  Bull. Chem. Soc. Jpn., 58, 735—744 (1985)

Aromatic Systems with 10π Electrons Derived from 3a-Azapentalene. Part 40. Studies on the 1,2,4-Triazolo[4,3-*b*][1,2,4]triazole Series

Mateo ALAJARIN,† Pedro MOLINA,† Alberto TARRAGA,† Mª Jesús VILAPLANA,† Mª de la Concepción FOCES-FOCES,†† Felix HERNANDEZ CANO,†† Rosa Mª CLARAMUNT,††† and José ELGUERO*

†*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Murcia, Murcia, Spain*

††*Departamento de Rayos X, Instituto de Química Física "Rocasolano", Serrano 119, Madrid-6, Spain*

†††*Química Organica, Universidad Nacional de Educación a Distancia, Ciudad Universitaria, Madrid-3, Spain*

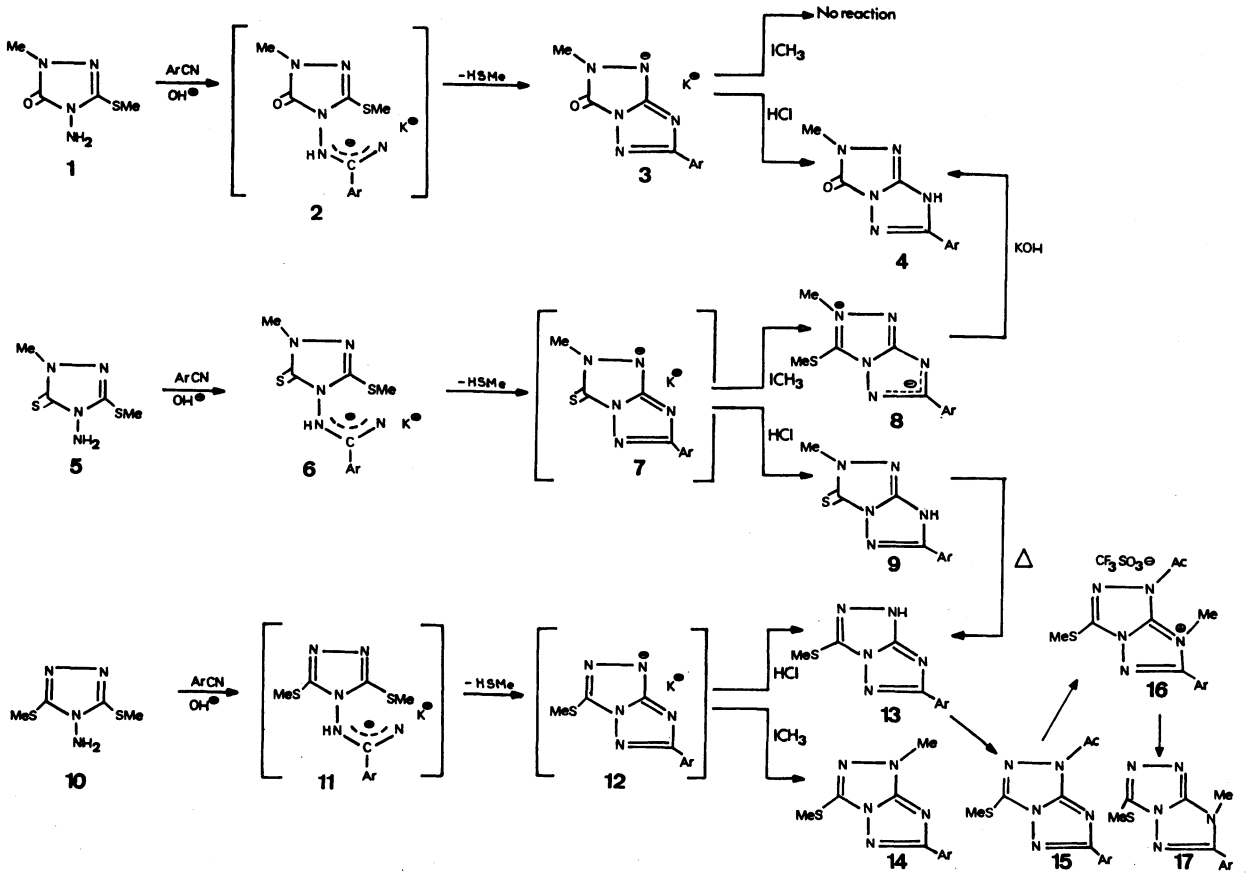
**Instituto de Química Médica, CSIC, Juan de la Cierva 3, Madrid-6, Spain*

(Received January 13, 1984)

The synthesis, structure, and reactivity of several 1,2,4-triazolo[4,3-*b*][1,2,4]triazole derivatives have been studied. Structures have been established throughout a careful carbon-13 NMR study, and for the most unusual one (inner salt of 2-methyl-3-methylthio-6-phenyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazolium hydroxide) by X-ray crystallography: the space group is P21/c, the cell constants are $a=12.6939(5)$, $b=16.0936(6)$, $c=12.0239$ (5) and $\beta=107.247(3)°$ and $Z=8$. The *S*-methyl group is directed towards the fusion of the five-membered rings at +/−syn conformations. The azapentalene moieties have the first atoms of the substituents on its plane and the 6-phenyl rings make an angle of −26.7 and −4.3° with it, in the two independent molecules respectively.

Continuing our interest in azapentalene derivatives[1] we have directed our attention to the 1,2,4-triazolo-[4,3-*b*][1,2,4]triazole ring. We have already obtained some results in these series,[2-4] but we want to present here a coherent view on the synthesis and reactivity of functional (oxo and thioxo) derivatives. Scheme 1 contains all the compounds and reactions studied.

The reaction of arenecarbonitriles in basic medium with 4-amino-3-methylthio-4*H*-1,2,4-triazole derivatives, **1**, **5**, and **10**, yields 6-aryl-1,2,4-triazolo[4,3-*b*]-[1,2,4]triazoles. The potassium salts lead by acidification the neutral molecules **4**, **9**, and **13**. In the first case, the cyclized form **3** was isolated and identified. In the second one, the intermediate amidine salt **6** was obtained. Thus, even in the third case, where the unstability of salts **11** and **12** prevents their isolation,



Scheme 1.

we have supposed the same mechanism. The first step is a nucleophilic addition of the *N*-amino group on the cyano group leading to the amidines **2**, **6**, and **11**. The cyclization step involves the departure of the methylthio group at position 3 with concomitant formation of the triazolotriazoles **3**, **7**, and **12**. These compounds carry at position 6 an aryl group and at position 3 an oxo **3**, thioxo **7** or methylthio group **12**. The tautomerism of the corresponding neutral molecules, **4**, **9**, and **13**, will be discussed later.

Table 1. Crystal data

Chemical formula	$C_{11}H_{11}N_5S$
Formula weight	245.3
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.6939(5)
b/Å	16.0936(6)
c/Å	12.0239(5)
β/°	107.247(3)
V/Å^3	2345.9(2)
D_{calcd}/g cm^{-3}	1.389
Z	8
μ/cm^{-1}	22.82

Compound **3** did not react with methyl iodide. The potassium salt **6** leads to a new mesoionic ring system **8**. The structure of this compound was established by radiocrystallography (see later). Nitrogens N_1, N_5, and N_7 could also have reacted with methyl iodide, but no *N*,*N*′-dimethyl derivative has been isolated. The high reactivity of the sulfur atom in mercaptotriazoles[5] could explain the formation of **8**, but having carried out the reaction on salt **6** it cannot be excluded that the *S*-methylation precedes the cyclization step. The methylation of salt **12** prepared either from **10** or from **13**, can yield three different *N*-methyl derivatives, but only 1-methyl-3-methylthio-6-aryl-1*H*-1,2,4-triazolo-[4,3-*b*][1,2,4]triazole **14** was actually isolated. The N_1 nitrogen atom is also the most reactive in the parent compound.[2] An isomer of **13** can be obtained using Olofson and Kendall's method.[6] The reaction of the azolide **15** with methyl trifluoromethanesulfonate yields the 7-methyl isomer **17** through the quaternary salt

