Reference Data

¹³C NMR Spectra of 1-Amino-1,2,3triazole Derivatives

2*—Identification of 4,5-Unsymmetrically Substituted 1-(*N*,*N*-Diaroyl)amino-1,2,3-triazoles

NESTOR A. RODIOS Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece

The ¹³C NMR spectra of some 1-(*N*,*N*diaroyl)amino-1,2,3-triazole derivatives are reported. The shifts of the methyl carbons attached to the triazole ring and those of C-4 and C-5 of the ring were used to distinguish between 4,5unsymmetrically substituted derivatives. The location of a methyl group on the 4or 5-position of the ring can be also deduced from the ¹J CH₃ value. A complete assignment of the aroyl carbons of the imide moiety is given.

INTRODUCTION

In connection with our work on 1-amino-1,2,3-triazole derivatives,¹ we have prepared a series of 1-(N,N-diaroyl)amino-1,2,3-triazoles and studied their conformation in solution by dipole moment measurements.²



 $\begin{array}{c} 1 \ R^{1} = R^{2} = H, X = H \\ 2 \ R^{1} = H, R^{2} = CH_{3}, X = H \\ 3 \ R^{1} = R^{2} = CH_{3}, X = H \\ 4 \ R^{1} = R^{2} = CH_{3}, X = p - CH_{3} \\ 5 \ R^{1} = R^{2} = CH_{3}, X = p - CH_{3} \\ 6 \ R^{1} = R^{2} = CH_{3}, X = p - CH_{3} \\ 6 \ R^{1} = R^{2} = CH_{3}, X = p - CH_{3} \\ 7 \ R^{1} = R^{2} = CH_{3}, X = p - NO_{2} \\ 8 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - OCH_{3} \\ 10 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - OCH_{3} \\ 10 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - OCH_{3} \\ 11 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - OCH_{3} \\ 12 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - OL_{3} \\ 13 \ R^{1} = C_{6}H_{5}, R^{2} = CH_{3}, X = p - NO_{2} \\ 14 \ R^{1} = p - CH_{3}O - C_{6}H_{4}, R^{2} = CH_{3}, X = H \\ 15 \ R^{1} = p - CH_{3}O - C_{6}H_{4}, R^{2} = CH_{3}, X = H \\ 16 \ R^{1} = p - Br - C_{6}H_{4}, R^{2} = CH_{3}, X = H \\ \end{array}$

These compounds are of interest, since it has been found that their 4-aryl-5-methyl derivatives, but not the 4-methyl-5-aryl isomers, can be used as intermediates * For Part 1, see Ref. 1. for the preparation of condensed 1,2,3triazolo heterocycles, such as the 4H-3,6-diaryl[1,2,3]triazolo[1,5-d][1,3,4]oxadiazines.³ We have found that ¹³C NMR spectroscopy can be used as a rapid and easy method for distinguishing between the two possible isomers, and now report our results.

EXPERIMENTAL

¹H NMR spectra, reported in δ units, were recorded on a Varian A 60A or CFT-20 spectrometer in CDCl₃ solutions. ¹³C NMR spectra were obtained at 40 °C with a Varian CFT-20 spectrometer, operating in the FT mode at 20 MHz, using 10 mm diameter tubes; 0.1–0.4 M solutions in CDCl₃ containing 0.5% TMS were recorded, with broad band proton noise decoupling. Accumulations of 20–70 K transients were obtained, depending on the concentration of the solution. A flip angle between 30–40°, corresponding to a pulse width of 7–9 μ s, was employed with 8K transforms for a 4 kHz sweep width.

Melting points were obtained on a Kofler hot-stage apparatus.

1-(N,N-Diaroyl)amino-1,2,3-triazoles 1-16 were prepared² by thermal isomerization of the corresponding 1,2,3-triazolyl isoimides¹ as follows. A 1-2 g amount of the 1,2,3-triazolyl isoimide¹ was heated in an oil-bath up to the melting point, and the melt was kept at this temperature for 1 h. After cooling, the solidified product was treated with CH₂Cl₂ and diethyl ether, and the white crystals formed were isolated by filtration. They were recrystallized from CH₂Cl₂-diethyl ether mixtures. The yields were 85-95%.

