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Synthesis of 2-Hetaryl-5-phenyl-1,3,4-oxadiazole and Bis-1,3,4-oxadiazole Derivatives and Their Use as Fluorescent Whiteners for Polyester Fibres

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SUMMARY

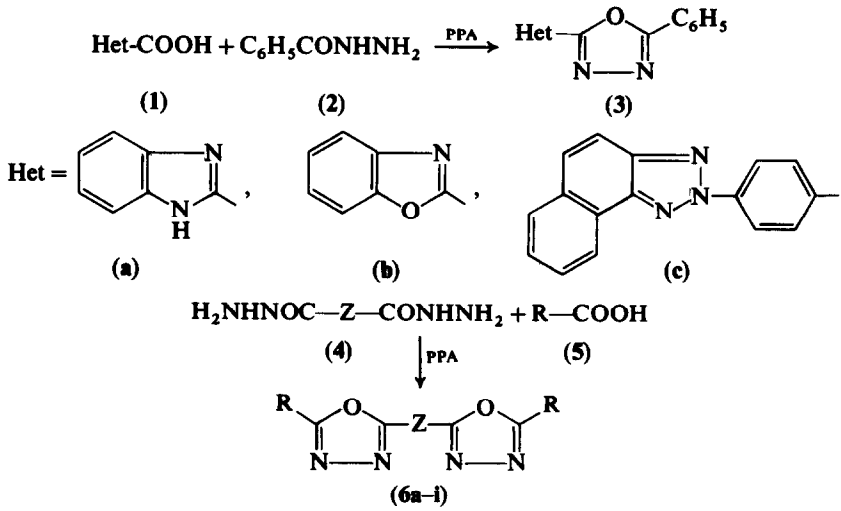
Heterocyclic carboxylic acids (**1**) *and benzoyl hydrazide* (**2**) *were condensed in the presence of polyphosphoric acid to give yellow to colourless compounds* (**3**) *which could be applied on polyester fibres as fluorescent whiteners. The dihydrazides* (**4**) *were condensed with aromatic acids* (**5**) *in the presence of polyphosphoric acid to yield bis-1,3,4-oxadiazole derivatives* (**6**). *These could also be used as fluorescent whiteners for polyester fibres. The spectroscopic properties in relation to the structural features of the compounds are discussed.*

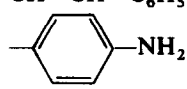
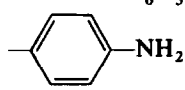
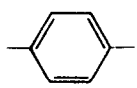
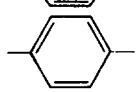
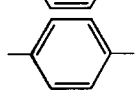
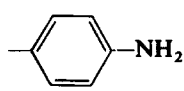
1. INTRODUCTION

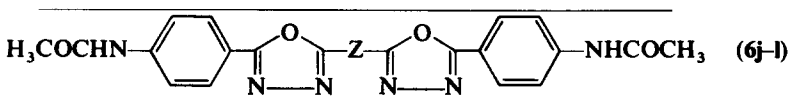
The use of colourless compounds which fluoresce in daylight as fluorescent whiteners to give a white appearance to yellow fabrics is of comparatively recent origin. Stilbene derivatives are commonly used for cotton.[1] The introduction of synthetic fibres has created a demand for water-insoluble fluorescent whiteners and a wide variety of heterocyclic compounds[2] have been reported to be useful as fluorescent whiteners. Many 1,3,4-oxadiazole derivatives have been described[3] as fluorescent whiteners for synthetic fibres.

On the basis that extended conjugation is one of the essential criteria for a compound to possess fluorescent properties, it was felt to be of interest to synthesise compounds having a fluorophore such as 1,3,4-oxadiazole and to couple it with an extended conjugated system and to

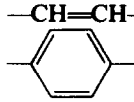
Dyes and Pigments 0143-7208/85/$03·30



Z	*R*	*Compd*
Direct bond	C_6H_5	**6a**
Direct bond	CH=CH—C_6H_5	**6b**
Direct bond		**6c**
—CH=CH—	C_6H_5	**6d**
—CH=CH—	CH=CH—C_6H_5	**6e**
—CH=CH—		**6f**
	C_6H_5	**6g**
	CH=CH—C_6H_5	**6h**
		**6i**



(6j–l)

Z	*Compd*
Direct bond	**6j**
—CH=CH—	**6k**
	**6l**

Scheme 1.

study the fluorescent properties of the compounds thus obtained. We report here the synthesis of 2-hetaryl-5-phenyl-1,3,4-oxadiazole derivatives and of bis-1,3,4-oxadiazole derivatives and their use as fluorescent whiteners for polyester fibres.