Table 2. Coordinates and thermal parameters as $U_{eq}=(1/3)$. $\sum(U_{ij}a_i^*a_j^*a_ia_j\cos(a_ia_j))$ ($\times 10^4$)

Atom	x	y	z	U_{eq}
N(1)	0.09162(22)	−0.23634(15)	0.20103(25)	695(10)
N(2)	0.08576(22)	−0.15356(15)	0.17071(23)	668(9)
C(3)	0.01914(26)	−0.10842(16)	0.21478(26)	646(10)
N(4)	−0.01858(20)	−0.16304(13)	0.27841(22)	603(8)
N(5)	−0.08870(21)	−0.16656(13)	0.34525(23)	633(9)
C(6)	−0.08198(23)	−0.24857(16)	0.37114(26)	607(10)
N(7)	−0.01471(20)	−0.29583(13)	0.32778(24)	646(9)
C(8)	0.02561(24)	−0.23971(16)	0.26780(27)	625(10)
C(9)	0.15011(36)	−0.12439(27)	0.09608(36)	808(15)
S(10)	−0.01335(9)	−0.00411(4)	0.19132(8)	786(3)
C(11)	0.02883(37)	0.03224(22)	0.33733(35)	809(14)
C(12)	−0.14938(23)	−0.28306(17)	0.43997(26)	623(10)
C(13)	−0.18411(28)	−0.36583(19)	0.42369(36)	753(13)
C(14)	−0.25149(31)	−0.39751(23)	0.48347(39)	832(15)
C(15)	−0.28502(34)	−0.34971(26)	0.56063(38)	875(16)
C(16)	−0.25151(35)	−0.26739(26)	0.57782(35)	862(15)
C(17)	−0.18419(29)	−0.23482(21)	0.51760(30)	736(12)
N(1′)	0.52857(26)	0.01220(16)	0.15301(25)	755(11)
N(2′)	0.56178(26)	0.09376(17)	0.15717(27)	779(11)
C(3′)	0.53118(26)	0.14014(18)	0.23462(32)	717(12)
N(4′)	0.47504(20)	0.08735(14)	0.28294(22)	614(8)
N(5′)	0.42056(20)	0.08536(14)	0.36437(23)	632(9)
C(6′)	0.38937(22)	0.00488(16)	0.35670(26)	593(9)
N(7′)	0.41809(21)	−0.04292(14)	0.27691(22)	635(9)
C(8′)	0.47351(25)	0.01079(17)	0.23139(27)	637(10)
C(9′)	0.62762(61)	0.11959(37)	0.08236(55)	1084(25)
S(10′)	0.56202(7)	0.24384(5)	0.26831(10)	845(4)
C(11′)	0.43396(43)	0.28823(28)	0.20403(79)	1552(37)
C(12′)	0.32998(22)	−0.02870(17)	0.43405(26)	608(10)
C(13′)	0.29265(25)	−0.11129(19)	0.42122(32)	692(11)
C(14′)	0.23707(29)	−0.14268(23)	0.49441(36)	805(14)
C(15′)	0.21825(31)	−0.09459(27)	0.58136(38)	852(15)
C(16′)	0.25438(30)	−0.01293(26)	0.59469(36)	839(14)
C(17′)	0.31025(26)	0.01932(22)	0.52234(31)	722(12)

16. In the case of the parent compound **18** a similar reaction yielded also the 7-methyl derivative **20**.[2]

Hydrolysis of the mesoionic compound **8** results in the formation of **4**. On heating compound **9** rearranges to compound **13** (this rearrangement takes place when the ^{13}C NMR spectrum of **9** is recorded at 80 °C to increase its solubility). The rearrangement **9** → **13** is another example of the well known *N* to *S* migration of alkyl groups in *N*-methylazolethiones.[7,8]

Determination of the Structure of Different Compounds

Carbon-13 NMR spectroscopy was used as the sole tool for establishing the different structures. However, due to its importance and unusual formula the structure of **8a** was determined by X-ray crystallography.

Table 1 presents the crystal data. Unit cell parameters were obtained from a least-squares refinement of 52 reflexions as measured on a Philips PW 1100 diffractometer with Cu $K\alpha$ radiation, up to 45° in θ. The intensities of 4347 reflexions with $\theta \leqslant 65°$ were measured with Cu $K\alpha$ radiation graphite monochromated and $\omega/2\theta$ scans. No deterioration of the sample was observed. Data were corrected for Lorentz and polarization factors but not for absorption. 3560 reflexions with $I \geqslant 2\sigma(I)$ were used in the analysis.

The structure was determined by direct methods[9] and refined by full matrix least-squares[10] anisotropically for all non-hydrogen atoms, leading to a final *R*-factor of 0.054 (R_w=0.058, with an empirical weighting scheme so as to give no trends in <w. Δ^2F>). All scattering factors were taken for neutral atoms.[11]

Final atomic parameters are given in Table 2.[12] There are two crystallographically independent molecules, **8a′** and **8a″**, in the unit cell, with bond lengths and angles as specified in Table 3.

Since the X-ray structures of aromatic azapentalenes are so scarce,[1] those of **8a′** and **8a″** deserve some comments, other than the fact that the mesoionic structure is established without ambiguity. The 1,2,4-triazolo-[4,3-*b*][1,2,4]triazole ring is planar in agreement with its aromatic nature. In order to make easy the discussion carbon C_{7a} has been numbered C_8 and substituents heavy atoms from C_9 to C_{17} (for the second molecule we have used dashed numbers) as represented in Fig. 1.

From the relationship between bond lengths and bond orders, it can be deduced that a canonical form, as the represented below, describes accurately the electronic structure of **8a**. Atoms C_9, S_{10}, and C_{12} lie on the plane of the azapentalene ring. The *S*-methyl group is directed towards N_5 and the dihedral angles 11–10–3–4 (11′–10′–3′–4′) are 58.9(3)° for **8a′** and −74.8(4)° for **8a″**. The 6-phenyl ring is planar. Bond distances and angles in this ring range in 1.367

Table 3. Bond distances (l/Å) and angles (ϕ/°) with the estimated standard deviations in parenthesis

Bond/Angle	Molecule **8a′**	Molecule **8a″**
S(10)-C(3)	1.732(3)	1.735(3)
S(10)-C(11)	1.776(4)	1.734(5)
C(3)-N(2)	1.338(5)	1.338(5)
C(3)-N(4)	1.343(4)	1.346(5)
N(2)-N(1)	1.377(3)	1.375(4)
N(2)-C(9)	1.479(6)	1.458(9)
N(1)-C(8)	1.322(5)	1.330(5)
C(8)-N(4)	1.377(4)	1.377(4)
C(8)-N(7)	1.348(4)	1.330(4)
N(4)-N(5)	1.366(4)	1.356(4)
N(5)-C(6)	1.353(3)	1.350(3)
C(6)-N(7)	1.358(4)	1.361(4)
C(6)-C(12)	1.465(5)	1.463(5)
C(3)-S(10)-C(11)	99.8(2)	100.1(2)
S(10)-C(3)-N(4)	128.3(2)	128.2(2)
S(10)-C(3)-N(2)	127.6(2)	127.4(3)
N(2)-C(3)-N(4)	104.1(2)	104.4(3)
C(3)-N(2)-C(9)	127.2(3)	127.5(3)
C(3)-N(2)-N(1)	114.3(3)	114.1(3)
N(1)-N(2)-C(9)	118.6(3)	118.4(3)
N(2)-N(1)-C(8)	101.9(2)	102.2(3)
N(1)-C(8)-N(7)	139.6(3)	139.1(3)
N(1)-C(8)-N(4)	111.6(3)	111.3(3)
N(4)-C(8)-N(7)	108.7(2)	109.6(3)
C(3)-N(4)-C(8)	108.1(2)	108.0(3)
C(8)-N(4)-N(5)	111.8(2)	111.2(2)
C(3)-N(4)-N(5)	140.1(2)	140.8(3)
N(4)-N(5)-C(6)	99.7(2)	100.1(2)
N(5)-C(6)-C(12)	119.5(3)	120.5(3)
N(5)-C(6)-N(7)	117.5(3)	117.1(3)
N(7)-C(6)-C(12)	123.0(2)	122.4(2)
C(8)-N(7)-C(6)	102.2(2)	102.0(2)

