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Synthesis of 7*H*-Benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one Derivatives and Study of Their Fluorescent Properties

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SUMMARY

*N-Aminonaphthalimide (**4a**) and N-amino-5-nitronaphthalimide (**4b**) prepared from acenaphthene (**1a**) and 5-nitroacenaphthene (**1b**) by oxidation, cyclization with acetic anhydride and subsequent treatment with hydrazine sulphate were reacted with a variety of carboxylic acid amides such as formamide, acetamide, benzamide, cinnamic amide, coumarin-3-carboxamide and urea using zinc chloride in ethanediol at 150°C to give the 10-substituted and 6-nitro-10-substituted-7H-benzo[de]-s-triazolo[5,1-a]-isoquinolin-7-ones (**6a**–**6f** and **6h**–**6m**), respectively. Acetylation of the 10-amino derivative **6f** and reductive acetylation of the 6-nitro-10-substituted derivatives **6h**–**6m** gave the 10-acetamido, 6-acetamido-, 6-acetamido-10-methyl, 6-acetamido-10-phenyl, 6-acetamido-10-(2-styryl), 6-acetamido-10-(coumarin-3-yl) and 6,10-bisacetamido derivatives (**6g**, **7a**–**7f**), respectively. The fluorescent properties of the compounds **6a**–**6e** and **7a**–**7f** were studied. Compounds **6a**, **6b** and **7e** were applied as fluorescent whiteners on polyester fibres and gave satisfactory results.*

1 INTRODUCTION

Certain fluorophoric heterocyclic systems fused with other fluorophoric heterocyclic moieties in appropriate positions result in augmentation of fluorescence in the newly developed heterocyclic compounds. We have previously reported on the synthesis and fluorescent properties of naphthalimide fused heterocycles such as (naphtho[1,2-*d*]triazolyl)naphthalimides,[1] tetrahydrobenzo[*de*]-γ-triazolo[4,5-*g*]isoquinolinones[1] and

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naphthalimidopyridones.[2] In continuation of our investigations we have now prepared a series of fused heterocycles based on two well-known fluorophoric systems, namely naphthalimide and 1,2,4-triazole (*s*-triazole) and report here the synthesis of 7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one derivatives and a study of their fluorescent properties.

