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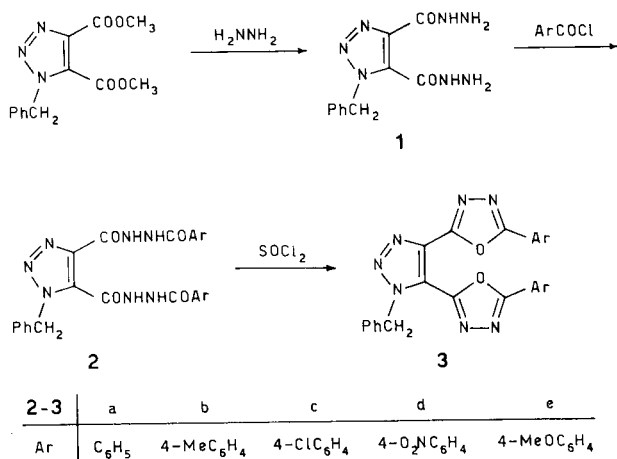
The synthesis of the title compounds **3** upon cyclodehydration with thionyl chloride of the corresponding bis-arylohydrazides **2** is described and their spectral properties are examined.

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The synthesis of 1,3,4-oxadiazole derivatives has attracted considerable attention mainly in connection with their wide range of applications [1,2] and especially their fluorescence and scintillation properties [3]. Although many 2,5-bis-substituted-1,3,4-oxadiazoles [1,4] and several polyaryles with alternating phenyl and 1,3,4-oxadiazole rings have been prepared [5-8] and their spectral behaviour has been reported, very little is known for analogous 1,3,4-oxadiazoles attached to a heterocyclic ring. For this reason we undertook the synthesis of the title bisoxadiazolyltriazoles **3** in order to examine their spectral properties in relation to other bis-1,3,4-oxadiazole systems.

Compounds **3** were prepared using 1-benzyl-4,5-bis(hydrazino)carbonyl-1,2,3-triazole (**1**) as starting material [9], according to Scheme 1. Thus, arylation of the bishydrazide **1** with the appropriate aryl chloride, in the presence of a mild base like pyridine, gave the corresponding 4,5-bis[*N'*-aryl-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazoles **2a-e** in very good yields (55-85%). Cyclization of the latter compounds has been effected using thionyl chloride as the dehydrating agent and gave the 4,5-bis[5-aryl-1,3,4-oxadiazol-2-yl]-1-benzyl-1,2,3-triazoles **3a-e** as the only isolated product (Table 1).

Scheme 1



The uv spectra of bisoxadiazolyltriazoles **3** consists of two main absorption bands. The first band with  $\lambda$  max at 206-216 nm could be attributed to the 1,2,3-triazole ring, in agreement with earlier reports [10]. The other absorption band is observed at longer wavelengths ( $\lambda$  max 267-299 nm), and it is characteristic of 2-aryl-1,3,4-oxadiazoles [6]. Similar absorption maxima have also been recorded for the 1,3-bis[5-aryl-1,3,4-oxadiazol-2-yl]ben-

zenes ( $\lambda$  max 250-286 nm) [7], whereas the more conjugated 1,4-bis[5-aryl-1,3,4-oxadiazol-2-yl]benzenes showed a bathochromic shift with  $\lambda$  max at 312-330 nm [8]. These results indicate that whereas for compounds **3** there is the possibility of conjugation between the triazole and the two oxadiazole rings, strong steric interactions probably prohibit this conjugation.

In ir spectra the title compounds **3** show the typical absorptions for the oxadiazole ring at 1580-1610 and 1020-1030 cm<sup>-1</sup> (C=N and C-O respectively), which are recorded with medium intensity [1], whereas the precursor compounds **2** exhibit strong absorptions at 3320-3260 cm<sup>-1</sup> (N-H), at 1690-1680 cm<sup>-1</sup> for the carbonyl group attached to the triazole ring and at 1660-1620 cm<sup>-1</sup> for the carbonyl next to the aryl group.