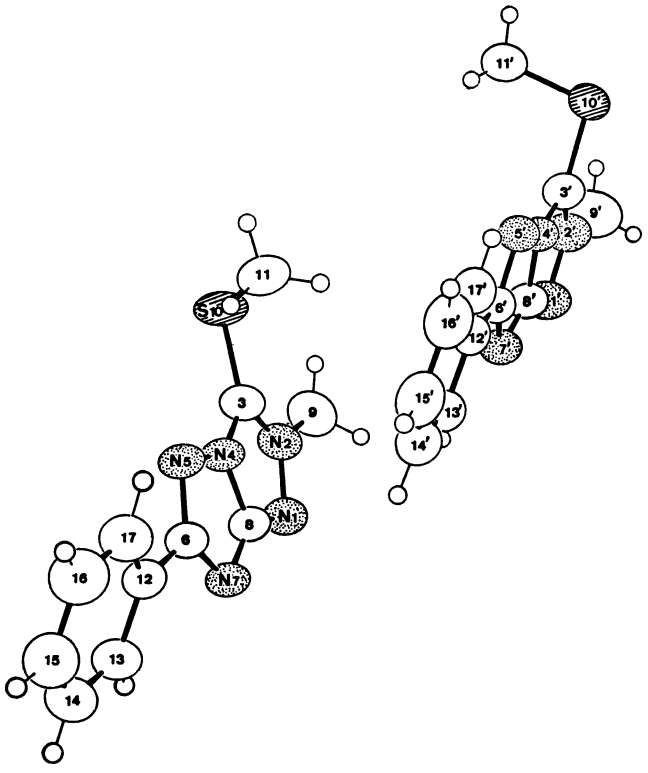
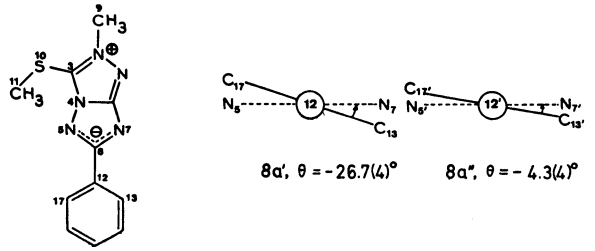


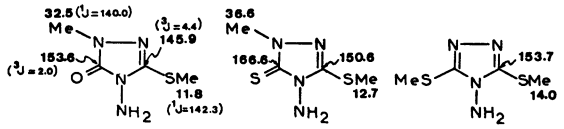
Fig. 1. Ortep drawing of the two molecules with atomic numbering.

(7)—1.404(4) Å and 118.5(3)—121.7(3)°. The dihedral angles about the 6—12 (6′—12′) bonds are −26.7 (4)° and −4.3(4)°.



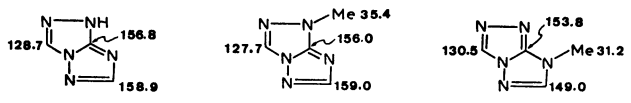
These small angles are expected[13] for a situation where hydrogen atoms on $C_{13(13')}$ and $C_{17(17')}$ are opposed to the lone pairs of $N_{5(5')}$ and $N_{7(7')}$.

To discuss the ^{13}C NMR results it is useful to divide the compounds of Scheme 1 into two classes: the 1,2,4-triazole derivatives **1**, **5** and **10** (solvent: DMSO-d_6) and the bicyclic compounds **3**, **4**, **8**, **9**, **13**, **14**, **15**, and **17**. The salts **16** have been isolated (see experimental part) but not studied due to its fragility. However, the position of the acetyl group, on N_1 and that of the methyl group, on N_7, follows from the structures of **15** and **17**. Salts **6**, 1,2,4-triazole derivatives, cyclize when dissolved in D_2O with release of methanethiol, so the ^{13}C spectrum obtained correspond to salt **7** and will be discussed together with the bicyclic compounds.



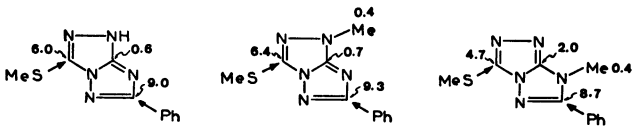
Compound **10** due to its symmetry shows a unique signal for carbons C_3 and C_5. The assignment of carbons C_3 (δ=150.6) and C_5 (δ=166.6) in compund **5** was straightforward from literature data.[14,15] The most difficult case was that of compound **1**, but the assignment was made unambiguous by selective proton decoupling. Irradiation of the SMe signal (δ=2.37, solvent DMSO-d_6) transforms the δ=145.9 quartet into a singlet.

The only ^{13}C NMR spectra of 1,2,4-triazolo[4,3-*b*]-[1,2,4]triazoles so far described are those of the parent compounds **18**, **19**, and **20**.[16,17]



The assignment problems concern exclusively the quaternary carbons C_3, C_6, C_{7a}, $C_{1'}$, and $C_{4'}$ (X≠H). The benzene-ring carbons ($C_{1'}$ and $C_{4'}$) have been assigned through the known[18] effects of the X-substituent (Table 4). The carbon bearing the phenyl group (C_6) appears as a triplet in the coupled spectra due to a $^3J_{CCCH}$ coupling with protons 2′ and 6′. Methylbenzenes[19] and methylpyridines[20] show similar couplings for the methyl carbon atom. Carbons C_3 and C_{7a} were assigned by internal comparison between the different derivatives of Table 4.

The effect of SMe and phenyl substituents (see below) are almost negligible on C_{7a} and internally consistent on carbons C_3 and C_6:



In benzene derivatives[21] the effect of an SMe group on the *ipso* carbon is +9.7 ppm and that of a phenyl group +13.0 ppm. On carbon C_2 of benzoxazoles, the phenyl produces an SCS of +8.4 ppm.[22] Thus the values obtained in the triazolotriazole series are quite normal, taking into account that we have neglected the long-range effects.

The chemical shifts of *N*-CH_3 groups in compounds **14** and **17** are characteristic of their positions N_1 and N_7 (compare with **19** and **20**[16]). Moreover, the carbons $C_{2'}$ and $C_{3'}$ in compound **17a** have identical chemical shifts (a similar situation is observed in ^1H NMR, see experimental part). This corresponds[23] to a hindered phenyl group. Only a methyl substituent on a neighbor nitrogen atom could produce such an effect. The acetyl derivative **15** displays a spectrum close to that of **14**, which proves the 1-acetyl-substituted structure.

Finally, concerning the annular tautomerism of **13**, the similitude of chemical shifts with **14** and the large differences with **17** (see, especially, C_6 and $C_{1'}$) favor the tautomer *N*(H)1. On the other side, compounds **4** and **9** seem to be *N*(H)7 tautomers (carbons C_6 and $C_{1'}$ appear as in **17**). Obviously, these conclusions concern exclusively DMSO solutions.

Experimental

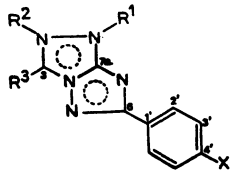
All melting points were determined with a Kofler hot-stage microscope and are uncorrected. Spectral characterization was performed with the following instruments: IR, Nicolet FT-5DX, ^1H-NMR (80 MHz), Varian FT-80, ^{13}C-NMR (20 MHz), Bruker WP80SY. Mass spectra (70 eV) were obtained with a Hewlett-Packard 5993 C instrument. Combustion analyses were performed with a Perkin-Elmer 240 °C instrument.

Materials. All the reagents, except those listed below were obtained from commercial sources and were used without purification. The 4-amino-1-methyl-3-methylthio-1*H*-1,2,4-triazole-5(4*H*)-thione **5**,[24] 4-amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium iodide,[24] 6-aryl-3-methylthio-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazoles **13**,[3] and 6-aryl-1-methyl-3-methylthio-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazoles **14**[3] were prepared according to the methods described in the literature.