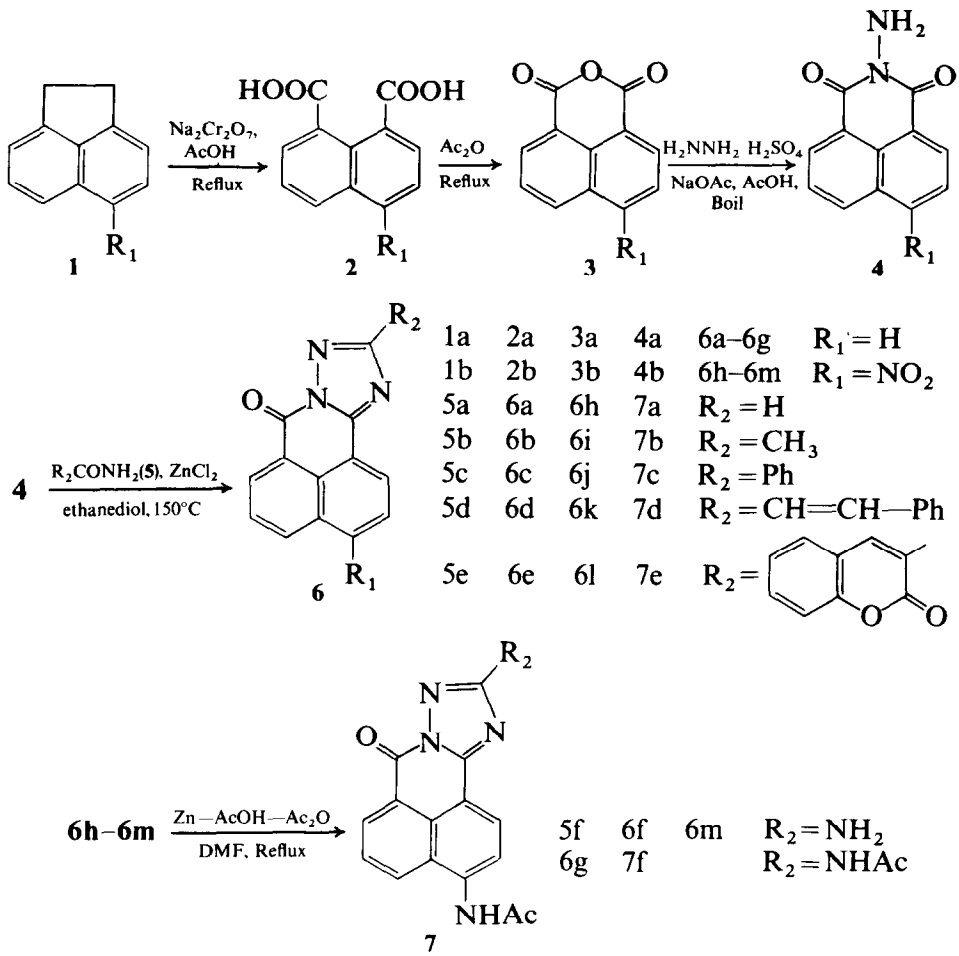
2 RESULTS AND DISCUSSION

The starting materials, *N*-aminonaphthalimide (**4a**) and *N*-amino-5-nitronaphthalimide (**4b**) were prepared from acenaphthene (**1a**) and 5-nitroacenaphthene (**1b**). 5-Nitroacenaphthene (**1b**)[3] was obtained by nitration of acenaphthene (**1a**) using nitric acid and acetic acid. Acenaphthene (**1a**) and 5-nitroacenaphthene (**1b**) were oxidized[3] with sodium dichromate in acetic acid to naphthalic acid (**2a**) and 4-nitronaphthalic acid (**2b**) which were then cyclized[3] to naphthalic anhydride (**3a**) and 5-nitronaphthalic anhydride (**3b**),[3] respectively, using acetic anhydride. Naphthalic anhydride (**3a**) was converted[4] to *N*-aminonaphthalimide (**4a**) by treatment with hydrazine sulphate and sodium acetate in acetic acid. This procedure was also used to obtain *N*-amino-5-nitronaphthalimide (**4b**) from 5-nitronaphthalic anhydride (**3a**).

The condensation of naphthalimide (**1a**) with formamide (**5a**) or benzamide (**5c**) using ammonium chloride as condensing agent has been described in the literature.[5] The resultant 7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]-isoquinolin-7-one has not, however, been exploited for its use in developing fluorescent compounds.

The condensation of *N*-aminonaphthalimide (**4a**) and *N*-amino-5-nitronaphthalimide (**4b**) with a variety of carboxylic acid amides was studied using various condensing agents at different temperatures. Ammonium chloride, polyphosphoric acid, zinc chloride, zinc chloride in ethanol and zinc chloride in ethanediol were used as condensing agents at different temperatures and the best results were obtained using zinc chloride in ethanediol at 150°C.

N-Aminonaphthalimide (**4a**) and *N*-amino-5-nitronaphthalimide (**4b**) were thus condensed with formamide (**5a**), acetamide (**5b**), benzamide (**5c**), cinnamic acid amide (**5d**), coumarin-3-carboxamide (**5e**) and urea (**5f**) using zinc chloride in ethanediol at 150°C to yield 7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6a**), 10-methyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6b**), 10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6c**), 10-(2-styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6d**), 10-(coumarin-3-yl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6e**), 10-amino-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6f**), 6-



Scheme 1

nitro-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6h**), 6-nitro-10-methyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6i**), 6-nitro-10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6j**), 6-nitro-10-(2-styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6k**), 6-nitro-10-(coumarin-3-yl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6l**) and 6-nitro-10-amino-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6m**), respectively.

The nitro group in compounds **6h–6m** is undesirable since the presence of a nitro group in a fluorescent compound generally quenches the fluorescence of the system. The amino group in compounds **6f** and **6m** is also undesirable since the primary amino group in a fluorescent compound which is applied to polyester fibre as a fluorescent whitener may be susceptible to attack by, for example, nitrous fumes, sunlight and oxidizing agents. Compound **6f**

containing the primary amino group was therefore acetylated to give the corresponding acetamido derivative, 10-acetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**6g**). Compounds **6h–6l** containing a nitro group and compound **6m** containing a nitro as well as a primary amino group were reductively acetylated using zinc, acetic acid and acetic anhydride in DMF. In this way were prepared 6-acetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7a**), 6-acetamido-10-methyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7b**), 6-acetamido-10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7c**), 6-acetamido-10-(2-styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7d**), 6-acetamido-10-(coumarin-3-yl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7e**) and 6,10-bisacetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (**7f**).

