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Synthesis of Phthalimid-3-yl and -4-yl Aminoethylenes and Pyrroloquinolines and a Study of Their Fluorescence Properties

D. W. Rangnekar and D. D. Rajadhyaksha

Dyes Research Laboratory, Department of Chemical Technology, University of Bombay, Matunga Road, Bombay 400 019, India

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SUMMARY

*3-Amino- (**5**) and 4-amino-*N*-phenylphthalimides (**6**) were condensed with diethyl ethoxymethylenemalonic diester (EMME) (**7a**), ethyl ethoxymethylenecyanoacetate (EMCA) (**7b**) and ethyl ethoxymethyleneacetoacetate (EMAA) (**7c**) to obtain 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-disubstituted ethylenes (**8**) and 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-disubstituted ethylenes (**9**), respectively. These aminoethylenes containing a 2-ethyl carboxylate substituent (**8a–8c**) and (**9a–9c**) were cyclized in Dowtherm A to give the corresponding 3-substituted 4-hydroxy-8-N-phenylpyrrolo[3,4-h]quinoline-7,9-diones (**10a–10c**) and 3-substituted 4-hydroxy-7-N-phenylpyrrolo[3,4-g]quinoline-6,8-diones (**11a–11c**), respectively. Compounds **5** and **6** were also condensed with ethyl orthoformate and compounds containing an active methylene or active methyl group such as phenyl acetonitrile (**12a**), 2-methylbenzimidazole (**12b**) and benzimidazol-2-yl acetonitrile (**12c**) to give different aminoethylene derivatives (**8**) and (**9**), respectively. The fluorescent properties of the compounds **8–11** were studied and some of these compounds were applied to polyester fibres as fluorescent dyes.*

1. INTRODUCTION

In our investigations into the synthesis of novel heterocyclic systems for use as fluorescent brightening agents and dyes, we have examined the utility of derivatives of 5-amino-1-*N*-(*p*-toluyl)naphthalimide by converting them to

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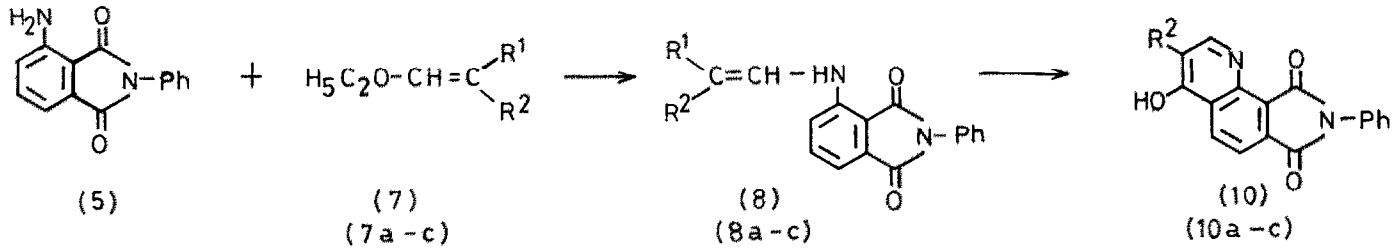
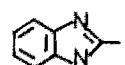
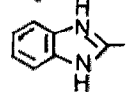


(5) + $CH(OC_2H_5)_3$ + $H_2C(R^1)(R^2)$ (12) (12a-c) ⟶ (8) ; (6) + $CH(OC_2H_5)_3$ + (12) ⟶ (9)

(8d-f) (12a-c) (9d-f)

R^1	R^2	Compd	R^1	R^2	Compd
$COOC_2H_5$	$COOC_2H_5$	7a, 8a, 9a, 10a, 11a	Ph	CN	8d, 9d, 12a
$COOC_2H_5$	CN	7b, 8b, 9b, 10b, 11b		H	8e, 9e, 12b
$COOC_2H_5$	$COCH_3$	7c 8c 9c 10c 11c		CN	8f 9f 12c