The previously unreported 3-methylthio-6-(*p*-nitrophenyl)-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazole **13h** was prepared from **10** and 4-nitrobenzonitrile. Yield, 41%; white needles, mp 280—282 °C; IR (Nujol) 3080, 1630, 1520, 1220, 980, 870, 840, 720 cm^{-1}.

*4-Amino-1-methyl-3-methylthio-1*H*-1,2,4-triazol-5(4*H*)-one* **1**. A solution of 4-amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium iodide (6.36 g, 20 mmol) and sodium methoxide (1.35 g, 25 mmol) in methanol (200 ml), was heated under reflux for 10 h. The reaction mixture was filtered, concen-

TABLE 4. CARBON-13 CHEMICAL SHIFS (IN ppm FROM TMS) OF 1,2,4-TRIAZOLO[4,3-*b*][1,2,4]TRIAZOLE DERIVATIVES



Compound	R^1	R^2	R^3	X	C_3	C_6	C_{7a}	Ar	R^1	R^2	R^3
3a[a]	⊖	Me	O	H	159.0	168.0	146.6	1′: 131.2 2′: 127.2 3′: 129.6 4′: 130.8	—	33.4	—
3b[a]	⊖	Me	O	Me	159.0	168.0	146.6	1′: 128.2 2′: 127.2 3′: 129.9 4′: 141.4 Me: 21.2	—	33.3	—
3d[a]	⊖	Me	O	OMe	c)	167.7	c)	1′: 124.1 2′: 128.8 3′: 114.7 4′: 162.1 OMe: 56.2	—	33.2	—
4a[b]	H	Me	O	H	145.2	155.2[d]	146.5	1′: 125.9 2′: 126.3 3′: 129.1 4′: 131.5	—	32.9[e]	—
4b[b]	H	Me	O	Me	145.4	155.6	146.8	1′: 123.4 2′: 126.4 3′: 129.6 4′: 141.6 Me: 21.0	—	32.9	—
4d[b]	H	Me	O	OMe	145.5	155.4	146.8	1′: 118.4 2′: 128.2 3′: 114.7 4′: 162.0 OMe: 55.5	—	32.9	—
7a[a]	⊖	Me	S	H	160.1	168.4	147.8	1′: 131.0 2′: 127.3 3′: 129.5 4′: 131.0	—	36.9	—
7b[a]	⊖	Me	S	Me	160.0	168.4	147.5	1′: 128.1 2′: 127.2 3′: 129.7 4′: 141.4 Me: 21.4	—	36.9	—
8a[b]	⊖	Me⊕	SMe	H	159.4[g]	168.9[d]	161.9	1′: 131.6 2′: 126.7 3′: 129.9 4′: 128.5	—	38.3[e]	15.5[f]
8b[b,h]	⊖	Me⊕	SMe	Me	160.8	168.9	161.7	1′: 128.7 2′: 126.4 3′: 128.7 4′: 139.2 Me: 21.0	—	37.9	15.1
8c[b]	⊖	Me⊕	SMe	Cl	c)	168.1	162.1	1′: 130.6 2′: 128.4* 3′: 128.6* 4′: 134.7	—	38.3	15.6
9a[b,h]	H	Me	S	H	154.2	156.8	149.0	1′: 125.5 2′: 126.9 3′: 129.4 4′: 132.2	—	36.6	—
9b[b]	H	Me	S	Me	153.6	157.1	149.6	1′: 122.9 2′: 126.5 3′: 129.7 4′: 142.0 Me: 21.0	—	36.3	—

Table 4. (Continued)

Compound	R^1	R^2	R^3	X	C_3	C_6	C_{7a}	Ar	R^1	R^2	R^3
9c[b]	H	Me	S	Cl	c)	156.0	149.4	1′: 124.8 2′: 128.5 3′: 129.3 4′: 136.7	—	36.4	—
9d[b]	H	Me	S	OMe	153.8	156.5	149.0	1′: 117.8 2′: 128.4 3′: 114.7 4′: 162.0 OMe: 55.5	—	36.3	—
13a[b]	H	—	SMe	H	134.7	167.9	157.4	1′: 131.1 2′: 126.2 3′: 128.1 4′: 129.3	—	—	13.5
13b[b]	H	—	SMe	Me	135.1	168.4	157.7	1′: 128.7 2′: 126.5 3′: 129.2 4′: 139.5 Me: 21.0	—	—	13.8
14a[b]	Me	—	SMe	H	c)	c)	157.1	1′: 130.9 2′: 126.6 3′: 128.7 4′: 130.3	35.8	—	14.1
14b[b]	Me	—	SMe	Me	134.1	168.3	156.7	1′: 128.3 2′: 126.4 3′: 129.2 4′: 139.7 Me: 20.9	35.5	—	13.8
15a[b]	COMe	—	SMe	H	140.4[g]	164.7[d]	155.0	1′: 130.2 2′: 126.6 3′: 128.8 4′: 130.4	168.4[g] 21.8[i]	—	13.1
15b[b]	COMe	—	SMe	Me	140.5	164.6	155.1	1′: 127.6 2′: 126.6 3′: 129.3 4′: 140.3 Me: 21.0	168.8 21.7	—	13.2
17a[b]	R^7=Me	—	SMe	H	135.2	157.7	155.8	1′: 125.3 2′: 129.1 3′: 129.1 4′: 131.4	R^7 31.6	—	15.4
17b[b]	R^7=Me	—	SMe	Me	135.1	157.8	155.8	1′: 122.4 2′: 128.9 3′: 129.6 4′: 141.5 Me: 21.0	R^7 31.5	—	15.3

a) Solvent: D_2O-dioxane; b) Solvent: DMSO-d_6; c) Not observed; d) Benzylic coupling (triplet, ^3J=3.5 Hz); e) N-CH_3 coupling (quartet, ^1J=142 Hz); f) S-CH_3 coupling (quartet, ^1J=144 Hz); g) Complex multiplet; h) At 80 °C; i) CO-CH_3 coupling (quartet, ^1J=133 Hz).

trated to one third of volume and cooled to 0 °C. The precipitated solid was filtered, dried, and recrystallized from methanol to give 4-amino-1-methyl-3-methylthio-1*H*-1,2,4-triazol-5(4*H*)-one **1** (2.78 g, 87%) as white needles, mp 175—176 °C.

IR (Nujol) 3320, 3210, 1720, 1650, 1560, 1420, 1270, 990, 970, 950, 890, 730 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ=5.29 (2H, s, NH_2), 3.30 (3H, s, N-CH_3), 2.37 (3H, s, S-CH_3).

Found: C, 29.91; H, 4.99; N, 34.82; S, 19.87%. Calcd for $C_4H_8N_4OS$: C, 29.99; H, 5.03; N, 34.97; S, 20.01%

General Procedure for the Preparation of Triazolotriazole Salts **3**. To a solution of 4-amino-1-methyl-3-methylthio-1*H*-1,2,4-triazol-5(4*H*)-one **1** (3.5 g, 21.8 mmol) in *t*-butyl alcohol (80 ml), equimolar amounts of potassium *t*-butoxide (2.44 g, 21.8 mmol) and the appropriate aromatic nitrile were added. The reaction mixture was heated under reflux with stirring for 6 h. After cooling, the precipitated solid was separated and recrystallized from ethanol to give the corresponding triazolotriazole salt **3** as crystalline solid in high yield (Table 5).

By this procedure, the following salts **3** were prepared:

3a as colorless prisms. IR(Nujol) 1680, 1600, 1460, 1440, 1280, 1180, 1120, 850, 830, 750 cm^{-1}.

3b as colorless prisms. IR(Nujol) 1680, 1600, 1460, 1440, 1380, 1280, 1120, 1070, 1030, 860, 780, 750, 710, 690 cm^{-1}.