The ¹H NMR parameters of compounds 1-16 are given in Table 2. Melting points and analytical data of the new compounds were as follows. 1, 193-195 °C; calc. for C₁₆H₁₂N₄O₂, C 65.75, H 4.14, N 19.17; found, C 68.89, H 4.22, N 19.42%. 2, 132-136 °C (lit.^{4a} 132–134 °C). 3, 97–99 °C (lit.^{4a} 94-96 °C). 4, 182-184 °C (lit.4a 184-186 °C). 5, 112-115 (lit.^{4b} 112-114 °C). 6, 148-150 °C (lit.4b 144-146 °C). 7, 188-191 °C (lit.^{4b} 187–190 °C). **8**, 155–158 °C (lit.^{4b} 153–157 °C). 9, 162–164 °C; calc. for C₂₅H₂₂N₄O₄, C 67.86, H 5.01, N 12.66; found, C 68.01, H 4.97, N 12.65%. 10, 185–196 °C; calc. for $C_{23}H_{16}Cl_2N_4O_2$, C 61.21, H 3.57, N 12.41; found, C 61.28, H 3.69, N 12.50%, 11, 147-150 °C; calc. for C₂₃H₁₆Cl₂N₄O₂, C 61.21, H 3.57, N 12.41; found, C 61.23, H 3.54, N 12.57%. 12, 175-185 °C; calc. for C23H16N6O6, C 58.48, H 3.41, N 17.79; found, C 58.46, H 3.60, N 17.80%. 13, 202-205 °C; calc. for

RESULTS AND DISCUSSION

The values of the ¹³C shifts and those of some coupling constants (values in parentheses) for the 1-(N,N-diaroyl)amino-1,2,3-triazoles **1–16** are given in Table 1. The assignments have been made by comparison with the analogous 1,2,3-triazolyl isoimides,¹ and by using the ¹H-coupled spectra as well as substituent chemical shift additivities.

Some substituent effects on the carbon chemical shifts are worth mentioning. Thus, the methyl group at the 5-position of the triazole ring in 2 causes a downfield shift of 9.1 ppm for C-5 and an upfield shift of 1.4 ppm for C-4, with respect to the unsubstituted compound 1. In the 4,5-dimethyl derivatives 3-7, both C-4 and C-5 are deshielded by approximately 6.5 and 5.0 ppm, respectively. In the 4-aryl-5-methyl derivatives 8-16, the aryl ring causes a downfield shift of approximately 11.0 ppm for C-4 and an upfield shift of approximately 4.0 ppm for C-5 with respect to the 5methyl derivative 2. The 4-aryl ring deshields 5-CH₃ by approximately 1.0 ppm, an effect that is also found in the ¹H NMR spectra of these compounds (Table 2). This might be explained by the tendency of the 4-phenyl ring to be coplanar with the triazole ring, thus causing the methyl group to be in the deshielding area of the phenyl ring.

It is also worth mentioning the difference found in the J(CH) values involving C-4 and C-5, as well as their attached methyl carbons. Thus, the J(CH) values of C-5 and 5-CH₃ are always larger than the corresponding J(CH) values of C-4 and 4-CH₃. Since the same behaviour has been found in other 1-substituted-1,2,3-triazole derivatives,^{1,5} it can be regarded as a general criterion for distinguishing between isomers of the 4,5-unsymmetrically substituted 1,2,3-triazoles.