To obtain compounds which may possess fluorescent properties it was decided to introduce known fluorophores like benzoxazole and a triazole and also benzimidazole as substituents at the 2-position of the 1,3,4-oxadiazole moiety. However, in the case of bis-1,3,4-oxadiazoles we have also synthesised series of bis-1,3,4-oxadiazoles having different linkages between the two oxadiazole moieties. The various linkages incorporated as a bridge between the two oxadiazole moieties are (1) direct, (2) ethylenic, and (3) 1,4-phenylene linkages. A comparative study was also made of the fluorescent properties of the compounds obtained in the three different series of bis-1,3,4-oxadiazoles. In the literature there are reports on the synthesis[4-12] of some bis-1,3,4-oxadiazoles, but these have been studied mainly for their polymeric properties.

The 2-hetaryl-5-phenyl-1,3,4-oxadiazoles (**3**) (Scheme 1) were synthesised by condensing heterocyclic carboxylic acids (**1**), such as benzimidazole-2-carboxylic acid, benzoxazole-2-carboxylic acid and naphtho[1,2-*c*]triazole-2-(phenyl-4-carboxylic acid) with benzoyl hydrazide (**2**) in the presence of polyphosphoric acid. The bis-1,3,4-oxadiazoles were synthesised, in a similar one-step method, by condensing dihydrazides (**4**) such as oxalyldihydrazide, fumaric acid dihydrazide and terephthalic acid dihydrazide, with various aromatic carboxylic acids (**5**), e.g. benzoic acid, cinnamic acid and *p*-aminobenzoic acid, in the presence of polyphosphoric acid. The amino derivatives **6c**, **6f** and **6i** were acetylated by refluxing in acetic anhydride to give the acetamido derivatives **6j**–**6l**.

2. RESULTS AND DISCUSSION

The various 2-hetaryl-5-phenyl-1,3,4-oxadiazoles and substituted bis-1,3,4-oxadiazole derivatives synthesised were pale yellow to colourless compounds possessing a blue to violet fluorescence in daylight. These compounds were applied on polyester fibre as fluorescent whiteners. In general the compounds showed moderate to fair whitening effect of the polyester fibre.

The PMR spectrum of **6l** in DMSO-d6 shows a broad singlet centred at

2·2 indicating two singlet (6H, aliphatic), and a multiplet between 7·5 and 8·4 (8H, aromatic). The two D_2O-exchangeable —NH— protons appear as a broad singlet at 9·5.

The mass spectra of compounds showed the corresponding molecular ion peaks in agreement with the molecular weights, thus confirming the structure of these compounds. The molecular ion peaks (m^+/e) of the compounds were as follows: **3a**, 262; **3b**, 263; **3c**, 389; **6a**, 290; **6e**, 368; **6g**, 366; **6h**, 418.

The IR spectra of compounds **3a–3c** (recorded in nujol mull) did not show peaks at 3340 cm^{-1} and 3460 cm^{-1} corresponding to the amino group of the dihydrazide, or at 1660 cm^{-1} corresponding to the keto group, additionally confirming the structures of the compounds. The spectra of compounds **6a–6h** were similar to those of **3a–3c**, the above bands also being absent, but additional bands at 3300 cm^{-1} and 3200 cm^{-1} (ν_{NH}) in **6c**, **6f** and **6i** and at 3260 cm^{-1} (ν_{NH}) and 1680 cm^{-1} ($\nu_{C=O}$) in **6j–6l** were in accord with the assigned structures.

The absorption maxima and the emission maxima of all the compounds **3a–3c** and **6a–6l** in their electronic spectra are given in Table 1.

The 2-hetaryl-5-phenyl-1,3,4-oxadiazole derivatives, compounds **3b** and **3c**, showed emission maxima in the blue region (436 and 430 nm)

TABLE 1
Absorption and Emission Spectra of Oxadiazole Derivatives

No. of compound	*Absorption max. (nm)*	*Absorbance, A*	*Emission max. (nm)*	*log E*
3a	276	0·644	465	4·324 0
3b	312	0·713	436	4·318 9
3c	360	0·600	430	4·294 5
6a	280	1·221	431	4·473 7
6b	260	0·640	428	4·226 4
6c	282	0·475	455	4·278 8
6d	332	1·437	430	4·563 7
6e	355	0·785	435	4·523 7
6f	360	0·521	452	4·331 0
6g	321	1·328	433	4·775 4
6h	326	0·508	428	4·230 3
6i	362	0·737	447	4·402 6
6j	315	0·648	440	4·432 5
6k	368	0·722	439	4·412 8
6l	342	0·645	438	4·463 4

indicating that these two compounds possess spectral properties in accord with those of commercially useful fluorescent whiteners. However, compound **3a** had emission maximum in the greenish-blue region (465 nm). The compounds **3b** and **3c** were applied to polyester fibre as fluorescent whiteners; compound **3b** showed a good whitening effect but **3c** showed only a moderate whitening effect. Compound **3a** gave a yellow tint to the polyester fibre.