The compounds **3** show in <sup>1</sup>H-nmr spectra peaks for the aromatic protons at the expected shift values, the *o*-aromatic protons attached to the oxadiazole rings being resonating at lower field ( $\delta$  7.60-8.25), whereas the benzylic protons attached to the triazole ring resonate at  $\delta$  6.16-6.20.

Scheme 2

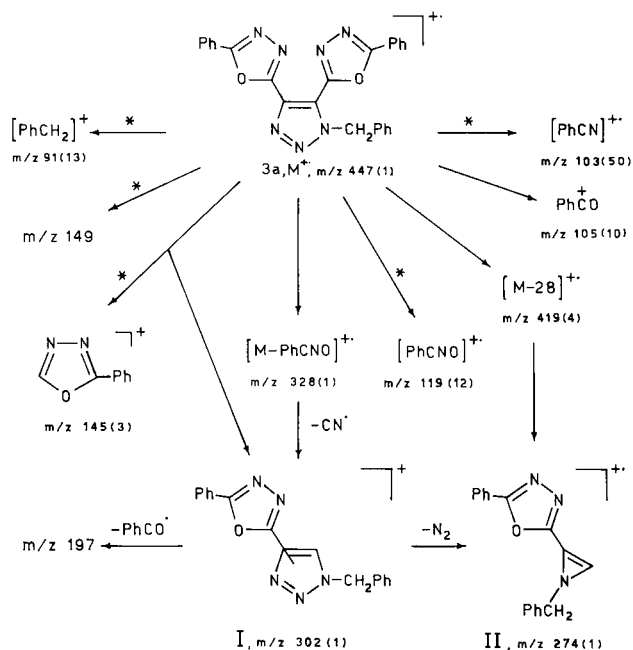


Table 1  
Physical, Spectral and Analytical Data of Compounds 3

Compound	Yield (%)	Mp (°C)	UV absorption spectra [a] $\lambda$ max/nm (log $\epsilon$ )	<sup>1</sup> H-nmr deuteriochloroform, ( $\delta$ ppm)	MS m/z (% Relative Intensity)	Formula M W	Elemental Analysis (%)											
							Calcd. (Found)	C	H	N								
<b>3a</b>	75	213-216	214 (4.16) 267 (4.32) 290 [b] (4.24)	6.20 (s, 2H), 7.20-7.60 (m, 11H), 8.00-8.25 (m, 4H)	447 (M <sup>+</sup> , 1), 419 (4), 328 (1), 302 (1), 274 (2), 253 (4), 197 (2), 149 (11), 145 (3), 119 (12), 105 (13), 103 (50), 91 (13), 77 (100)	C <sub>25</sub> H <sub>17</sub> N <sub>7</sub> O <sub>2</sub> 447.2	67.08 (66.96)	3.83 (3.70)	21.92 (22.02)									
										<b>3b</b>	61	212-215	2.40 (s, 6H), 6.15 (s, 2H), 7.08-7.28 (m, 9H), 7.63-8.12 (m, 4H)	475 (M <sup>+</sup> , 1), 380 (1), 326 (1), 149 (37), 141 (41), 119 (23), 117 (21), 91 (33), 78 (100)	C <sub>27</sub> H <sub>21</sub> N <sub>7</sub> O <sub>2</sub> 475.2	68.18 (67.88)	4.45 (4.45)	20.63 (20.48)
<b>3d</b>	41	287-291	6.20 (s, 2H), 7.18 (m, 5H), 8.15-8.48 (m, 8H)	507 (M <sup>+</sup> , -), 311 (100), 210 (7), 167 (14), 150 (92), 104 (42), 79 (85)	C <sub>25</sub> H <sub>15</sub> N <sub>9</sub> O <sub>6</sub> 537.2	55.85 (55.62)	2.81 (2.78)	23.46 (23.38)										
									<b>3e</b>	91	180-184	3.86 (s, 6H), 6.18 (s, 2H), 6.86-7.08 (dd, 4H), 7.18-7.50 (m, 5H), 7.95-8.12 (m, 4H)	507 (M <sup>+</sup> , 1), 439 (1), 296 (1), 278 (1), 209 (7), 149 (32), 133 (11), 91 (15), 76 (100)	C <sub>27</sub> H <sub>21</sub> N <sub>7</sub> O <sub>4</sub> 507.2	63.87 (63.66)	4.17 (4.13)	19.33 (19.24)	

[a] In absolute ethanol solution. [b] Shoulder.

