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Reference Data

^{1}H and ^{13}C NMR Spectroscopy of Substituted Tris-1,3,4-oxadiazoles

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1,3,5-Tris(5-substituted-1,3,4-oxadiazol-2-yl)benzenes were prepared by the dehydration of the corresponding hydrazides. The structures of these compounds were elucidated by IR, ^{1}H and ^{13}C NMR spectroscopy. © 1997 by John Wiley & Sons, Ltd.

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INTRODUCTION

The interest in 1,3,4-oxadiazole chemistry stems from their biological activities and their wide use in medicine, agriculture and industry.[1–6] Recently, we reported the synthesis and the characterization of substituted bis-1,3,4-oxadiazoles.[7–9] Reports concerned with the synthesis of substituted tris-1,3,4-oxadiazoles have, in comparison, remained rare.[10,11] In continuation of our efforts in this area, we report here results on the synthesis and spectroscopic characterization of substituted tris-1,3,4-oxadiazoles.

RESULTS AND DISCUSSION

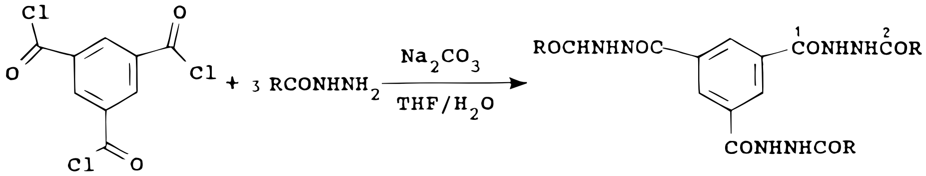
The reaction of 1,3,5-benzenetricarboxylic acid trichloride (**1**) with three equivalents of the acid hydrazides **2a–h** gave the corresponding 1,3,5-benzenetris(2′-substituted carbohydrazides) **3a–h** (Table 1). The structures of these compounds were studied by IR, ^{1}H and ^{13}C NMR and the results are given in Tables 2 and 3. The IR spectra of **3a–h** display moderate absorptions in the range 3300–3140 cm^{-1}, assigned to NH stretching, and in the range 1680–1640 cm^{-1}, assigned to the C=O and aromatic bonds.

The ^{13}C NMR spectra exhibit characteristic signals in the range 157.1–169.2 ppm, assigned to C-1 and C-2 of the hydrazide carbonyls. The chemical shift of C-2 was found to be strongly dependent on the nature of the substituent R, when R = 2-furyl or 2-thienyl, C-2 resonates in the range 157.1–160.6 ppm. For R = phenyl or substituted phenyl the C-2 signal is at δ 164.2–165.6 ppm. For R = alkyl, C-2 resonates at 168.3–169.2 ppm.

Dehydration of **3a–h** with phosphorus oxychloride in acetonitrile afforded the substituted tris-1,3,4-oxadiazoles **4a–h** in good yields (Table 4). The structures of these compounds were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy and the results are given in Tables 5 and 6. The IR spectra of **4a–h** display moderate to strong absorptions in the range 1640–1600 cm^{-1}, assigned to C=N bonds, in addition to strong absorptions in the range 1580–1540 cm^{-1}, assigned to aromatic bonds. The ^{1}H and ^{13}C NMR were in full agreement with the assigned structures.

The ^{13}C NMR spectra exhibit characteristic signals for C-2 of the oxadiazole ring at δ 164.1–161.4 ppm, whereas the C-5 signals are at δ 166.5–157.5 ppm and show a strong dependence on the nature of substituent R as in the case of **3a–h**.

Table 1. Structures, yields and melting points of substituted 1,3,5-benzenetris(2′-substituted carbohydrazides) 3a–h



3 a—h

Compound 3	Ar	Yield (%)	M.p. (°C)
a	C_6H_5	95	206–210
b	p-$CH_3C_6H_4$	98	193–196
c	p-$CH_3OC_6H_4$	87	199–202
d	p-$O_2NC_6H_4$	83	314–316
e	2-Furyl	98	245[a]
f	2-Thienyl	97	212[a]
g	$C_6H_5CH_2$	74	313–314
h[b]	CH_3	57	328–331

[a] Decomposition above this temperature.
[b] Triacetyl derivative.