The emission maxima of the substituted bis-1,3,4-oxadiazoles directly linked (**6a–6c** and **6j**) were in the range of 428–440 nm (i.e. blue region) except for compound **6c** which had an emission maximum in the greenish-blue region (455 nm). The compounds **6a**, **6b** and **6j** were therefore applied on polyester fibre as fluorescent whiteners and on this substrate compounds **6b** and **6j** were found to have a moderate whitening effect whereas **6a** was not satisfactory.

The emission spectra of substituted bis-1,3,4-oxadiazoles containing an ethylenic linkage (**6d–6f**, **6k**) were also in the blue region (430–439 nm) except for compound **6f** which had an emission maximum at 452 nm (greenish-blue region). The compounds **6d**, **6e** and **6k** were applied on polyester fabric as fluorescent whiteners but did not give good results.

The substituted bis-1,3,4-oxadiazoles linked through a phenyl ring (**6g–6i**, **6l**) showed emission maxima in the range 428–438 nm (i.e. blue region), except for compound (**6i**) which showed in the greenish-blue region (447 nm). Compound **6g** showed a poor whitening effect whereas the compounds **6h** and **6l** had fair to moderate whitening properties on polyester.

Despite the differences in the effective conjugation in the bis-oxadiazoles, increasing in the order direct linkage, ethylenic and 1,4-phenylene, no appreciable change in the spectral properties of corresponding derivatives was observed with changes in the nature of the linking bridge between the two oxadiazole moieties. This may be attributable to the quenching effect of the extended conjugated system.

In general, all the bis-oxadiazoles containing amino groups (compounds **6c**, **6f** and **6i**) had emission in the greenish-blue and this substitution pattern is thus unsatisfactory for the compounds to be used as whiteners. Whilst emission of the other compounds was in general in the blue area suitable for use of the compounds as whiteners, properties of all the bis-oxadiazoles linked through an ethylenic bridge were unsatisfactory. Of the bis-oxadiazoles linked either directly or through a phenylene bridge, the phenyl substituted compounds **6a** and **6g** had poor whitening

characteristics and more satisfactory results were obtained with the acetamidophenyl (compounds **6j** and **6l**) and styryl (**6b** and **6h**) substituted derivatives.

3. EXPERIMENTAL

All the melting points are uncorrected and are in °C. Visible and emission spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer and Aminco Bowman spectrophotofluorimeter respectively. Infrared spectra were recorded on a Perkin-Elmer Model 397 spectrometer. The PMR spectra were recorded on a Varian 60 MHz instrument EM-360-L using TMS as internal standard and the chemical shifts are cited in a δ (ppm) scale.

3.1. Preparation of starting materials

Benzoylhydrazide,[13] benzimidazole-2-carboxylic acid,[14] benzoxazole-2-carboxylic acid,[15] naphtho[1,2-*c*]triazole-2-(phenyl-4-carboxylic acid),[16] oxalyldihydrazide,[17] fumaric acid dihydrazide[18] and terephthalic acid dihydrazide[19] were prepared by known methods.

3.2. 2-(2′-Benzimidazolyl)-5-phenyl-1,3,4-oxadiazole (3a)

A mixture of benzoyl hydrazide (1·36 g, 0·01 mole) and benzimidazole-2-carboxylic acid (2·62g, 0·01 mole) was added to freshly prepared polyphosphoric acid (P_2O_5 18·0 g, H_3PO_4 10 g) at 80 °C. The reaction mixture was stirred at this temperature for 3·5 to 4 h, cooled to 60° and slowly poured onto ice water to isolate the product. The product was filtered, washed with water and crystallised from glacial acetic acid to give **3a** as yellow grains (73%), m.p. 234°. Calculated for $C_{15}H_{10}N_4O$: C, 68·70; H, 3·82; N, 21·37. Found: C, 68·56; H, 3·75; N, 21·25%.

3.3. 2-(2′-Benzoxazolyl)-5-phenyl-1,3,4-oxadiazole (3b)

This was synthesised in a similar manner to the above and was recrystallised from an ethanol–chloroform mixture (1:1) as buff coloured flakes (75%), m.p. 240°. Calculated for $C_{15}H_9N_4O$: C, 68·44; H, 3·42; N, 15·97. Found: C, 68·30; H, 3·35; N, 15·81%.