Various substituted-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-ones, **6a–6e** and **7a–7f**, were yellow compounds and exhibited fluorescence in daylight or in ultraviolet radiation. Thus, compounds **6a**, **6b** and **7e** exhibited a blue fluorescence in daylight, compounds **7a–7d** and **7f** exhibited a greenish-blue fluorescence in daylight, compounds **6c–6e** exhibited fluorescence only in UV radiation, whereas compounds **6h–6m** did not exhibit fluorescence properties.

The absorption maxima and fluorescence emission maxima of compounds **6a–6e** and **7a–7f** in DMF were recorded and are given in Table 1. The absorption maxima of compounds **6a–6e** and **7a–7f** were in the range 337–370 nm and their fluorescence emission maxima in the range 363–460 nm. The fluorescence maxima of compounds **6c–6e** were between 363 and 378 nm, those of compounds **7a–7d** and **7f** between 448 and 460 nm whereas those of compounds **6a**, **6b** and **7e** were between 435 and 440 nm. Although compounds **6c–6e** did not satisfy the general requirement of fluorescent compounds suitable as fluorescent whiteners for polyester fibres, compounds **6a**, **6b** and **7a–7e** did satisfy the requirement. The most satisfactory compounds were **6a**, **6b** and **7e**.

The amount (Q) of a compound dissolved in a solvent (100 ml) required for 100 units of intensity indicated that compounds **6a–6c** and **7d–7e** compared well with the standard fluorescent compound 7-diethylamino-4-methylcoumarin, whereas compounds **6d–6e**, **7a–7c** and **7f** did not stand comparison.

When compounds **6a**, **6b** and **7c** were applied on polyester fibres as fluorescent whiteners, the whitening effect was found to be excellent (grades 3), whereas the other compounds either did not give a whitening effect or gave a yellow tint to the fibre. It may thus be concluded that some of the compounds synthesized in this present study may be used as satisfactory fluorescent whiteners for polyester fibres.

TABLE 1
Absorption and Fluorescence Emission Spectra of 7H-Benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one Derivatives

Compound	*Absorption max. (nm)*	*Fluorescence emission max. (nm)*	*log ε*	*Q (mg)*
6a	365	435	4·26	1·01
6b	343	440	4·25	1·05
6c	337	363	4·38	1·66
6d	341	370	4·41	2·71
6e	345	378	4·30	3·76
7a	370	458	4·01	4·05
7b	350	450	4·05	3·01
7c	356	448	4·05	3·04
7d	350	454	4·12	2·06
7e	340	440	3·80	2·05
7f	350	460	4·02	4·62
Std[a]	376	458	4·40	1·68

[a] 7-Diethylamino-4-methylcoumarin.

3 EXPERIMENTAL

All melting points are uncorrected and are in °C. Absorption and fluorescence emission spectra in DMF solutions were recorded on a Beckman Model 25 spectrophotometer and an Aminco Bowman spectrophotofluorimeter respectively.

3.1 Preparation of starting materials

N-Aminonaphthalimide (**4a**),[3] m.p. 262° (literature[3] m.p. 262°) and 5-nitronaphthalic anhydride (**3b**),[3] m.p. 229° (literature[3], m.p. 228–229°) were prepared by known methods.

3.2 *N*-Amino-5-nitronaphthalimide (4b)

Finely powdered 5-nitronaphthalic anhydride (**3b**) (6·29 g, 0·03 mol) was added in small portions with vigorous stirring to a mixture of hydrazine sulphate (5·8 g, 0·04 mol), sodium acetate (3·3 g, 0·04 mol) and glacial acetic acid (100 ml). The mixture was boiled to dissolve the contents and the hot solution was allowed to cool to room temperature, when bright yellow needles separated. The crystalline product was filtered, washed with acetic

acid–water (1:1), then with water and dried. The resulting solid was crystallized from acetic acid to yield fine bright yellow needles (95%), m.p. 215–217°. Calculated for $C_{12}H_7N_3O_3$: C, 59·75; H, 2·9; N, 17·4. Found: C, 59·9; H, 3·1; N, 17·3%.