Scheme 1

various amino acrylates and thence to the corresponding fused naphthalimidoquinolines.[1] The results of this study were encouraging and prompted us to investigate the use of the 3-amino- (**5**) and 4-amino-1-*N*-phenylphthalimides (**6**). A number of fluorescent whiteners derived from phthalimide have been reported in the literature.[2-5]

We report here the synthesis of phthalimid-3-yl and 4-yl aminoethylenes derived from 3-amino-1-*N*-phenylphthalimide (**5**) and 4-amino-1-*N*-phenylphthalimide (**6**), respectively, and the synthesis of the pyrroloquinolines corresponding to ethyl 1-*N*-(1-*N*-phenylphthalimido-3-yl and -4-yl)aminoethylene-2-carboxylate derivatives (Scheme 1).

2. RESULTS AND DISCUSSION

Compounds **5** and **6** were obtained by nitration of phthalic anhydride, isolation of 3-nitrophthalic anhydride (**1**)[6,7] and 4-nitrophthalic anhydride (**2**),[8,9] their fusion with aniline to give 3-nitro-1-*N*-phenylphthalimide (**3**)[10] and 4-nitro-1-*N*-phenylphthalimide (**4**)[11] followed by reduction with stannous chloride and hydrochloric acid to the amino compounds **5**[12] and **6**.[13]

Compounds **5** and **6** were then converted to 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-disubstituted ethylenes (**8**) and 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-disubstituted ethylenes (**9**), respectively, using two different methods. In the first method, the readily available diethyl ethoxymethylenemalonic diester (EMME; **7a**), ethyl ethoxymethylenecyanoacetate (EMCA; **7b**) and ethyl ethoxymethyleneacetoacetate (EMAA; **7c**) were condensed with **5** and **6**, respectively, to give the corresponding ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-carboxylate derivatives (**8a–8c**) and 1-*N*-(1-*N*-phenylphthalimid-4-yl)aminoethylene-2-carboxylate derivatives (**9a–9c**), i.e. diethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-dicarboxylate (**8a**), ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-carbonitrile-2-carboxylate (**8b**), ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-aceto-2-carboxylate (**8c**), diethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)aminoethylene-2-dicarboxylate (**9a**), ethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)aminoethylene-2-carbonitrile-2-carboxylate (**9b**) and ethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino ethylene-2-aceto-2-carboxylate (**9c**), respectively.

In a second method, compounds **5** and **6** were reacted with ethyl orthoformate and a suitable active methylene or active methyl group containing compounds *in situ*. The formation of arylaminoacrylates by the reaction of an arylamine, ethyl orthoformate and an active methylene group containing compound *in situ* was earlier reported[14] by us. Following

a similar procedure, compounds **5** and **6** were reacted with ethyl orthoformate and phenyl acetonitrile (**12a**), 2-methylbenzimidazole (**12b**) and benzimidazol-2-yl acetonitrile (**12c**), respectively, in refluxing xylene to yield 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-phenylethylene-2-carbonitrile (**8d**), 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-(benzimidazol-2-yl)ethylene (**8e**), 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-(benzimidazol-2-yl)ethylene-2-carbonitrile (**8f**), 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-phenylethylene-2-carbonitrile (**9d**), 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-(benzimidazol-2-yl)ethylene (**9e**) and 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-(benzimidazol-2-yl)ethylene-2-carbonitrile (**9f**), respectively.

In order for heterocyclic compounds to possess fluorescent properties, in general either the heterocyclic moieties should be linked together with suitable linkages to increase the overall conjugation or they should be fused together, thus increasing the conjugation and bringing rigidity to the structures. We have previously reported[15] the synthesis and application of suitably linked 1,3,4-oxadiazoles, and in this present work the compounds **8a–8c** and **9a–9c** were cyclized to give the fused heterocycles pyrrolo[3,4-*h*]quinolines (**10a–10c**) and pyrrolo[3,4-*g*]quinolines (**11a–11c**).

The ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl and -4-yl)aminoethylene-2-carboxylate derivatives **8a–8c** and **9a–9c** were refluxed in Dowtherm A to effect cyclization to the pyrrolo[3,4-*h*]quinolines (**10a–10c**) and pyrrolo-[3,4-*g*]quinolines (**11a–11c**), i.e. ethyl 4-hydroxy-8-*N*-phenylpyrrolo[3,4-*h*]quinoline-7,9-dione-3-carboxylate (**10a**), 4-hydroxy-8-*N*-phenylpyrrolo-[3,4-*h*]quinoline-7,9-dione-3-carbonitrile (**10b**), 3-aceto-4-hydroxy-8-*N*-phenylpyrrolo[3,4-*h*]quinoline-7,9-dione (**10c**), 4-hydroxy-7-*N*-phenyl-pyrrolo[3,4-*g*]quinoline-6,8-dione-3-carboxylate (**11a**), 4-hydroxy-7-*N*-phenylpyrrolo[3,4-*g*]quinoline-6,8-dione-3-carbonitrile (**11b**) and 3-aceto-4-hydroxy-7-*N*-phenylpyrrolo[3,4-*g*]quinoline-6,8-dione (**11c**), respectively.

The PMR of compound **11b** in DMSO-d_6 showed a sharp peak centred at 7·7 corresponding to three aromatic protons of the 7-*N*-phenyl ring situated away from two keto groups of the pyrrole ring (3H, aromatic); a doublet centred between 7·9 and 8·1 corresponding to three aromatic protons, two of the 7-*N*-phenyl ring situated close to two keto groups of the pyrrole ring and one at C-9 of the pyrrolo[3,4-*g*]quinoline residue (3H, aromatic); a sharp singlet centred at 8·5 corresponding to two aromatic protons, one situated at C-3 and one at C-5 of the pyrrolo[3,5-*g*]quinoline residue (2H, aromatic).

The mass spectra of the compounds showed the required molecular ion peaks and the IR spectra of the compounds in Nujol mull were also in accord with the assigned structures. Thus, compounds **8a–8c** and **9a–9c** showed a sharp peak at 1680 cm^{-1} and the compounds **8d–8f**, **9d–9f**,

10a–10c and **11a–11c** showed a strong peak at 1670 cm^{-1} corresponding to the carbonyl of the imide (phthalimide and pyrrolimide). Compounds **8a–8f** and **9a–9f** showed no absorption corresponding to a primary amino group, but they showed a peak between 3100 and 3350 cm^{-1} corresponding to the secondary amino group. The IR spectra of compounds **8a–8c** and **9a–9c** showed a sharp peak at 1740 cm^{-1} corresponding to the ester group and that of compounds **8b**, **9b**, **8d**, **9d**, **8f** and **9f** showed a sharp peak between 2220 and 2250 cm^{-1} corresponding to a cyano group, i.e. **8b** and **9b**, 2220 cm^{-1}; **8d**, 2240 cm^{-1}; **9d**, 2230 cm^{-1}; and **8f** and **9f**, 2250 cm^{-1}. A broad peak corresponding to the hydroxy group was observed in the spectra of compounds **10a**, **11a**, **10b** and **11b** between 3500 and 3400 cm^{-1} and of compounds **10c** and **11c** at 3500 cm^{-1}. Absorption at 1730 cm^{-1} due to the carbonyl of the ester residue was observed in the spectra of compounds **10a** and **11a** and the cyano group was apparent in the spectrum of **10b** at 2250 cm^{-1} and of compound **11b** at 2240 cm^{-1}. A sharp peak corresponding to a ketone carbonyl group was present at 1700 cm^{-1} for **10c** and at 1710 cm^{-1} for **11c**.

