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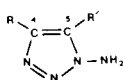
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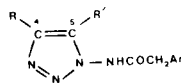
$^{13}\text{C}$  nmr chemical shifts are used for the structural assignment of isomeric 1-amino-1,2,3-triazoles and 1-(*N*-arylacetylamino)-1,2,3-triazoles unsymmetrically substituted with phenyl, methyl or hydrogen in the 4,5-positions of the triazole ring. A signal at  $11 \pm 0.6$  ppm indicates a 4-methyl triazole derivative, whereas a signal at  $7.9 \pm 1$  ppm indicates a 5-methyl triazole. A signal at  $120 \pm 0.5$  ppm (C-5) indicates a hydrogen in the 5-position (unsubstituted triazole).

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The main purpose of this work is the identification of isomeric 1-amino- (I) and 1-(*N*-arylacetylamino)-1,2,3- (or *v*-) triazoles (II) unsymmetrically substituted with phenyl, methyl or hydrogen in the 4,5-positions of the triazole ring by means of carbon-13 nmr spectroscopy.



I



II

Ia R, R' = CH<sub>3</sub>  
Ib R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>  
Ic R = CH<sub>3</sub>, R' = C<sub>6</sub>H<sub>5</sub>  
Id R = C<sub>6</sub>H<sub>5</sub>, R' = H  
Ie R = *p*-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>, R' = H  
If R, R' = C<sub>6</sub>H<sub>5</sub>

IIa R, R' = CH<sub>3</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
IIb R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
IIc R = CH<sub>3</sub>, R' = C<sub>6</sub>H<sub>5</sub>, Ar = C<sub>6</sub>H<sub>5</sub>  
IId R, R' = CH<sub>3</sub>, Ar = *p*-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>

It has been shown (1) that by the oxidation of some bis-arylacetylaminohydrazone of  $\alpha$ -dicarbonyl compounds, two isomeric 1-(*N*-phenacetylamino)-*v*-triazoles were formed (IIb, IIc), which were identified after acid hydrolysis as the corresponding 1-amino-*v*-triazoles.

The problem of this structural assignment in analogously substituted 1-( $\alpha$ -aryloxy-arylideneamino)-*v*-triazoles (triazolyl isoimides) was solved by benzene induced shifts in the  $^1\text{H}$ -nmr spectra (2) or by dipole moment measurements (3). However, in the present case these methods could not be used, due to, among other reasons, the very low solubility of the compounds in benzene and in non-polar solvents. We have found that for this structural problem,  $^{13}\text{C}$  nmr spectroscopy can be used as a simple and reliable method.

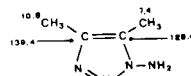
The chemical shifts (in ppm from internal TMS) of the amines (I) and amides (II) studied in deuteriochloroform for the methyl carbons in the 4,5-positions of the triazole ring are found in the range of 7-11.5 ppm depending on the position of the methyl group, whereas the shifts for the triazole C-4 and C-5 are in the range of 120-145 ppm. It is mentioned that the signals for methyl carbons attached to the triazole ring appear at much higher field than those for methyl groups attached to phenyl groups which resonate at  $\sim 20$  ppm and they are easily differentiated.

The carbonyl carbon in amides (II) resonates at  $\sim 170$  ppm, whereas the methylene carbon at  $\sim 41$  ppm. The methyl carbon shifts, as well as those of C-4 and especially of C-5, are of diagnostic importance and they are used for the identification of these isomeric triazole derivatives.

Authentic samples (4,5) of 1-amino-4-phenyl-5-methyl-*v*-triazole (Ib) and 1-amino-4-methyl-5-phenyl-*v*-triazole (Ic) showed signals for methyl carbons at 8.9 (5-CH<sub>3</sub>) and at 11.5 (4-CH<sub>3</sub>) ppm, respectively, proving thus, that the higher field peak corresponds to C-CH<sub>3</sub> at the 5-position. On the other hand, 1-amino-4,5-dimethyl-*v*-triazole (Ia) gave two peaks for methyl carbons at 7.4 and 10.6 ppm, which could be assigned by the previous analogy as 5-CH<sub>3</sub> and 4-CH<sub>3</sub>, respectively. The signals for the triazole carbons in this compound were at 139.4 and 129.4 ppm. Elguero, *et al.* (6,7), have found that the shifts for C-4 and C-5 in 1-methyl-1,2,3-triazole are 133.6 and 124.1 ppm, respectively, whereas the carbon shifts in 1-acetyl-1,2,3-triazole (7) are 134.2 for C-4 and 121.1 ppm for C-5.

Furthermore, the carbon shift for C-5 in 1-alkyl-4-vinyl-*v*-triazoles was found (8) to be at 119-121 ppm. Considering that the shift effect of methyl group is  $\sim +9$  ppm (9) and ignoring the "o-effect", which however in some aromatic systems is  $\sim 1$  ppm, it is found from the signals at 139.4 and 129.4 ppm that the shifts for C-4 and C-5 in 1-amino-*v*-triazole should be at  $\sim 130$  and  $\sim 120$  ppm, respectively, in good agreement with the values previously mentioned. The 1-amino-4,5-diphenyl-*v*-triazole (If) gave two signals for the triazole carbons at 143.6 and 132.8 ppm. Considering the substituent effect of the phenyl group equal to  $\sim +13$  ppm (9), the values  $\sim 130$  and  $\sim 120$  ppm for C-4 and C-5 are again found. The aromatic carbons show a set of eight peaks between 130.9 and 126.8 ppm.