CONCLUSIONS

The ¹³C NMR data of 1-(*N*,*N*-diaroyl)amino-1,2,3-triazoles can be used to

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Carbon 1	2	m	4	ŝ	9	7	80	6	10	F	12	13	14	15	16
C-4tr 13; (198	3.7 132.3 .6. (196.2.	140.3	140.1	140.1	Ð	141.0	143.5	143.4	143.8	143.5	144.2	143.5	143.4	142.6	142.5
10	.2 ^a) 3.6 ^b	~													
C-5tr 12((200	5.1 135.2 .2, (14.6, ^a	131.4	131.5	σ	131.5	131.2	131.4	σ	131.5	131.5	131.2	131.9	130.6	131.7	131.7
15	(7a) 7.9 ^c)														
4-CH ₃ –	1	10.8	10.7	10.7	10.7	10.7	ł		ļ	ł	1	I	I	I	1
5-CH ₃ –	- 7.7	7.3	(0.021) 7.2	7.2	(120.4) 7.1	7.2	8.6	8.6	8.6	9.0	8.7	8.5	8.6	8.7	8.6
•	(130.7)	,	(130.2)		(130.5)		(130.7)	(130.7)	(130.8)		(130.5)	(131.5)	(130.6)	(130.5)	(130.6)
C-1, 13.	1.6 131.7	131.9	128.6	123.9	129.8	136.4	131.8	123.8	129.7	132.4	136.3	129.5	131.7	131.7	131.7
C-2' D-6' 12!	.3 129.2	129.2	129.5	131.9	130.6	130.1	129.3	131.9	130.7	138.7 130.3	130.1	145.0 127.6	129.3	129.3	129.3
C-3' C-5' 12	1.9 128.9	128.9	129.5	114.2	129.3	124.1	128.9	114.3	129.4	129.3 126.9	124.2	124.5 131.5º	128.9	129.0	128.9
C-4/ 133	133.7	133.8	144.5	164.0	140.5	150.7	133.8	164.1	140.6	132.6	150.7	134.69	133.7	133.9	133.8
C=0 165	1.4 169.4	169.5	169.5	169.0	168.4	167.5	169.5	168.9	168.5	167.9	167.5	164.7	169.5	169.4	169.4
C-1" –	1	I	1		1		130.9	131.0	q	130.9	σ	130.4	123.4	129.3 ^f	129.8
C-2"							176.0	1 7 G R	126.0	176 0	176.8	176 B	128.2	128.1	128.2
ں-وڑ 1	1	ł	l	1	I	I	6.021	0.021	2021	6.021	0.021	0.021	7.071	1.021	0.021
ں-ع، ۲.		-					128.8	128.7	128.8	128.8	128.9	128.9	114.2	129.0	131.9
C-5,															
C-4"	1	1	-	I	I	ł	128.1	128.0	128.3	128.2	128.7	128.3	159.6	134.2	122.3
×			21.7 (127.3)	55.5				55.5 (144.7)					55.3 ^h (144.1)		
^a ² /(CCH)(H ₂) ^a ³ /(C,4, 5-CH ₃)(H) ² /(C-5, 5-CH ₃)(H) ² /(C-5, 5-CH ₃)(H) ¹ Masked by the ^a Masked by the ^b Masked by the ^c from the off-res ¹ The OCH ₃ groun	z). z). C-2' peak. C-4 peak. onance spect ay be interchi	rum. anged.													