In the mass spectra of the compounds **3** the whole fragmentation pattern is in agreement with that expected for the 1,2,3-triazole [11] and 1,3,4-oxadiazole [12] ring systems. Thus, these compounds besides the molecular ion  $M^{+}$  give peaks corresponding to  $[M-N_2]^+$  and  $[M-ArCNO]^+$ , as well as the fragments  $[ArCN]^+$ ,  $[ArCNO]^+$ ,  $[ArCO]^+$  and  $[PhCH_2]^+$ . They also give peaks corresponding to ions **I** and **II** shown in Scheme 2, where a fragmentation pattern for compound **3a** is shown.

Bis-oxadiazolyltriazoles **3** also exhibit strong fluorescence in ethanolic solutions on stimulation by uv-irradiation [1,2], which is detectable even at concentrations as low as  $10^{-7}$  M. The compound **3e** upon excitation at 275 nm shows an emission spectrum (Figure 1), which at  $\lambda_{max}$  420 nm has two fold fluorescence intensity of that recorded for a sulfate quinine solution with the same concentration, at  $\lambda_{max}$  460 nm.

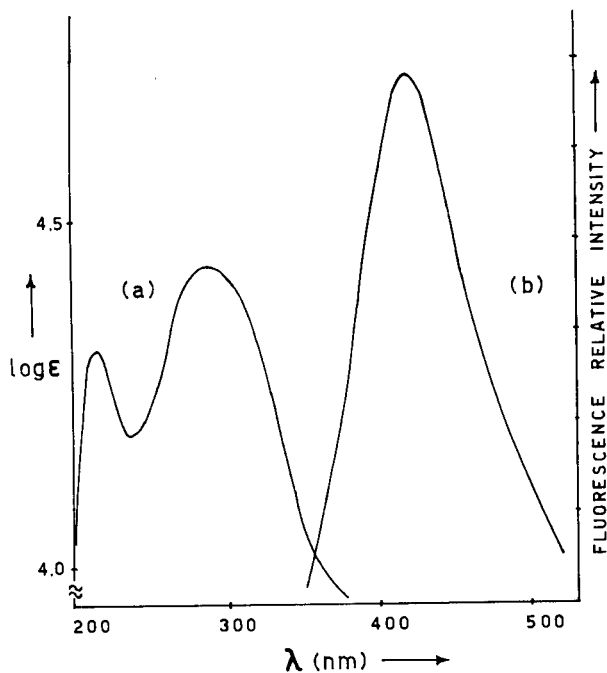


Figure 1. Absorption (a) and fluorescence (b) spectrum of compound **3e**.

## EXPERIMENTAL

Melting points were determined on a Kofler hot stage apparatus and are uncorrected. The ir spectra were measured with Perkin-Elmer 297 spectrometer and the  $^1H$ -nmr spectra, reported in  $\delta$  units, were recorded on a AW-80 Bruker spectrometer using TMS as internal standard. The uv spectra were carried out with a Shimadzu UV 210A double beam spectrophotometer and the fluorescence spectra recorded on a Perkin-Elmer 3000 spectrometer. The mass spectra were measured with a Hitachi-Perkin-Elmer model RMU-6L spectrometer, with an ionization energy of 70 eV, at temperature in the ion source between 180-350°. Elemental microanalyses were performed with a Perkin-Elmer 240B CHN analyser.

Synthesis of 4,5-bis[*N'*-aroyl-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazoles **2a-e**.

### General Procedure.

Aroyl chloride (3.3 mmoles) was added gradually to a stirred solution of the bishydrazide **1** (825 mg, 3 mmoles) in dry pyridine (20 ml). The mixture stirred for 12 hours at room temperature and the solvent removed *in vacuo*. The residual light yellow oil was crystallized with time or upon addition of diethyl ether and was recrystallized to give compounds **2a-e**.