3c as colorless prisms. IR(Nujol) 1680, 1600, 1520, 1460, 1430, 1380, 1200, 1125, 845, 810, 765, 740 cm^{-1}.

3d as colorless prisms. IR(Nujol) 1680, 1600, 1460, 1440,

Table 5. Triazolotriazole and amidine salts **3** and **6**

Compound	X	Yield/%	Mp θ_m/°C	Found/%				Molecular formula	Calcd/%			
				C	H	N	S		C	H	N	S
3a	H	80	>350	47.25	3.12	27.42		$C_{10}H_8N_5OK$	47.37	3.15	27.63	
3b	4-CH_3	85	>350	49.25	3.54	25.92		$C_{11}H_{10}N_5OK$	49.38	3.74	26.18	
3c	4-Cl	80	>350	41.57	2.33	24.20		$C_{10}H_7N_5ClOK$	41.72	2.43	24.33	
3d	4-OCH_3	82	>350	46.53	3.49	24.50		$C_{11}H_{10}N_5O_2K$	46.59	3.52	24.70	
3e	2-CH_3	87	>350	49.29	3.60	26.12		$C_{11}H_{10}N_5OK$	49.38	3.74	26.18	
3f	2,4-$(CH_3)_2$	75	>350	51.06	4.17	24.60		$C_{12}H_{12}N_5OK$	51.17	4.26	24.87	
6a	H	74	>350	41.48	3.83	21.94	20.25	$C_{11}H_{12}N_5S_2K$	41.62	3.81	22.06	20.19
6b	4-CH_3	69	>350	43.40	4.12	21.05	19.22	$C_{12}H_{14}N_5S_2K$	43.47	4.25	21.12	19.34
6c	4-Cl	64	>350	37.45	3.03	19.76	18.10	$C_{11}H_{11}N_5ClS_2K$	37.54	3.15	19.90	18.22
6d	4-OCH_3	61	>350	41.33	4.02	20.01	18.30	$C_{12}H_{14}N_5OS_2K$	41.47	4.06	20.15	18.45
6e	2-CH_3	58	>350	43.38	4.20	21.01	19.18	$C_{12}H_{14}N_5S_2K$	43.47	4.25	21.12	19.34
6f	2,4-$(CH_3)_2$	56	>350	45.13	4.51	10.13	18.66	$C_{13}H_{16}N_5S_2K$	45.19	4.66	20.26	18.55

Table 6. 1,2,4-triazolo[4,3-*b*][1,2,4]triazol-3-one and 1,2,4-triazolo[4,3-*b*][1,2,4]-triazole-3-thione derivatives **4** and **9**

Compound	X	Yield/%	Mp θ_m/°C	Found/%				Molecular formula	Calcd/%			
				C	H	N	S		C	H	N	S
4a	H	83	299—300	55.57	3.91	32.55		$C_{10}H_9N_5O$	55.81	4.18	32.55	
4b	4-CH_3	79	323—324	57.70	4.52	30.29		$C_{11}H_{11}N_5O$	57.64	4.80	30.56	
4c	4-Cl	81	>350	48.12	3.17	28.10		$C_{10}H_8N_5ClO$	48.09	3.20	28.05	
4d	4-OCH_3	75	327—330	53.71	4.29	28.80		$C_{11}H_{11}N_5O_2$	53.87	4.48	28.57	
4e	2-CH_3	75	278—279	57.40	4.60	30.48		$C_{11}H_{11}N_5O$	57.64	4.80	30.56	
4f	2,4-$(CH_3)_2$	70	294—296	59.17	5.14	28.70		$C_{12}H_{13}N_5O$	59.25	5.34	28.80	
9a	H	92	300—302	52.01	3.90	30.17	13.72	$C_{10}H_9N_5S$	51.93	3.92	30.28	13.86
9b	4-CH_3	95	268—270	53.77	4.50	28.44	13.10	$C_{11}H_{11}N_5S$	53.86	4.52	28.55	13.07
9c	4-Cl	98	330—333	45.09	2.97	26.18	11.92	$C_{10}H_8N_5ClS$	45.20	3.03	26.35	12.06
9d	4-OCH_3	87	287—289	50.51	4.22	26.76	12.12	$C_{11}H_{11}N_5OS$	50.56	4.24	26.80	12.27
9e	2-CH_3	85	215—217	53.76	4.40	28.49	12.99	$C_{11}H_{11}N_5S$	53.86	4.52	28.55	13.07
9f	2,4-$(CH_3)_2$	83	220—222	55.55	5.01	26.89	12.22	$C_{12}H_{13}N_5S$	55.57	5.05	27.00	12.36

1260, 1040, 860, 770 cm^{-1}.

3e as colorless prisms. IR(Nujol) 1680, 1600, 1460, 1440, 1380, 1280, 1180, 1115, 855, 830, 750 cm^{-1}.

3f as colorless prisms. IR(Nujol) 1680, 1600, 1460, 1440, 1280, 1230, 1175, 1110, 1030, 850, 830, 800, 750, 680 cm^{-1}.

*General Procedure for the Preparation of 6-Aryl-2-methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazol-3(2*H*)-ones* **4**. To a well stirred solution of triazolotriazole salt **3** (10 mmol) in water (80 ml), 1 M† hydrochloric acid was added dropwise until pH=5. The precipitated solid was collected by filtration, dried, and recrystallized from ethanol to give pure 6-aryl-2-methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazol-3(2*H*)-one **4** as crystalline solid in high yield (Table 6).

By this procedure, the following compounds **4** were prepared:

4a as colorless prisms. IR(Nujol) 3070, 1695, 1650, 1500, 970, 840, 780, 730, 680 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.9—7.6 (5H, m), 3.40 (3H, s), MS *m/z* (%), 215 (M^+, 100), 103 (82).

4b as colorless prisms. IR (Nujol) 3080, 1710, 1650, 970, 835, 730, 680, 640 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.60 (2H, d), 7.15 (2H, d), 3.38 (3H, s), 2.33 (3H, s). MS *m/z* (%), 229 (M^+, 100), 117 (91).

4c as colorless needles. IR (Nujol) 3090, 1710, 1660, 1500, 1470, 1100, 970, 835, 730, 700, 660 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.90 (2H, d), 7.20 (2H, d), 3.39 (3H, s). MS *m/z* (%), 249 (M^+, 100), 251 (M^++2, 31), 137 (85), 139 (25).

4d as colorless prisms. IR (Nujol) 3080, 1705, 1660, 1620, 1590, 1505, 1260, 1185, 1030, 965, 835, 735, 710, 660, 650, 630 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.88 (2H, d), 7.10 (2H, d), 3.85 (3H, s), 3.39 (3H, s). MS *m/z* (%), 245 (M^+, 100), 133 (80).

4e as colorless prisms. IR (Nujol) 3100, 1710, 1660, 1500, 970, 830, 770, 710, 680, 660 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.5—7.2 (4H, m). 3,39 (3H, s), 2.39 (3H, s). MS *m/z* (%) 229 (M^+, 100), 117 (90).

4f as colourless prisms. IR (Nujol) 3070, 1710, 1660, 1500, 1340, 970, 830, 730, 710, 680, 670 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.5—7.2 (3H, m), 3.40 (3H, s), 2.48 (3H, s), 2.34 (3H, s). MS *m/z* (%), 243 (M^+, 100), 131 (82).

General Procedure for the Preparation of Amidine Salts **6**. To a well-stirred solution of 4-amino-1-methyl-3-methylthio-1*H*-1,2,4-triazole-5(4*H*)-thione **5** (3.52 g, 20 mmol) in *t*-butyl alcohol (100 ml), equimolar amounts of potassium *t*-butoxide (2.24 g, 20 mmol) and the appropriate aromatic nitrile, were added. The reaction mixture was heated under reflux for 3 h. After cooling, the precipitated solid was separated by filtration and recrystallized from ethanol to give the cor-

† 1 M=1 mol dm^{-3}.