3.3 7*H*-Benzo[de]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6a)

A mixture of *N*-aminonaphthalimide (**4a**) (2·12 g, 0·01 mol), formamide (0·68 g, 0·015 mol), zinc chloride (1 g, 0·8 mol) and ethanediol (5 ml) was heated to 150° and the temperature maintained until reaction was complete (4h, checked by TLC). The reaction mixture was cooled to room temperature, when pale yellow needles separated. These were filtered, washed with acetic acid and then with water and dried. The product was recrystallized from DMF–water (1:2) as fine pale yellow needles (78%), m.p. 192–193° (literature[5] m.p. 240°C). Calculated for $C_{13}H_7N_3O$: C, 70·6; H, 3·2; N, 19·0. Found: C, 70·45; H, 3·1; N, 18·7%.

The other 7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-ones (**6b–6f** and **6h–6m**) were synthesized following the above procedure.

3.4 10-Methyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6b)

Crystallized from DMF–water (1:2) as fine pale yellow needles (75%), m.p. 207–208° (literature[5] m.p. 208–210°). Calculated for $C_{14}H_9N_3O$: C, 71·5; H, 3·8; N, 17·9. Found: C, 69·7; H, 3·6; N, 18·3%.

3.5 10-Phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6c)

Crystallized from DMF–water (1:2) as fine pale yellow needles (70%), m.p. 260° (literature[5] m.p. 260°). Calculated for $C_{19}H_{11}N_3O$: C, 76·8; H, 3·7; N, 14·1. Found: C, 76·0; H, 3·6; N, 14·0%.

3.6 10-(2-Styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6d)

Crystallized from DMF–water (1:2) as pale yellow needles (68%), m.p. 215–217°. Calculated for $C_{21}H_{13}N_3O$: C, 78·0; H, 4·0; N, 13·0. Found: C, 77·85; H, 3·9; N, 13·1%.

3.7 10-(Coumarin-3-yl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6e)

Crystallized from DMF–Water (1:1) as pale yellow needles (68%), m.p.

220–222°. Calculated for $C_{22}H_{11}N_3O_3$: C, 72·3; H, 3·0; N, 11·5. Found: C, 72·0; H, 3·1; N, 11·4%.

3.8 10-Amino-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6f)

Crystallized from DMF–water (1:2) as off-white needles (64%), m.p. > 300°. Calculated for $C_{13}H_8N_4O$: C, 66·1; H, 3·4; N, 23·7. Found: C, 65·9; H, 3·2; N, 23·8%.

3.9 5-Nitro-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6h)

Crystallized from DMF–water (1:2) as yellow needles (54%), m.p. 299–300°. Calculated for $C_{13}H_6N_4O_3$: C, 58·6; H, 2·25; N, 21·1. Found: C, 58·55; H, 2·1; N, 21·0%.

3.10 6-Nitro-10-methyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6i)

Crystallized from DMF–water (1:2) as yellow needles (58%), m.p. >300°. Calculated for $C_{14}H_8N_4O_3$: C, 60·0; H, 2·85; N, 20·0. Found: C, 60·3; H, 2·8; N, 19·9%.

3.11 6-Nitro-10-phenyl-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6j)

Crystallized from DMF–water (1:2) as bright yellow needles (62%), m.p. >300°. Calculated for $C_{19}H_{10}N_4O_3$: C, 66·3; H, 2·9; N, 16·3. Found: C, 66·1; H, 3·1; N, 16·3%.

3.12 6-Nitro-10-(2-styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6k)

Crystallized from DMF–water (1:2) as bright yellow needles (63%), m.p. >300°. Calculated for $C_{21}H_{12}N_4O_3$: C, 68·5; H, 3·3; N, 13·6. Found: C, 68·65; H, 3·4; N, 13·65%.