4,5-Bis[*N'*-benzoyl-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazole (**2a**).

Recrystallization from pyridine-ethanol gave compound **2a** in 81% yield, mp 257-260°; ir (nujol): 3300 and 3180 (NH), 1680 and 1650 (C=O)  $cm^{-1}$ ; ms:  $m/z$  483 ( $M^{+}$ , 1), 379 (1), 319 (1), 214 (6), 136 (6), 105 (100).

Anal. Calcd. for  $C_{25}H_{21}N_7O_4$ : C, 62.08; H, 4.38; N, 20.29. Found: C, 61.87; H, 4.29; N, 20.13.

4,5-Bis[*N'*-(*p*-methylbenzoyl)-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazole (**2b**).

Recrystallization from ethanol afforded compound **2b** in 55% yield, mp 239-243°; ir (nujol): 3260 and 3180 (NH), 1690 and 1670 (C=O)  $cm^{-1}$ ; ms:  $m/z$  511 ( $M^{+}$ , 1), 420 (3), 392 (2), 362 (2), 278 (7), 153 (100).

Anal. Calcd. for  $C_{27}H_{25}N_7O_4$ : C, 63.37; H, 4.93; N, 19.17. Found: C, 63.41; H, 4.95; N, 19.05.

4,5-Bis[*N'*-(*p*-chlorobenzoyl)-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazole (**2c**).

Recrystallization from ethanol gave compound **2c** in 60% yield, mp 263-266°; ir (nujol): 3260 and 3180 (NH), 1690 and 1660 (C=O)  $cm^{-1}$ ; ms:  $m/z$  553/551 ( $M^{+}$ , -), 223 (8), 212 (12), 181 (22), 169 (40), 91 (100).

Anal. Calcd. for  $C_{25}H_{19}N_7O_4Cl_2$ : C, 54.34; H, 3.47; N, 17.76. Found: C, 54.42; H, 3.52; N, 17.69.

4,5-Bis[*N'*-(*p*-nitrobenzoyl)-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazole (**2d**).

Recrystallization from ethanol afforded compound **2d** in 58% yield, mp 271-275°; ir (nujol): 3240 and 3160 (NH), 1690 and 1670 (C=O)  $cm^{-1}$ ; ms:  $m/z$  573 ( $M^{+}$ , -), 337 (1), 312 (10), 207 (1), 104 (100).

Anal. Calcd. for  $C_{25}H_{19}N_7O_6$ : C, 52.34; H, 3.34; N, 21.99. Found: C, 52.39; H, 3.42; N, 22.07.

4,5-Bis[*N'*-(*p*-methoxybenzoyl)-*N*-hydrazinocarbonyl]-1-benzyl-1,2,3-triazole (**2e**).

Recrystallization from ethanol gave compound **2e** in 85% yield, mp 233-234°; ir (nujol): 3240 and 3160 (NH), 1690 and 1670 (C=O)  $cm^{-1}$ ; ms:  $m/z$  543 ( $M^{+}$ , -), 324 (1), 282 (5), 192 (20), 165 (7), 135 (100).

Anal. Calcd. for  $C_{27}H_{25}N_7O_6$ : C, 59.64; H, 4.64; N, 18.05. Found: C, 59.79; H, 4.48; N, 17.98.

Synthesis of 4,5-Bis[5-aryl-1,3,4-oxadiazol-2-yl]-1-benzyl-1,2,3-triazoles **3a-e**.

### General Procedure.

Freshly distilled thionyl chloride (1 ml, 14 mmoles) was added gradually to a suspension of the corresponding compound **2** (1 mmole) in 15 ml dry benzene and the mixture reflux until a clear

solution obtained (2-15 hours). The solvent and the excess thionyl chloride then evaporated *in vacuo* and the remaining crude solid **3** was recrystallized from benzene. Yields and other data are given in Table 1.

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