Table 7. Inner salt of 6-aryl-2-methyl-3-methylthio-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]-triazolium hydroxydes **8**

Compound	X	Yield/%	Mp θ_m/°C	Found/%				Molecular formula	Calcd/%			
				C	H	N	S		C	H	N	S
8a	H	82	165—167	53.74	4.50	28.41	12.93	$C_{11}H_{11}N_5S$	53.86	4.52	28.55	13.07
8b	4-CH_3	74	158—160	55.52	4.96	26.84	12.12	$C_{12}H_{13}N_5S$	55.58	5.05	27.00	12.36
8c	4-Cl	77	160—162	47.12	3.61	24.91	11.33	$C_{11}H_{10}N_5ClS$	47.23	3.60	25.03	11.46
8d	4-OCH_3	91	185—187	52.23	4.65	25.39	11.48	$C_{12}H_{13}N_5OS$	52.35	4.76	25.43	11.64
8e	2-CH_3	57	151—153	55.50	5.02	26.89	12.30	$C_{12}H_{13}N_5S$	55.58	5.05	27.00	12.36
8f	2,4-$(CH_3)_2$	61	175—177	57.01	5.47	25.49	11.56	$C_{13}H_{15}N_5S$	57.12	5.53	25.62	11.73

responding amidine salt **6**, as crystalline solid in moderated yields (Table 5).

By the above procedure, the following salts **6** were obtained:

6a as colorless prisms. IR (Nujol) 3180, 1590, 1580, 1460, 1200, 1120, 1010, 835, 750, 705 cm^{-1}.

6b as colorless prisms. IR (Nujol) 3210, 1590, 1460, 1330, 1130, 1010, 830, 755 cm^{-1}.

6c as colorless prisms. IR (Nujol) 3210, 1595, 1450, 1400, 1280, 1130, 1110, 1020, 1000, 840, 760 cm^{-1}.

6d as colorless prisms. IR (Nujol) 3200, 1590, 1580, 1460, 1255, 1175, 1030, 1000, 855, 760 cm^{-1}.

6e as colorless prisms. IR (Nujol) 3200, 1590, 1450, 1325, 1190, 1120, 1000, 830, 745, 720 cm^{-1}.

6f as colorless prisms. IR (Nujol) 3180, 1590, 1580, 1450, 1190, 1120, 1010, 835, 735, 720 cm^{-1}.

*General Procedure for the Preparation of Inner Salt of 6-Aryl-2-methyl-3-methylthio-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazolium Hydroxides* **8**. To a well-stirred solution of amidine salt **6** (10 mmol) in water (100 ml), methyl iodide (13 mmol) and enough ethanol (about 20 ml) were added to give a clear solution. The resulting solution was kept at room temperature for 24 h. The solvent was partially removed under reduced pressure and the separated solid was filtered, dried and recrystallized from ethanol to give pure **8** as crystalline solid in good yield (Table 7).

By this procedure the following mesoionic compounds **8** were prepared:

8a as white prisms. IR (Nujol) 1590, 1580, 1410, 1350, 1280, 1080, 990, 790, 755, 715 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=8.3—7.4 (5H, m), 4.00 (3H, s), 2.75 (3H, s). MS *m/z* (%) 245 (M^+, 38), 212 (25), 129 (44), 103 (34), 77 (100).

8b as white prisms. IR (Nujol) 1585, 1460, 1400, 1330, 1180, 1105, 1030, 980, 830, 755, 730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=7.70 (2H, d), 7.40 (2H. d), 4.05 (3H, s), 2.75 (3H, s), 2.40 (3H, s). MS *m/z* (%) 259 (M^+, 26), 226 (79), 185 (30), 143 (51), 117 (43), 81 (76), 69 (100).

8c as white prisms. IR (Nujol) 1580, 1570, 1470, 1420, 1320, 1020, 990, 840, 760, 730 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=7.80 (2H, d), 7.60 (2H, d), 4.00 (3H, s), 2.70 (3H, s). MS *m/z* (%) 281 (M^++2, 6), 279 (M^+, 18), 248 (5), 246 (15), 165 (8), 163 (8), 139 (10), 137 (30), 70 (100).

8d as white prisms. IR (Nujol) 1610, 1590, 1430, 1405, 1350, 1310, 1250, 1180, 1020, 850, 740, 680 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=7.90 (2H, d), 7.20 (2H, d), 3.95 (3H, s), 3.80 (3H, s), 2.70 (3H, s). MS *m/z* (%) 275 (M^+, 31), 270 (12), 244 (5), 242 (8), 159 (21), 133 (13), 69 (100).

8e as white needles. IR (Nujol) 1590, 1460, 1330, 1260, 1190, 1025, 990, 820, 750, 735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=8.1—7.3 (4H, m), 4.00 (3H, s), 2.70 (3H, s), 2.65 (3H, s). MS *m/z* (%) 259 (M^+, 43), 226 (12), 143 (72), 117 (25), 69 (100).

8f as white needles. IR (Nujol) 1585, 1560, 1455, 1420, 1325, 1200, 1020, 980, 830, 760 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ=8.0—7.1 (3H, m), 4.00 (3H, s), 2.75 (3H, s), 2.65 (3H, s), 2.40 (3H, s). MS *m/z* (%) 273 (M^+, 70), 258 (43), 157 (33), 131 (30), 69 (100).

*General Procedure for the Preparation of 6-Aryl-2-methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazole-3(2*H*)-thiones* **9**. To a well-stirred solution of amidine salt **6** (10 mmol) in water (100 ml), 1 M hydrochloric acid was added dropwise until pH=5. The precipitated solid was collected by filtration, dried, and recrystallized from ethanol to give pure **9** as crystalline solid in high yield (Table 6).

By the above procedure, the following compounds **9** were prepared:

9a as white prisms. IR (Nujol) 3080, 1655, 1605, 1465, 1430, 1380, 1120, 960, 830, 780, 690 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.9—7.3 (5H, m), 3.83 (3H, s). MS *m/z* (%) 231 (M^+, 55), 198 (11), 172 (42), 103 (100), 77 (21).

9b as white needles. IR (Nujol) 3080, 1650, 1610, 1460, 1320, 1200, 1125, 960, 830, 825, 730 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.70 (2H, d), 7.30 (2H, d), 3.80 (3H, s), 2.40 (3H, s). MS *m/z* (%) 245 (M^+, 61), 212 (8), 186 (32), 117 (100), 70 (48).

9c as white needles. IR (Nujol) 3080, 1655, 1605, 1470, 1400, 1100, 960, 840, 830, 730 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O)) δ=7.90 (2H, d), 7.60 (2H, d), 3.80 (3H, s). MS *m/z* (%) 267 (M^++2, 32), 265 (M^+, 100), 234 (4), 232 (12), 208 (21), 206 (63), 139 (10), 137 (30).

9d as white needles. IR (Nujol) 3070, 1650, 1605, 1490, 1460, 1250, 1175, 1025, 950, 850, 845, 810, 735 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=7.70 (2H, d), 7.30 (2H, d), 3.85 (3H, s), 3.75 (3H, s). MS *m/z* (%) 261 (M^+, 100), 228 (8), 202 (56), 133 (42).

9e as white prisms. IR (Nujol) 3080, 1650, 1460, 1310, 1120, 1050, 950, 825, 770, 720 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=8.1—7.3 (4H, m), 3.82 (3H, s), 2.65 (3H, s). MS *m/z* (%) 245 (M^+, 100), 212 (7), 186 (34), 158 (25), 143 (11), 117 (44).

9f as white prisms. IR (Nujol) 3080, 1650, 1610, 1460, 1370, 1300, 1200, 1120, 955, 830, 735, 720 cm^{-1}. ^{1}H-NMR (DMSO-d_6/D_2O) δ=8.0—7.1 (3H, m), 3.80 (3H, s), 2.65 (3H, s), 2.40 (3H, s). MS *m/z* (%) 259 (M^+, 100), 226 (13), 200 (28), 172 (36), 131 (76), 116 (62).

