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Reference Data

^{1}H and ^{13}C 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 ^{1}H and ^{13}C NMR spectroscopy. The measured and calculated ^{13}C chemical shifts of the aromatic carbons were compared.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C 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 ^{13}C 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.

RESULTS AND DISCUSSION

The condensation of aryl azides (**1a–l**) with ethyl acetoacetate (**2**) afforded the corresponding 1-aryl-4-carboxy-5-methyl-1,2,3-triazoles (**3a–l**) (Table 1). The structures of these compounds were confirmed by MS, IR and ^{1}H and ^{13}C NMR and the results are given in Tables 2 and 3. The IR spectra of **3a–l** 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 ^{1}H 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 ^{13}C 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 effects[8] 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.

^{1}H NMR spectra were recorded at room temperature at 80 MHz on a Bruker FT-AC 80 instrument. ^{13}C 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.

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

The ^{13}C 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–l** were prepared as described in the literature;[12] six are new compounds.

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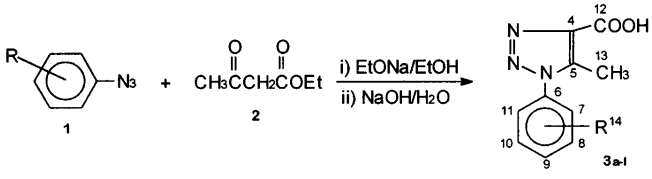
Table 1. Structures, yields and melting points of 1-aryl-4-carboxy-5-methyl-1,2,3-triazoles **3a–l**



Compound **3**	Ar	Yield (%)	M.p. (°C)
a	*p*-ClC_6H_4	80	200–201
b	*p*-$CH_3OC_6H_4$	71	179–180
c	*p*-$CH_3C_6H_4$	56	182–183
d	*p*-BrC_6H_4	64	201–202
e	*m*-ClC_6H_4	67	187–188
f	*o*-ClC_6H_4	55	165–166
g	*m*-BrC_6H_4	58	185–186
h	*o*-BrC_6H_4	51	157–158
i	C_6H_5	45	148–149
j	*o*-$CH_3OC_6H_4$	50	169–170
k	*m*-$CH_3C_6H_4$	47	159–160
l	*o*-$CH_3C_6H_4$	43	145–146

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Table 2. MS, IR and ^{1}H NMR spectral data for compounds **3a–l**

Compound[a] **3**	MS (*m/z*)	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)
c	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, $ArCH_3$)
l	217	3479, 1686, 1574	7.48 (m, 4H, Ar), 2.30 (s, 3H, CH_3), 1.96 (s, 3H, $ArCH_3$)

[a] Satisfactory microanalyses were obtained for all the compounds.

Table 3. ^{13}C NMR spectral data for compounds **3a–l**

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
l	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. ^{13}C NMR chemical shift increments ($\Delta\delta$, ppm) induced by the heterocyclic ring on the aromatic carbons

Compound	C-*i*	C-*o*	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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