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Table 2. ^{1}H NMR spectral data for compounds 3a–h

Compound[a] 3	IR (cm^{-1}) (KBr disc)	^{1}H NMR (DMSO-d_6) δ (ppm), J (Hz)[b]
a	3240, 1655	10.73 (s, 6H, NH), 8.67 (s, 3H, Ar), 7.52–8.01 (m, 15H, Ar)
b	3210, 1670, 1640	10.57, 10.80 (b, 6H, NH), 8.68 (s, 3H, Ar), 7.87 (d, 6H, J = 8.0 Hz, Ar), 7.34 (d, J = 8.0 Hz, Ar), 2.39 (s, 9H, CH_3)
c	3320, 1680, 1640	10.49, 10.75 (b, 6H, NH), 8.68 (s, 3H, Ar), 7.95 (d, 6H, J = 8.7 Hz, Ar), 7.07 (d, 6H, J = 8.7 Hz, Ar), 3.84 (s, 9H, OCH_3)
d	3200, 1680, 1635	11.09 (b, 6H, NH), 8.75 (s, 3H, Ar), 8.40 (d, 6H, J = 8.8 Hz, Ar), 8.20 (d, 6H, J = 8.8 Hz, Ar)
e	3300, 1680	10.86 (b, 6H, NH), 8.63 (s, 3H, Ar), 7.29 (d, 3H, J = 3.2 Hz), 6.72 (b, 3H)
f	3210, 1640	10.86, 10.64 (b, 6H, NH), 8.60 (s, 3H, Ar), 7.87 (d, 6H, J = 4.9 Hz), 7.23 (t, 3H, J = 4.4 Hz)
g	3140, 1640, 1600	10.34, 9.98 (b, 6H, NH), 8.52 (s, 3H, Ar), 7.21–7.34 (m, 15H, Ph), 3.57 (s, 6H, CH_2)
h	3220, 1680, 1640	10.63, 10.35 (b, 6H, NH), 8.49 (s, 3H, Ar), 1.96 (s, 9H, CH_3)

[a] Satisfactory microanalyses were obtained for all the compounds.
[b] All spectra were recorded at 298 K.

EXPERIMENTAL

Melting points were measured on an electrothermal digital melting point apparatus. ^{13}C NMR spectra were recorded in the PFT mode at ambient temperature with internal deuterium lock using a Bruker WP 80-SY spectrometer (20 MHz). The pulse duration was 3 μs and the sweep width was 4500 Hz. The ^{1}H NMR spectra were recorded on a Bruker WP 80-SY spectrometer (80 MHz). The pulse duration was 1 μs and the sweep width was 800–1050 Hz. All chemical shifts were determined on the δ scale (ppm) relative to internal tetramethylsilane. The ^{13}C chemical shifts assignments are based on coupling information, substituent effects and data reported earlier for related compounds.[9] IR spectra were recorded on a Pye Unicam SP 30 spectrophotometer as potassium bromide pellets.

Compounds

Acid hydrazides **2a**–**h** were prepared as described in the literature.[12]

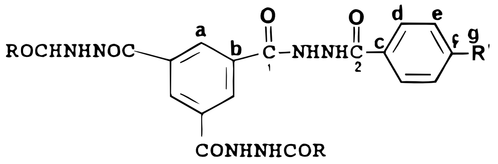
General procedure for the preparation of compound 3a–h

A solution of 1,3,5-benzenetricarboxylic acid trichloride **1** (2.66 g, 0.01 mol) in tetrahydrofuran (THF) (20 ml) was added with stirring to a solution of one of the acid hydrazides **2a**–**h** (0.03 mol) and potassium carbonate (4.2 g, 0.03 mol) in a mixture of water (120 ml) and THF (40 ml). The reaction mixture was stirred for 1–3 h. The resulting solid was collected by filtration, washed with water and dried. Recrystallization from dimethyl sulfoxide–water (1 : 1) afforded the products as white powders.