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Table 2. ¹	H NMR sh	ifts (ô, pp	m from T	MS) and c	coupling co	onstants (F	łz, in pare	entheses) (of compou	nds 1-16						
Protons	- r	от	e 0	400	500	900	7 00	80	on.	10	11	12	13	14	15	16
4-CH ₃	/9// /21 2/	2	2.23 (2H c)	2.23	2777 (3H c)	2.23 (2H c)	2.23 (3H c)	1	I	I	I	ł	1	1	I	ł
5-CH,	7.67ª	2.21	2.17	2.14	2.15	2.10	2.15	2.40	2.38	2.37	2.55	2.41	2.61	2.37	2.38	2.39
0	(2H, s)	(3H, d) (0 EE)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)	(3H, s)
2′.6′	7.80	(cc.n) 7.85	7.95	7.80	7.83	7.84	7.97	7.89	7.88	7.82	7.67	7.99	7.65 ^d	7.88	7.82	7.88
	(4H, m)	(4H, m)	(4H, m)	(4H, d°)	(4H, d ^c)	(4H, d ^c)	(4H, d°)	(4H, m)	(4H, d°)	(4H, d ^c)	(4H, m)	(4H, d°)	(8H, m)	(4H, m)	(4H, m)	(4H, m)
				(8.0)	(8.6)	(8.4)	(8.8)		(8.8)	(8.8)		(6.3)				
3',(4'),5'	7.40	7.42	7.57	7.37	6.87	7.43	8.30	7.40	6.88	7.41	7.35	8.28	8.24 ^e	7.47	7.43	7.48
	(eH, m)	(eH, m)	(eH, m)	(4H, d ^c)	(4H, d°)	(4H, d°)	(4H, d ^c)	(9H, m)	(4H, d°)	(7H, m)	(9H, m)	(4H, d ^c)	(2H, m)	(eH, m)	(eH, m)	(eH, m)
				(8.0)	(8.6)	(8.4)	(8.8)		(8.8)	(8.8)		(6.3)				
2",6"	۱	I	I		1		1	7.7	7.69	7.68	4	7.60	8	7.59	7.56	7.51
•								(2H. m)	(2H, m)	(2H, m)		(2H, m)		(2H, d°)	(2H, d°)	(4H, s)
														(8.7)	(6.2)	
3",(4"),5"	-	-		1	1	1	١	ť	7.39	ء	ء	7.38	7.41	6.95	7.34	7.51
									(3H, m)			(3H, m)	(3H, m)	(2H, d°)	(2H, d ^c)	(4H, s)
														(8.7)	(9.2)	
×	۱	1		2.38	3.81	1	ł	I	3.80					3.91 ⁱ		
				(6H, s)	(6H, s)				(6H, s)					(3H, s)		
• H-4 and b H-4 mask • AA'BB' si given as th d H-4, H-5' f H-2'', H-6' f H-2'', H-6' f H-2'', H-6' f H-2'', H-6' f H-3'', H-6' f H-3'', H-6' f H-6'' f H-6'' H-6'' H-6	H-5 of the t (ed by the (jin system,) - J value. , H-6' of the le two aroy masked by masked by ' masked by	riazole ring aromatic pr the separa two aroy! groups. the peak t the peak	i gave one otons at δ fition betwe groups. of H-2′, H-1 of H-4′, H-1 peak of H-	s singlet at 5 = 7.42. 9en the two 6' at 8 = 7.6 -3', H-6' at 3. -3', H-4', H-	δ = 7.67, ir o main pea 67. 5 ⁸ = 7.65. 5 ⁴ at δ ≈ 7.	tegrating iks of each 4.	for 2H. AA' or BB	r part of th	ne spectrur	'si						

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determine the position of the substituents in 4,5-unsymmetrically substituted derivatives, $R^1 \neq R^2$. This can be found on the basis of the chemical shifts of C-4 and C-5 of the triazole ring, or on the shifts of their attached methyl groups. Thus, the 5-methyl derivatives show a peak for 5-CH₃ between 7.0 and 8.5 ppm, whereas in the 4-methyl derivatives 4-CH₃ absorbs at approximately 11.0 ppm. In the 4-aryl derivatives C-4 absorbs at 142.5-144.0 ppm, and in the 4methyl derivatives C-4 absorbs at 140.0-141.0 ppm. The position at which a methyl group is attached on to the triazole ring can also be determined by its ¹J(CH₃) value, REFERENCE DATA where ${}^{1}J(CH) = 130.5$ Hz demonstrates a

where ${}^{1}J(CH) = 130.5$ Hz demonstrates a methyl group in the 5-position, and ${}^{1}J(CH) = 128.5$ Hz shows a methyl group in the 4-position of the ring.

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