, ArH); cmr (DMSO-d_6): δ ppm 15.3 (SCH_3), 21.6 (SCH_3 ester), 59.3 (NCH_2), 151.7 (triazole C_5), 161.3 (triazole C_3), 204.8 (C=S); uv (ethanol): λ max nm (ϵ 10^{-3}) 253 (15.4), 274 (13.8); uv (10% ethanol + 90% 0.1 *N* hydrochloric acid): λ max nm (ϵ 10^{-3}) 254 (15.9), 279 (14.8).

Anal. Calcd. for $C_{18}H_{18}N_4S_3$ (MW 386.55): C, 55.93; H, 4.69; N, 14.49; S, 24.89. Found: C, 56.11; H, 4.83; N, 14.63; S, 24.58.

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