Basic Hydrolysis of Compounds **8**. A solution of inner salt of 6-aryl-2-methyl-3-methylthio-7*H*-1,2,4-triazolo[4,3-*b*]-[1,2,4]triazolium hydroxide **8** (5 mmol) in 10 % methanolic potassium hydroxide (75 ml) was heated under reflux until evolution of methanethiol was ceased (about 5 h). Then, the solvent was removed under reduced pressure and the residual material was dissolved in water (60 ml). The resulting solution was acidified by dropwise addition of 1 M hydrochloric acid until pH=5. The precipitated solid was collected by filtration, dried and crystallized from ethanol to give 6-aryl-2-methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazol-

3(2*H*)-one **4** in almost quantitative yield.

General Procedure for the Preparation of 1-Acetyl-6-aryl-3-methylthio-1,2,4-triazolo[4,3-b][1,2,4]triazoles **15**. A solution of 6-aryl-3-methylthio-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]-triazole **13** (20 mmol) in acetic anhydride (100 ml) was heated under reflux for 1 h with stirring. After cooling, the precipitated solid was collected by filtration, dried under vacuum at 100 °C, and crystallized from ethanol to give pure **15** as crystalline solid in high yield (Table 4).

By this procedure the following compounds **15** were obtained:

15a as white plates. IR (Nujol) 1750, 1570, 1490, 1420, 1310, 1130, 990, 790, 740, 710, 680 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=8.1—7.5 (5H, m), 2.90 (3H, s), 2.75 (3H, s).

15b as white needles. IR (Nujol) 1740, 1585, 1570, 1490, 1430, 1420, 1320, 1205, 1125, 835, 760, 745 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=7.90 (2H, d), 7.50 (2H, d), 2.90 (3H, s), 2.75 (3H, s), 2.40 (3H, s).

15c as white needles. IR (Nujol) 1745, 1570, 1420, 1320, 1210, 1125, 1020, 910, 850, 745 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=7.90 (2H, d), 7.60 (2H, d), 2.95 (3H, s), 2.75 (3H, s).

15e as white needles. IR (Nujol) 1730, 1585, 1570, 1480, 1410, 1380, 1325, 1125, 900, 760, 730 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=8.1—7.4 (4H, m), 2.90 (3H, s), 2.75 (3H, s), 2.65 (3H, s).

15f as white needles. IR (Nujol) 1740, 1570, 1495, 1420, 1320, 1210, 1130, 990, 910, 840, 760, 730 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=7.9—7.1 (3H, m), 2.90 (3H, s), 2.75 (3H, s), 2.65 (3H, s), 2.40 (3H, s).

15g as white needles. IR (Nujol) 1730, 1585, 1570, 1485, 1410, 1380, 1330, 1205, 1125, 1045, 900, 735, 710 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=8.1—7.4 (4H, m), 2.95 (3H, s), 2.75 (3H, s).

15h as white plates. IR (Nujol) 1745, 1575, 1520, 1420, 1350, 1310, 1130, 990, 870, 860, 740, 720 cm^{-1}. ^1H-NMR ($CDCl_3$/CF_3CO_2H) δ=7.90 (2H, d), 7.60 (2H, d), 2.90 (3H, s), 2.75 (3H, s).

General Procedure for the Preparation of 1-Acetyl-6-aryl-7-methyl-3-methylthio-7H-1,2,4-triazolo[4,3-b][1,2,4]triazol-7-ium Trifluoromethanesulfonates **16**. To a solution of 1-acetyl-6-aryl-3-methylthio-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazole **15** (10 mmol) in dry dichloromethane (75 ml), methyl trifluoromethanesulfonate (12 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. Occasionally the trifluoromethanesulfonate salt **16** precipitated in the course of the reaction. If not, the solvent was removed under reduced pressure and the residual material was crystallized from dichloromethane–diethyl ether to give the pure **16** as crystalline solid in high yield (Table 8).

By this procedure the following compounds **16** were prepared:

16a as colorless prisms. IR (Nujol) 1755, 1640, 1530, 1460, 1370, 1300, 1230, 1210, 1160, 1130, 1030, 950, 780, 730, 710, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=7.8—7.5 (5 H, m), 4.15 (3H, s), 2.85 (3H, s), 2.75 (3H, s).

16b as colorless prisms. IR (Nujol) 1770, 1620, 1520, 1310, 1270, 1230, 1160, 1030, 980, 840, 770, 740, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=8.0 (2H, d), 7.5 (2H, d), 4.15 (3H, s), 2.90 (3H, s), 2.75 (3H, s), 2.40 (3H, s).

16c as colorless prisms. IR (Nujol) 1765, 1610, 1540, 1360, 1270, 1230, 1160, 1030, 1010, 965, 910, 840, 730, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=7.90 (2H, d), 7.60 (2H, d), 4.10 (3H, s), 2.90 (3H, s), 2.75 (3H, s).

16e as colorless prisms. IR (Nujol) 1765, 1615, 1550, 1370, 1310, 1270, 1240, 1230, 1160, 1030, 970, 910, 770, 760, 740, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=8.2—7.4 (4H, m), 4.15 (3H, s), 2.85 (3H, s), 2.75 (3H, s), 2.65 (3H, s).

16f as colorless prisms. IR (Nujol) 1770, 1620, 1520, 1420, 1310, 1270, 1230, 1180, 1160, 1030, 970, 830, 780, 760, 720, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=7.9—7.0 (3H, m), 4.15 (3H, s), 2.90 (3H, s), 2.75 (3H, s), 2.65 (3H, s),

Table 8. 3-Methylthio-6-arylthio-6-aryl-1,2,4-triazolo[4,3-*b*][1,2,4]triazole derivatives **15**, **16**, and **17**

Compound	X	Yield/%	Mp θ_m/°C	Found/%				Molecular formula	Calcd/%			
				C	H	N	S		C	H	N	S
15a	H	88	193—195	52.64	4.02	25.47	11.58	$C_{12}H_{11}N_5OS$	52.73	4.06	25.62	11.73
15b	4-CH_3	68	174—175	54.21	4.49	24.19	10.98	$C_{13}H_{13}N_5OS$	54.34	4.56	24.37	11.16
15c	4-Cl	70	199—200	46.78	3.22	22.59	10.31	$C_{12}H_{10}N_5ClOS$	46.83	3.27	22.75	10.42
15e	2-CH_3	82	140—142	54.28	4.52	24.19	11.03	$C_{13}H_{13}N_5OS$	54.34	4.56	24.37	11.16
15f	2,4-$(CH_3)_2$	95	200—202	55.69	4.93	23.18	10.49	$C_{14}H_{15}N_5OS$	55.80	5.02	23.24	10.64
15g	2-Cl	67	130—131	46.85	3.21	22.62	10.33	$C_{12}H_{10}N_5ClOS$	46.83	3.27	22.75	10.42
15h	4-O_2N	47	220—222	45.14	3.12	26.33	9.93	$C_{12}H_{10}N_6O_3S$	45.28	3.17	26.40	10.07
16a	H	70	156—158	38.54	3.18	16.05	14.53	$C_{14}H_{14}N_5F_3O_4S_2$	38.44	3.23	16.01	14.66
16b	4-CH_3	81	110—112	39.83	3.51	15.39	14.07	$C_{15}H_{16}N_5F_3O_4S_2$	39.91	3.57	15.51	14.20
16c	4-Cl	89	185—186	35.52	2.69	14.73	13.40	$C_{14}H_{13}N_5ClF_3O_4S_2$	35.64	2.78	14.84	13.59
16e	2-CH_3	51	115—117	39.85	3.51	15.38	14.08	$C_{15}H_{16}N_5F_3O_4S_2$	39.91	3.57	15.51	14.20
16f	2,4-$(CH_3)_2$	81	101—103	41.18	3.85	14.94	13.66	$C_{16}H_{18}N_5F_3O_4S_2$	41.29	3.90	15.04	13.78
16g	2-Cl	63	149—150	35.59	2.69	14.72	13.43	$C_{14}H_{13}N_5ClF_3O_4S_2$	35.64	2.78	14.84	13.59
16h	4-O_2N	37	129—130	34.77	2.70	17.36	13.13	$C_{14}H_{13}N_6F_3O_6S_2$	34.86	2.72	17.42	13.29
17a	H	86	113—115	53.80	4.47	28.37	12.94	$C_{11}H_{11}N_5S$	53.86	4.52	28.55	13.07
17b	4-CH_3	91	128—129	55.44	4.96	26.83	12.19	$C_{12}H_{13}N_5S$	55.58	5.05	27.00	12.36
17c	4-Cl	96	110—112	47.12	3.52	24.89	11.29	$C_{11}H_{10}N_5ClS$	47.23	3.60	25.03	11.46
17e	2-CH_3	74	112—114	55.53	5.01	26.82	12.27	$C_{12}H_{13}N_5S$	55.58	5.05	27.00	12.36
17f	2,4-$(CH_3)_2$	81	92— 93	56.97	5.46	25.49	11.61	$C_{13}H_{15}N_5S$	57.12	5.53	26.62	11.73
17g	2-Cl	67	98— 99	47.05	3.56	24.92	11.33	$C_{11}H_{10}N_5ClS$	47.23	3.60	25.03	11.46
17h	4-O_2N	93	148—150	45.43	3.38	28.83	10.89	$C_{11}H_{10}N_6O_2S$	45.51	3.47	28.95	11.04