It is of interest to note that the C-5 shift in Id is at 120.6 ppm and at 120.1 ppm in Ie. This peak became a doublet in an off-resonance decoupled spectrum, proving thus that the higher field peak at  $\sim 120$  ppm corresponds to C-5 of the triazole ring. Thus, the carbon shifts in Ia are as shown below.



Ia

An explanation of this up-field shift for C-5 and 5-CH<sub>3</sub> might be given considering that C-5 in the triazole ring is attached to a nitrogen of sp<sup>3</sup>-hybridization (amino nitrogen), whereas C-4 is attached to a nitrogen of sp<sup>2</sup>-hybridization (imino nitrogen). This is also valid in some other nitrogen heterocycles like imidazole, pyrazole, benzothiazole. It is mentioned that the shifts for C-4 and C-5 in 1-methylimidazole (6) are 129.3 and 119.7 ppm, respectively.

By plotting the total charge densities, calculated by the CNDO/2 method for C-4 and C-5 of the amino-triazole (Ia) (their charges being equal to 3.9528 and 3.9876) versus the shifts 139.4 and 129.4 ppm, the following simple expression is found:  $\delta_c = -287 \cdot q_{\pi+\sigma} + 1274$  (ppm). Using this equation and substituting the total charge densities of C-4 (3.9750) and C-5 (4.0135), calculated for 1-amino-*v*-triazole, the shifts  $\delta_{c-4} = 133.2$  and  $\delta_{c-5} = 122.1$  are produced, in very good agreement with those previously mentioned. We have also found analogous expressions for similarly substituted triazole derivatives, like the compounds Ib and Id. It is worth mentioning that a similar expression was used (10) for the correlation of chemical shifts with charge densities in some azolium salts.

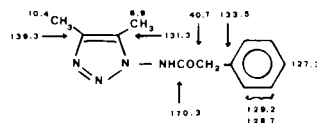
The CNDO/2 calculations were made by using X-ray data (11) for the triazole ring dimensions.

The conclusions which can be drawn from the above discussion on the spectra of 1-amino-*v*-triazoles are the following. The presence of a methyl group in the 5-position of the triazole ring is accompanied by a signal for a methyl carbon at  $7.9 \pm 1$  ppm, whereas the presence of a methyl group in the 4-position is accompanied by a signal at  $11 \pm 0.6$  ppm. Although the difference in chemical shifts is small, the shifts are quite characteristic and independent of the other substituent (phenyl or hydrogen). The presence of a hydrogen in the 5-position gives rise to a signal for C-5 at  $120 \pm 0.5$  ppm. If the substituent at C-4 is a methyl group, the signals for C-CH<sub>3</sub> and C-5 are conclusive for the structure. If the substituent at C-4 is a phenyl group, the signal at  $\sim 120$  ppm is conclusive again. However, if the phenyl group is at the 5-position, the signals for C-4 and C-5 are predicted to be at  $\sim 130$  ppm in the range where the phenyl carbons also resonate. In this case, the conclusion for the structure can be taken indirectly by the absence of a signal at  $\sim 120$  ppm. The shift at 120 ppm might be confused with the aromatic carbon in the *p*-position of a -OCH<sub>3</sub> or -NH<sub>2</sub> group, which also resonates at  $\sim 120$  ppm. The distinction in this case between C-5 and C-*para* is possible with an off-resonance decoupled spectrum, where the peak for triazole C-5 becomes a doublet.

It is shown that these data are readily applicable to arylacetylaminio-*v*-triazoles. Thus, the amides IIb and IIc, which upon acid hydrolysis are converted to the known amino-triazoles Ib and Ic, showed signals for methyl car-

bons at 8.3 and 11.1 ppm, respectively, proving that in IIb the methyl group is located in the 5-position, whereas in IIc it is in the 4-position of the triazole ring.

The carbon shifts of phenacetylaminio-triazole (IIa) are shown below, whereas in the table the methyl carbon shifts of some amino (I) and arylacetylaminio-triazoles (II) are given.



IIa

It is worth mentioning that analogous shifts (12) for the 4-CH<sub>3</sub> or 5-CH<sub>3</sub> and C-5 also show the 4,5-unsymmetrically substituted triazolyl isoimides and this method can be also used for their structural assignment.

Table

Carbon Methyl Shifts (ppm/TMS) of 1-Amino-*v*-triazoles (I) and 1-(*N*-Arylacetylaminio)-*v*-triazoles (II) in Deuteriochloroform

Compound	$\delta$ CH <sub>3</sub> -4	$\delta$ CH <sub>3</sub> -5
Ia	10.6	7.4
Ib		8.9
Ic	11.5	
IIa	10.4	6.9
IIb		8.3
IIc	11.1	
IId	10.4	7.0

## EXPERIMENTAL

<sup>13</sup>C Nmr spectra were obtained at 40° with a Varian Associates CFT-20 spectrometer operating in the Fourier transform mode at 20 MHz, using 10 mm diameter sample tubes. Solutions of 0.1-0.7M in deuteriochloroform containing 1% TMS were employed with broad-band proton noise decoupling. Accumulations of 20000 to 75000 transients were obtained depending on the concentration of the solution. A flip angle between 30° and 40° corresponding to pulse width 6-8μseconds was applied.

The preparation of arylacetylaminio-1,2,3-triazoles (II) was previously described (1). The 1-amino-1,2,3-triazoles (I) were obtained by acid hydrolysis either of the corresponding arylacetylaminio-1,2,3-triazoles (1) or of the triazolyl isoimides.

The samples used for the spectra had the following melting points (°C): (Ia) 89-91; (Ib) 140-142; (Ic) 69-71; (Id) 121-122; (Ie) 123-124; (If) 126-128; (IIa) 163-165; (IIb) 142-143; (IIc) 140-141; (IId) 212-214.

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