3.4. 2-{4′-(Naphtho[1,2-*c*]triazol-2″-yl)}-5-phenyl-1,3,4-oxadiazole (3c)

A mixture of naphtho[1,2-*c*]triazole-2-(phenyl-4′-carboxylic acid) (2·89 g, 0·01 mole) and benzoyl hydrazide (1·36 g, 0·01 mole) was added to freshly prepared polyphosphoric acid (P_2O_5, 26 g; H_3PO_4, 15 g) at 120°. The reaction mixture was heated to 180° and was stirred at this temperature for 1–1·5 h. The reaction mixture was then cooled to 80° and slowly added to ice water. The product was filtered, washed thoroughly with water until acid-free and then dried. It was recrystallised from dimethylformamide to give **3c** as colourless crystals (79 %), m.p. 320°. Calculated for $C_{24}H_{15}N_5$: C, 74·04; H, 3·86; N, 17·99. Found: C, 73·89; H, 3·99; N, 18·15 %.

3.5. 2,2′-Bis(5-phenyl-1,3,4-oxadiazole) (6a)

A mixture of oxalyldihydrazide (1·18 g, 0·01 mole) and benzoic acid (1·22 g, 0·01 mole) was added at 120° to freshly prepared polyphosphoric acid (P_2O_5, 18 g; H_3PO_4, 9·0 g). The reaction mixture was stirred and the temperature raised to 180°. The mixture was cooled to 80° after 1 h, then slowly added to ice water, and the product filtered, washed with water and recrystallised from a benzene–methanol mixture (1:2) to give **6a** as colourless plates (79 %), m.p. 265° (literature[11] m.p. 268–70°). Calculated for $C_{16}H_{10}N_4O_2$: C, 66·20; H, 3·45; N, 21·54. Found: C, 66·33; H, 3·37; N, 21·35 %.

The synthesis of other bis-1,3,4-oxadiazoles was carried out similarly using the typical procedure described above.

3.6. 2,2′-Bis(5-styryl-1,3,4-oxadiazole) (6b)

Crystallised from dimethylformamide as colourless crystals (77 %), m.p. 320°. Calculated for $C_{20}H_{14}N_4O_2$: C, 70·17; H, 4·09; N, 16·37. Found: C, 70·30; H, 4·28; N, 16·48 %.

3.7. 2,2′-Bis(5-(*p*-aminophenyl)-1,3,4-oxadiazole) (6c)

Crystallised from acetic acid as colourless needles (72 %), m.p. 285°. Calculated for $C_{16}H_{12}N_6O_2$: C, 60·00; H, 3·75; N, 26·25. Found: C, 59·87; H, 3·68; N, 26·08 %.

3.8. 1,2-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)ethylene (6d)

Crystallised from acetic acid as colourless crystals (70%), m.p. 295° (literature[6] m.p. 307–9°). Calculated for $C_{18}H_{12}N_4O_2$: C, 68·35; H, 3·78; N, 17·72. Found: C, 68·15; H, 3·89; N, 17·59%.

3.9. 1,2-Bis(5-styryl-1,3,4-oxadiazol-2-yl)ethylene (6e)

Crystallised from chlorobenzene as pale yellow crystals (75%), m.p. >360°. Calculated for $C_{22}H_{16}N_4O_2$: C, 71·74; H, 4·35; N, 15·22. Found: C, 71·60; H, 4·27; N, 15·10%.

3.10. 1,2-Bis[5-(*p*-aminophenyl)-1,3,4-oxadiazol-2-yl]ethylene (6f)

Crystallised from dimethylformamide as colourless crystals (72%), m.p. >360°C. Calculated for $C_{18}H_{14}N_6O_2$: C, 62·43; H, 4·05; N, 24·28. Found: C, 62·57; H, 4·12; N, 24·11%.

3.11. 1,4-Bis(5-phenyl-1,3,4-oxadiazol-2-yl)benzene (6g)

Crystallised from acetic acid as colourless needles (80%), m.p. 298° (literature[10] m.p. 311–13°). Calculated for $C_{22}H_{14}N_4O_2$: C, 72·13; H, 3·83; N, 15·30. Found: C, 72·20; H, 3·78; N, 15·40%.

3.12. 1,4-Bis(5-styryl-1,3,4-oxadiazol-2-yl)benzene (6h)

Crystallised from dimethylformamide as colourless crystals (77%), m.p. 280° (dec.) (literature[10] m.p. 295–7°). Calculated for $C_{26}H_{18}N_4O_2$: C, 74·64; H, 4·31; N, 13·39. Found: C, 75·45; H, 4·42; N, 13·51%.