3.13 6-Nitro-10-(3-coumarinyl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6l)

Crystallized from DMF–water (1:1) as yellow needles (58%), m.p. 255–258°. Calculated for $C_{22}H_{10}N_4O_5$: C, 64·4; H, 3·3; N, 13·7. Found: C, 65·4; H, 2·3; N, 13·4%.

3.14 6-Nitro-10-amino-7*H*-benzo [*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (6m)

Crystallized from DMF–water (1:2) as pale yellow needles (64%), m.p. >300°. Calculated for $C_{13}H_7N_5O_3$: C, 55·5; H, 2·5; N, 24·9. Found: C, 55·4; H, 2·6; N, 24·7%.

3.15 10-Acetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*-]isoquinolin-7-one (6g)

A mixture of compound **6f** (2·36 g, 0·01 mol), glacial acetic acid (7 ml) and acetic anhydride (7 ml) was refluxed until reaction was complete (5h, checked by TLC). The reaction mixture was poured onto crushed ice (about 150 g) with stirring when an off-white solid separated. The product was recrystallized from DMF–water (1:2) as off-white needles (60%), m.p. 288–289°. Calculated for $C_{15}H_{10}N_4O_2$: C, 64·75; H, 3·6; N, 20·1. Found: C, 64·6; H, 3·6; N, 20·1%.

3.16 6-Acetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (7a)

Zinc dust (2·0 g, 0·011 g atom) was added in portions with stirring to a mixture of compound **6h** (2·66 g, 0·01 mol), DMF (5 ml), glacial acetic acid (4 ml), acetic anhydride (7 ml) and a drop of pyridine. The reaction mixture was then refluxed until the reaction was complete (4h, checked by TLC). The reaction mixture was filtered hot and the filtrate was poured onto crushed ice (about 150 g) with stirring when yellow crystals separated. The crystalline solid was filtered, washed with water and dried. The product was recrystallized from DMF–water (1:2) as pale yellow crystals (58%), m.p. 211–212°. Calculated for $C_{15}H_{10}N_4O_2$: C, 64·75; H, 3·6; N, 20·1. Found: C, 64·6; H, 3·6; N, 20·1%.

The other 6-acetamido derivatives, **7b**–**7e** and 6,10-bisacetamido derivative **7f** were synthesized following the above procedure.

3.17 6-Acetamido-10-methyl-7*H*-benzo[*de*]-*s*-triazolo-[5,1-*a*]isoquinolin-7-one (7b)

Crystallized from DMF–water (1:2) as pale yellow crystals (62%), m.p. 221–222°. Calculated for $C_{16}H_{12}N_4O_2$: C, 65·75; H, 4·1; N, 19·2%. Found: C, 65·6; H, 4·0; N, 19·1%.

3.18 6-Acetamido-10-phenyl-7*H*-benzo[*de*]-*s*-triazolo-[5,1-*a*]isoquinolin-7-one (7c)

Crystallized from DMF–water (1:2) as yellow crystals (65%), m.p. >300°.

Calculated for $C_{21}H_{14}N_4O_2$: C, 71·2; H, 3·95; N, 15·8. Found: C, 71·2; H, 4·0; N, 16·0%.

3.19 6-Acetamido-10-(2-styryl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (7d)

Crystallized from DMF–water (1:2) as yellow crystals (59%), m.p. 210–212°. Calculated for $C_{23}H_{16}N_4O_2$: C, 67·0; H, 3·9; N, 13·6. Found: C, 67·3; H, 4·1; N, 13·75%.

3.20 6-Acetamido-10-(3-coumarinyl)-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (7e)

Crystallized from DMF–water (1:1) as pale yellow crystals (55%) m.p. 215–216°. Calculated for $C_{24}H_{14}N_4O_4$: C, 68·25; H, 3·3; N, 13·3. Found: C, 68·1; H, 3·4; N, 13·15%.

3.21 6,10-Bisacetamido-7*H*-benzo[*de*]-*s*-triazolo[5,1-*a*]isoquinolin-7-one (7f)

Crystallized from DMF–water (1:2) as yellow brown crystals (52%) m.p. > 300°. Calculated for $C_{17}H_{13}N_5O_3$: C, 60·9; H, 3·9; N, 20·9. Found: C, 61·1; H, 4·0; N, 21·1%.

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