General procedure for the preparation of compounds 4a–h

A solution of one of compounds **3a**–**h** (7.5 mmol) and phosphorus oxychloride (46 g, 0.3 mol) in acetonitrile (100 ml) was heated under reflux for 2–5 h. The reaction mixture was cooled to room temperature and then rapidly added to an ice–water slush (150 ml). The precipitate was filtered, washed with cold water and dried. Recrystallization from dimethyl sulfoxide–water (9 : 1) afforded the products.

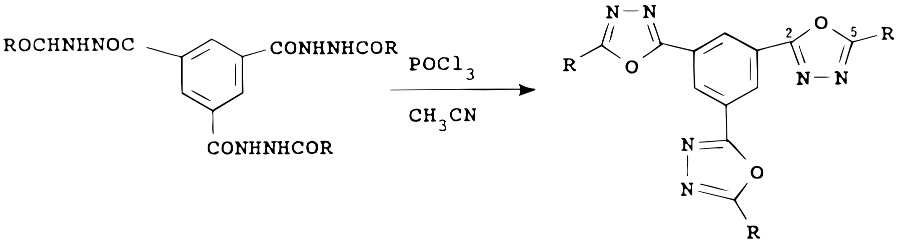
Table 3. ^{13}C NMR spectral data for compounds 3a–h



Compound[a] 3	C-1	C-2	C-a	C-b	C-c	C-d	C-e	C-f	C-g
a	164.8	165.6	129.6	131.8	133.5	128.4	127.4	132.4	
b	164.9	165.6	127.8	129.2	141.9	129.0	127.5	133.5	21.0
c	164.9	165.2	124.5	129.7	133.5	129.3	113.7	162.0	55.3
d	164.8	164.2	123.4	128.4	138.1	129.1	123.7	131.3	
e	164.8	157.1	129.6	133.4	146.2	114.6	111.8	145.7	
f	164.9	160.6	128.1	129.9	137.1	133.4	129.7	131.6	
g	164.3	169.2	126.4	129.5	135.6	128.9	128.1	133.1	40.3
h	164.4	168.3	129.4	133.4					20.5

[a] All spectra were recorded in DMSO-d_6 at 298 K.

Table 4. Structures, yields and melting points of 1,3,5-tris(5-substituted-1,3,4-oxadiazole-2-yl)benzenes 4a–h



4 a–h

Compound 4	R	Yield (%)	M.p. (°C)
a	C_6H_5	80	311–314
b	$4\text{-}CH_3C_6H_4$	93	281–285
c	$4\text{-}CH_3OC_6H_4$	96	299–302
d	$4\text{-}O_2NC_6H_4$	43	271–274
e	2-Furyl	86	292–296
f	2-Thienyl	85	329–330
g	$C_6H_5CH_2$	78	132–134
h	CH_3	62	215–219