2.40 (3H, s).

16g as colorless prisms. IR (Nujol) 1770, 1620, 1530, 1370, 1310, 1270, 1230, 1160, 1030, 970, 910, 780, 760, 730, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=8.2—7.4 (4H, m), 4.10 (3H, s), 2.90 (3H, s), 2.75 (3H, s).

16h as white needles. IR (Nujol) 1770, 1620, 1550, 1520, 1360, 1320, 1270, 1160, 1040, 975, 910, 870, 860, 730, 640 cm^{-1}. ^1H-NMR ($CDCl_3$) δ=7.90 (2H, d), 7.70 (2H, d), 4.10 (3H, s), 2.85 (3H, s), 2.75 (3H, s).

General Procedure for the Preparation of 6-Aryl-7-methyl-3-methylthio-7H-1,2,4-triazolo[4,3-b][1,2,4]triazoles **17**. To a solution of 1-acetyl-6-aryl-7-methyl-3-methylthio-1*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazol-7-ium trifluoromethanesulfonate **16** (10 mmol) in water (250 ml), ethanol was added until a clear solution was obtained at 70 °C. Then a saturated aqueous solution of sodium carbonate was added dropwise with stirring, until pH=9. After cooling to 0 °C, the precipitated solid was collected by filtration, dried, and recrystallized from chloroform-hexane to give the pure **17** as crystalline solid in high yield (Table 8).

By the above procedure, the following compounds **17** were obtained:

17a as white prisms. IR (Nujol) 1590, 1470, 1330, 1320, 1170, 1045, 1020, 955, 785, 720, 710 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=7.7—7.2 (5H, m), 3.80 (3H, s), 2.75 (3H, s); ($CDCl_3$) δ=7.60 (5H, s), 3.75 (3H, s), 2.65 (3H, s). The fact that the phenyl appears as a singlet is characteristic of a phenyl out-of-plane (For another example in the azapentalene series, see Ref. 25).

17b as white needles. IR (Nujol) 1590, 1480, 1460, 1270, 1175, 1070, 990, 970, 840, 730 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=7.90 (2H, d), 7.65 (2H, d), 3.80 (3H, s), 2.70 (3H, s), 2.50 (3H, s).

17c as white needles. IR (Nujol) 1590, 1495, 1320, 1180, 1170, 1090, 1000, 945, 835, 720 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=8.00 (2H, d), 7.80 (2H, d), 3.80 (3H, s), 2.70 (3H, s).

17e as white prisms. IR (Nujol) 1590, 1490, 1370, 1320, 1170, 1050, 1030, 950, 785, 740, 730 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=7.8—7.4 (4H, m), 3.65 (3H, s), 2.70 (3H, s), 2.35 (3H, s).

17f as white prisms. IR (Nujol) 1590, 1500, 1370, 1320, 1180, 1140, 1060, 1000, 970, 840, 745, 735, 730 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=7.9—7.3 (3H, m), 3.60 (3H, s), 2.75 (3H, s), 2.45 (3H, s), 2.35 (3H, s).

17g as white prisms. IR (Nujol) 1600, 1500, 1430, 1370, 1320, 1180, 1095, 1040, 970, 780, 745, 720 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=8.0—7.6 (4H, m), 3.70 (3H, s), 2.75 (3H, s).

17h as yellow plates. IR (Nujol) 1590, 1540, 1530, 1470, 1350, 1170, 1060, 950, 860, 760, 720, 710 cm^{-1}. ^1H-NMR (DMSO-d_6) δ=7.90 (2H, d), 7.65 (2H, d), 3.80 (3H, s), 2.70 (3H, s).

We thank Mrs. M. D. Casado, Mrs. M. L. Jimeno, and Mrs. M. Plaza for recording the ^{13}C NMR spectra.

References

1) J. Elguero, R. M. Claramunt, and A. J. H. Summers, *Adv. Heterocycl. Chem.*, **22**, 183 (1978).
2) R. M. Claramunt, J. P. Fayet, M. C. Vertut, P. Mauret, and J. Elguero, *Tetrahedron*, **31**, 545 (1975).
3) P. Molina, M. Alajarin, and M. J. Vilaplana, *Synthesis*, **1983**, 415.
4) P. Molina and A. Tárraga, *Synthesis*, **1983**, 411.
5) K. Schofield, M. R. Grimmett, and B. T. R. Keene, "The Azoles," Cambridge University Press, Cambridge (1976).
6) R. A. Olofson and R. V. Kendall, *J. Org. Chem.*, **35**, 2246 (1970).
7) A. Maquestiau, Y. Van Haverbeke, and J. D. Vanovervelt, *Bull. Soc. Chim. Belg.*, **86**, 961 (1977).
8) C. Guimon, G. Pfister-Guillouzo, and M. Begtrup, *Can. J. Chem.*, **61**, 1197 (1983).
9) P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq, and H. H. Woolfson, "The MULTAN-80 System," Univ. of York, England and Louvain, Belgium, (1980).
10) J. M. Stewart, P. A. Maclin, C. W. Dickinson, H. L. Ammon, H. Heck, and H. Flack, "The X RAY-76 System," Univ. of Maryland, USA, (1976).
11) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, Vol. IV, (1974).
12) The H positions, the anisotropic model and the observed and calculated structure factors are deposited at the office of this Bulletin as Document No. 8501.
13) T. Avignon, L. Bouscasse, and J. Elguero, *Tetrahedron*, **34**, 1139 (1978).
14) H. Kristinsson and T. Winkler, *Helv. Chim. Acta*, **66**, 1129 (1983).
15) R. Faure, E. J. Vincent, G. Assef, J. Kister, and J. Metzger, *Org. Magn. Reson.*, **9**, 688 (1977).
16) R. Faure, E. J. Vincent, R. M. Claramunt, and J. Elguero, *Org. Magn. Reson.*, **9**, 508 (1977).
17) In Ref. 16 the value of carbon C_{7a} chemical shift in compound **19** was erroneously printed at δ 146.0 instead of the true value (δ 156.0).
18) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972), p. 197.
19) M. J. Shapiro, *J. Org. Chem.*, **43**, 212 (1978).
20) Y. Takeuchi, *Org. Magn. Reson.*, **7**, 181 (1975).
21) W. W. Paudler and M. V. Jovanovic, *Org. Magn. Reson.*, **19**, 192 (1982).
22) J. Llinares, J. P. Galy, R. Faure, E. J. Vincent, and J. Elguero, *Can. J. Chem.*, **57**, 937 (1979).
23) R. N. Butler, T. McEvoy, E. Alcalde, R. M. Claramunt, and J. Elguero, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2886.
24) P. Molina and M. Alajarin, *Synthesis*, **1983**, 414.
25) E. Alcalde, R. M. Claramunt, J. Elguero, and C.P.S. Huber, *J. Heterocycl. Chem.*, **15**, 395 (1978).