Reference Data

¹H and ¹³C NMR—Spectroscopy of Substituted 1,2,3-Triazoles

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ABSTRACT: 1-Aryl-4-carboxy-5-methyl-1,2,3-triazoles were prepared by the condensation of aryl azides with ethyl acetoacetate. The structures of these compounds were characterized by MS, IR and ¹H and ¹³C NMR spectroscopy. The measured and calculated ¹³C chemical shifts of the aromatic carbons were compared.

KEYWORDS: NMR; ¹H NMR; ¹³C NMR; 1,2,3-triazoles

INTRODUCTION

1,2,3-Triazole derivatives form an interesting class of compounds on account of their biological activities and their wide use in medicine, agriculture and industry.¹⁻⁴ In the past, we investigated the ¹³C NMR spectra of substituted 1,2,4-triazoles.⁵⁻⁷ In connection with our efforts in this area, we report now the spectroscopic characterization of substituted 1,2,3-triazoles. © 1998 John Wiley & Sons, Ltd.

RESULTS AND DISCUSSION

The condensation of aryl azides (1a–1) with ethyl acetoacetate (2) afforded the corresponding 1-aryl-4-carboxy-5-methyl-1,2,3-triazoles (3a–1) (Table 1). The structures of these compounds were confirmed by MS, IR and ¹H and ¹³C NMR and the results are given in Tables 2 and 3. The IR spectra of 3a–1 display an intense peak around 1690 cm⁻¹ due to the C=O function and a broad peak in the region 2566–3097 cm⁻¹ (bonded OH) or a sharp peak around 3500 cm⁻¹ (free OH). The absorption band in the range 1562–1578 cm⁻¹ is assigned to N=N and aromatic bonds.

The ¹H NMR spectra show the presence of the triazole methyl group in the range δ 2.30–2.51 ppm, whereas the aromatic protons resonate at δ 7.15–7.85 ppm. The ¹³C NMR spectra exhibit characteristic signals for C-4 and C-5 of the triazole ring at δ 135.85–136.62 and 138.93– 140.37 ppm, respectively. The C-12 signal of the carboxy group is at δ 162.43–162.64 ppm.

Compound **3i** was utilized to determine the influence of the heterocyclic ring on the aromatic carbons. The chemical shift increments induced by the heterocyclic ring are given in Table 4. The *para* carbon resonates at lower field than *ortho* and *meta* carbons, which reflects the electron-withdrawing ability of the 1,2,3-triazole group.

By adding the substituent effects⁸ of Cl, Br, CH_3 and CH_3O to the chemical shifts of **3i**, the chemical shifts of the aromatic carbons were calculated for **3a-h** and **3j-l**. The average error of the prediction was *ca*. 1 ppm. The larger deviations between the measured and the calculated shifts are observed for *ortho*-substituted derivatives due to the steric hindrance.

Finally, it was found that the C-6 chemical shifts could not be well correlated with Hammett's constants of the substituents.

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EXPERIMENTAL

Melting points were determined on a Kofler melting point apparatus and are uncorrected. MS was performed on an HP-5988A spectrometer (electron ionization at 70 eV). IR spectra were obtained in KBr discs on a Nicolet 170SX FT-IR spectrometer.

¹H NMR spectra were recorded at room temperature at 80 MHz on a Bruker FT-AC 80 instrument. ¹³C NMR spectra were obtained at 100.61 MHz on a Bruker AM 400 spectrometer operating in the complex pulse decoupling (CPD) mode. Spectra were recorded for solutions of about 20 mg of each compound in 0.5 ml of DMSO- d_6 and 5 mm NMR tubes were used. All chemical shifts were determined on the δ scale (ppm) relative to internal TMS.

¹H NMR spectra were recorded with spectral width 1362.4 Hz, acquisition time 1.5 s, pulse width for a 90° pulse 3.0 μ s and relaxation delay 1.0 s. Typical conditions for recording ¹³C NMR spectra were spectral width 23.8 kHz, acquisition time 0.688 s, pulse width for a 90° pulse 5.0 μ s, relaxation delay 2.0 s and number of data points 32 K.

The ¹³C chemical shift assignments were made on the basis of the additivity effects induced by the substituents, the signal intensities and data reported earlier for related compounds.⁹⁻¹¹ Compounds **3a-I** were prepared as described in the literature;¹² six are new compounds.