Table 5. IR and ^{1}H NMR spectral data for compounds 4a–h

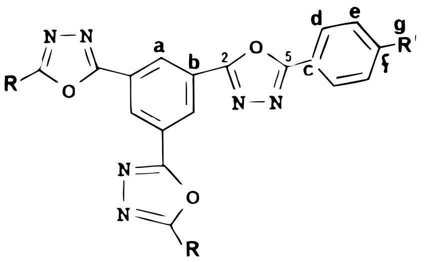
Compound[a] 4	IR (cm^{-1}) (KBr disc)	^{1}H NMR (DMSO-d_6)[b] δ (ppm), J (Hz)
a	1610, 1550	8.80 (s, 3H, Ar), 8.11–8.15 (m, 9H, Ar), 7.57–7.62 (m, 6H, Ar)
b	1620, 1550	8.73 (s, 3H, Ar), 7.98 (d, 6H, J = 8.0 Hz, Ar), 7.38 (d, 6H, J = 8.05 Hz, Ar), 2.39 (s, 9H, CH_3)
c	1620, 1510	8.77 (s, 3H, Ar), 8.07 (d, 6H, J = 8.5 Hz, Ar), 7.14 (d, 6H, J = 8.5 Hz, Ar), 3.88 (s, 9H, OCH_3)
d	1600, 1520	8.80 (s, 3H, Ar), 8.40–8.44 (m, 12H, Ar)
e	1625, 1540	8.63 (s, 3H, Ar), 8.05 (d, 3H, J = 1.4 Hz), 7.49 (d, 3H, J = 3.4 Hz), 6.81 (b, 3H)
f	1580, 1540	8.65 (s, 3H, Ar), 7.95 (t, 6H, J = 4.9 Hz), 7.27 (t, 3H, J = 4.4 Hz)
g	1640, 1550	8.55 (s, 3H, Ar), 7.40 (bm, 15H, Ph), 4.14 (s, 6H, CH_2)
h	1640, 1580	8.37 (s, 3H, Ar), 2.63 (s, 9H, CH_3)

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

[b] All spectra were recorded at 298 K.

Reference Data

Table 6. ^{13}C NMR spectral data for compounds 4a–h



Compound[a] 4	C-2	C-5	C-a	C-b	C-c	C-d	C-e	C-f	C-g
a	164.1	166.6	124.9	127.6	133.7	130.8	128.7	128.5	
b	161.9	164.7	125.8	126.3	142.2	126.8	126.3	129.5	20.9
c	162.9	165.1	126.3	126.7	129.0	115.9	115.3	162.3	55.8
d	163.8	165.5	124.4	128.3	133.0	130.9	128.8	149.6	
e	161.4	157.5	125.4	126.4	147.3	115.5	112.6	138.2	
f	161.9	161.2	123.9	125.7	132.1	131.2	126.7	128.7	
g	162.6	166.4	125.7	126.2	134.2	128.9	128.7	127.2	30.8
h	162.0	164.7	125.4	125.6					20.5

[a] All spectra were recorded in DMSO-d_6 at 298 K.

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References

1. F. Pochat, *Synthesis* **2**, 146 (1984).
2. L. V. Nargund, G. R. Reddy and V. Hariprasad, *J. Pharm. Sci.* **83**, 246 (1994).
3. A. R. Blem, H. L. Plant and R. R. Riegis, *US Pat.* 4914703 (1990); *Chem. Abstr.* **113**, 147259b (1990).
4. L. S. Yadav, R. K. Tripathi and H. S. Rajesh, *J. Agric. Food Chem.* **39**, 1863 (1991).
5. W. D. Rangnekar and C. R. Phadke, *Dyes Pigm.* **6**, 293 (1985).
6. K. Nagai, M. Oota, H. Sakom and Ch. Adachi, *Jpn. Pat.* 06107648 (1994); *Chem. Abstr.* **121**, 134124u (1994).
7. M. Al-Talib, H. Tashtoush and N. Odeh, *Synth. Commun.* **20**, 1811 (1990).
8. H. Tashtoush, M. Al-Talib and N. Odeh, *Liebigs Ann. Chem.* **1992**, 291.
9. H. Tashtoush, M. Al-Talib and N. Odeh, *Magn. Reson. Chem.* **30**, 910 (1992).
10. K. Natio and A. Miura, *J. Phys. Chem.* **97**, 6240 (1993).
11. K. Natio, *Jpn. Pat.* 05202011 (1993); *Chem. Abstr.* **120**, 90771a (1994).
12. H. T. Clarke and A. W. Davis, *Organic Synthesis*, Vol. 1, p. 261. Wiley, New York (1941).