3.13. 1,4-Bis[5-(*p*-aminophenyl)-1,3,4-oxadiazol-2-yl]benzene (6i)

Crystallised from dimethylformamide as pale yellow needles (78%), m.p. >360°. Calculated for $C_{22}H_{16}N_6O_2$: C, 66·67; H, 4·04; N, 21·21. Found: C, 66·51; H, 4·12; N, 21·05%.

3.14. 2,2′-Bis[5-(*p*-acetamidophenyl)-1,3,4-oxadiazole] (6j)

2,2′-Bis[5-(*p*-aminophenyl)-1,3,4-oxadiazole] (**6c**, 1·6 g, 0·005 mole) was

refluxed in acetic anhydride (5 ml) and acetic acid (2 ml) for 2·5–3 h. The product obtained was filtered, washed with water and dried and crystallised from acetic acid to give **6j** as colourless needles (86%), m.p. >360°. Calculated for $C_{20}H_{16}N_6O_2$: C, 64·52; H, 4·30; N, 22·58. Found: C, 64·56; H, 4·28; N, 22·51%. The compounds **6k** and **6l** were prepared by a similar procedure to that described above.

3.15. 1,2-Bis[5-(*p*-acetamidophenyl)-1,3,4-oxadiazol-2-yl]ethylene (6k)

Crystallised from dimethylformamide as colourless needles (83%), m.p. >360°. Calculated for $C_{22}H_{18}N_6O_4$: C, 61·39; H, 4·18; N, 19·53. Found: C, 61·12; H, 4·27; N, 19·40%.

3.16. 1,4-Bis[5-(*p*-acetamidophenyl)-1,3,4-oxadiazol-2-yl]benzene (6l)

Crystallised from dimethylformamide as colourless needles (84%), m.p. >360°. Calculated for $C_{26}H_{20}N_6O_4$: C, 65·00; H, 4·17; N, 17·50. Found: C, 64·87; H, 4·28; N, 17·63%.

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REFERENCES

1. G. Evans (Ciba–Geigy AG), Eur. Pat. Appl. 24380; *Chem. Abstr.*, **95**, 63695 (1981).
2. K. Warning, D. Guenther and R. Erckel (Hoechst AG), Ger. Offen. 2908364; *Chem. Abstr.*, **94**, 158320 (1981).
3. K. Tonegawa (Osaka Seika Industries Co. Ltd), Japanese Patent 72 21 234; *Chem. Abstr.*, **77**, 128101 (1972).
4. S. Motoo, S. Toshiyuki and S. Koichiro, *Kogyo Kagaku Zasshi*, **69**, 2225 (1966); *Chem. Abstr.*, **67**, 117411 (1967).
5. J. Preston, *J. Heterocyclic Chem.*, **2**, 441 (1965).
6. O. Manabe, T. Nagakoshi and H. Hiyama, *Yuki Gosei Kagaku, Kyoshi Shi*, **26**, 355 (1968); *Chem. Abstr.*, **69**, 67291 (1968).
7. P. Leggate and D. Owen, *Mol. Cryst.*, **4**, 357 (1968); *Chem. Abstr.*, **69**, 86167 (1968).

8. H. El Kadem, M. A. E. Shaban and M. A. M. Nassr, *J. Chem. Soc. (C)*, 1416 (1969).
9. G. Vasvari and S. Holly, *Acta Chim. (Budapest)*, **66**, 459 (1970); *Chem. Abstr.*, **74**, 125577 (1971).
10. J. Kranz and H. Weidinger, *Festschrift Carl Wuroter zum 60 Geburtstag*, 119 (1960); *Chem. Abstr.*, **56**, 10132 (1962).
11. H. Weidinger and J. Kranz, *Ber.*, **96**, 1049 (1963).
12. S. Motoo and S. Toshiyuki, *J. Polym. Sci., Part B*, **4**, 869 (1966).
13. T. Cutrius and H. Franzen, *Ber.*, **35**, 3241 (1902).
14. A. Bistrzycki and G. Przeworski, *Ber.*, **45**, 3483 (1908).
15. S. Skraup and M. Moser, *Ber.*, **55**, 1080 (1922).
16. M. P. Schmidt and A. Hagenbocker, *Ber.*, **54**, 2199 (1921).
17. S. Curtius-Schofer, *J. prakt. Chem.* (*2*), **51**, 194 (1850).
18. L. Rodenhausen, *J. prakt. Chem.* (*2*), **52**, 451 (1851).
19. K. Dorunbung, *J. prakt. Chem.* (*2*), **54**, 81 (1851).