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R N3	0 0 ∥ ∥ + CH₃CCH₂COEt - 2	i) EtONa/EtOH ii) NaOH/H₂O	$N \xrightarrow{4} COOH$ $N \xrightarrow{5} CH3$ $11 \xrightarrow{6} 7 R^{14}$ $3 = 1$
Compound 3	Ar	Yield (%)	M.p. (°C)
a b c d e f g h i j k	$\begin{array}{c} p\text{-CIC}_{6}H_{4} \\ p\text{-CH}_{3}\text{OC}_{6}H_{4} \\ p\text{-CH}_{3}\text{C}_{6}H_{4} \\ p\text{-BrC}_{6}H_{4} \\ m\text{-CIC}_{6}H_{4} \\ m\text{-BrC}_{6}H_{4} \\ m\text{-BrC}_{6}H_{4} \\ c_{6}H_{5} \\ o\text{-CH}_{3}\text{OC}_{6}H_{4} \\ m\text{-CH} \subset H \end{array}$	80 71 56 64 67 55 58 51 45 50 47	$\begin{array}{c} 200-201\\ 179-180\\ 182-183\\ 201-202\\ 187-188\\ 165-166\\ 185-186\\ 157-158\\ 148-149\\ 169-170\\ 159-160\\ \end{array}$
ī	o-CH ₃ C ₆ H ₄	43	145–146

 Table 1. Structures, yields and melting points of 1-aryl-4carboxy-5-methyl-1,2,3-triazoles 3a–I

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Reference Data

Compound ^a 3	MS (<i>m</i> / <i>z</i>)	IR (cm ⁻¹) (KBr disc)	¹ H NMR (DMSO- d_6) δ (ppm), J (Hz)
a	237/239	2573–3076, 1694, 1565	7.68 (s, 4H, Ar), 2.49 (s, 3H, CH ₃)
b	233	2570–3027, 1684, 1569	7.54 (d, 2H, J = 8.83 Hz, Ar), 7.15 (d, 2H, J = 8.83 Hz, Ar), 3.85 (s, 3H, OCH ₃), 2.46 (s, 3H, CH ₃)
с	217	2566-3076, 1683, 1566	7.45 (s, 4H, Ar), 2.47 (s, 3H, CH ₃), 2.40 (s, 3H, ArCH ₃)
d	281/283	2570–3097, 1694, 1564	7.85 (d, 2H, $J = 8.56$ Hz, Ar), 7.59 (d, 2H, $J = 8.56$ Hz, Ar), 2.50 (s, 3H, CH ₃)
e	237/239	2570-3089, 1698, 1565	7.65 (m, 4H, Ar), 2.51 (s, 3H, CH ₃)
f	237/239	3488, 1690, 1576	7.70 (m, 4H, Ar), 2.33 (s, 3H, CH ₃)
g	281/283	2568-3089, 1698, 1562	7.71 (m, 4H, Ar), 2.51 (s, 3H, CH ₃)
h	281/283	3488, 1690, 1576	7.71 (m, 4H, Ar), 2.32 (s, 3H, CH ₃)
i	203	3550, 1697, 1570	7.63 (s, 5H, Ar), 2.50 (s, 3H, CH ₃)
j	233	3498, 1689, 1578	7.41 (m, 4H, Ar), 3.79 (s, 3H, OCH ₃), 2.30 (s, 3H, CH ₃)
k	217	3488, 1689, 1567	7.45 (m, 4H, Ar), 2.49 (s, 3H, CH ₃), 2.40 (s, 3H, ArCH ₃)
1	217	3479, 1686, 1574	7.48 (m, 4H, Ar), 2.30 (s, 3H, CH ₃), 1.96 (s, 3H, ArCH ₃)

Table 2. MS, IR and ¹H NMR spectral data for compounds 3a-I

^a Satisfactory microanalyses were obtained for all the compounds.

Table 3. ¹³C NMR spectral data for compounds 3a–I

Compound ^a											
3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14
a	136.60	139.22	134.71	127.29	129.75	134.12	129.75	127.29	162.52	9.67	
b	136.28	139.05	128.10	126.97	114.74	160.18	114.74	126.97	162.64	9.64	55.61
c	136.44	138.94	132.88	125.28	130.10	139.87	130.10	125.28	162.64	9.70	20.75
d	136.62	139.14	134.54	127.48	132.68	123.24	132.68	127.48	162.48	9.66	
e	136.56	139.26	136.43	125.45	133.89	130.06	131.30	124.32	162.47	9.64	
f	136.13	140.32	132.79	132.52	132.79	130.54	129.77	128.76	162.44	9.11	
g	136.52	139.31	136.52	128.24	122.07	132.99	131.55	124.72	162.50	9.68	
h	136.10	140.07	134.17	120.70	133.60	132.89	129.76	129.25	162.43	9.19	
i	136.49	138.96	135.28	125.44	129.68	130.00	129.68	125.44	162.56	9.69	
j	135.85	140.37	123.49	153.65	112.89	132.33	120.94	128.48	162.62	9.10	56.01
k	136.49	138.93	135.26	125.85	139.61	129.47	130.64	122.49	162.64	9.74	20.76
1	136.07	139.63	135.05	134.15	130.77	131.32	127.36	127.17	162.58	9.16	16.65

^a All spectra were recorded at 297 K.

Table 4. ¹³C NMR chemical shift increments ($\Delta \delta$, ppm) induced by the heterocyclic ring on the aromatic carbons

Compound	C-i	С-о	C-m	C-p
4-Carboxy-5-methyl-1-phenyl-1,2,3-triazole	6.78	-3.06	1.18	1.50

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