The absorption and fluorescence emission maxima of the compounds **8–11** are given in Table 1. The absorption maxima of the phthalimid-3-yl

TABLE 1
Absorption and Fluorescence Emission Spectra of Phthalimid-3-yl and -4-yl Aminoethylenes and Pyrroloquinolines

Compound	*Absorption* λ_{max} *(nm)*	*Molar extinction coefficient* $(E \times 10^{-4})$	*Fluorescence emission* λ_{max} *(nm)*
8a	398	1·758	510
8b	404	2·364	502
8c	400	1·911	518
8d	425	1·659	501
8e	445	1·494	495
8f	460	1·835	490
9a	408	2·273	507
9b	412	2·554	498
9c	407	2·687	514
9d	460	2·869	498
9e	470	3·079	489
9f	448	3·189	482
10a	428	1·132	487
10b	448	1·258	479
10c	436	1·223	491
11a	443	1·263	474
11b	456	1·658	463
11c	451	1·487	478

and -4-yl aminoethylenes **8a–8f** and **9a–9f** are in the range 398–470 nm and these compounds had fluorescent emission maxima in the green region (482–514 nm). The pyrroloquinolines **10a–10c** and **11a–11c** showed absorption maxima in the range 428–456 nm and fluorescence emission maxima were in the bluish-green to green region (463–487 nm). Most of the compounds are thus pale yellow to bright yellow in colour and they were applied as fluorescent dyes to polyester, on which they gave light greenish-yellow to bright yellow colorations, having poor to moderate pick-up. The resultant dyeings had moderately good fastness to both light and sublimation.

3. EXPERIMENTAL

All the melting points are uncorrected and are recorded in °C. Absorption and fluorescence 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 spectrum was recorded on Varian 60 MHz instrument EM-360-L using TMS as internal standard and the chemical shifts are cited in δ(ppm).

3.1. Preparation of starting materials

3-Nitrophthalic anhydride (**1**),[6,7] 4-nitrophthalic anhydride (**2**),[8,9] 3-nitro-1-*N*-phenylphthalimide (**3**),[10] 4-nitro-1-*N*-phenylphthalimide (**4**),[11] 3-amino-1-*N*-phenylphthalimide (**5**)[12] and 4-amino-1-*N*-phenylphthalimide (**6**)[13] were prepared by known methods.

3.2. Diethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-dicarboxylate (8a)

To a stirred solution of 3-amino-1-*N*-phenylphthalimide (**5**) (2·38 g, 0·01 mol) in dry xylene (20 ml) was added a solution of diethyl ethoxymethylenemalonic diester (EMME; **7a**) (2·33 g, 0·011 mol) in dry xylene (10 ml) followed by a drop of piperidine. The mixture was heated to reflux until the reaction was complete (8·5 h) (monitored by TLC). The boiling reaction liquor was filtered hot, the filtrate concentrated and cooled to give a yellow crystalline solid, which was recrystallized from xylene in bright yellow crystals (65%), m.p. 311–3°. Calculated for $C_{22}H_{20}N_2O_6$: C, 64·7; H, 4·9; N, 6·9. Found: C, 64·5; H, 4·7; N, 6·75%.

The compounds **8b–8c** and **9a–9c** were synthesized following the above typical procedure.

3.3. Ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)aminoethylene-2-carbonitrile-2-carboxylate (8b)

Recrystallized from xylene as yellow crystals (60%), m.p. 327–8°. Calculated for $C_{20}H_{15}N_3O_4$: C, 66·5; H, 4·2; N, 11·6. Found: C, 66·4; H, 4·3; N, 11·5%.

3.4. Ethyl 1-*N*-(1-*N*-phenylphthalimid-3-yl)amino-2-acetoethylene-2-carboxylate (8c)

Recrystallized from xylene to give bright yellow crystals (59%), m.p. > 340°. Calculated for $C_{21}H_{18}N_2O_5$: C, 66·7; H, 4·8; N, 7·4. Found: C, 66·1; H, 4·4; N, 7·35%.

3.5. Diethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)aminoethylene-2-dicarboxylate (9a)

Recrystallized from DMF as bright yellow crystals (68·5%), m.p. 293°. Calculated for $C_{22}H_{20}N_2O_6$: C, 64·7; H, 4·9; N, 6·9. Found: C, 64·9; H, 5·0; N, 7·1%.

3.6. Ethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)aminoethylene-2-carbonitrile-2-carboxylate (9b)

Recrystallized from DMF as yellow crystals (75%), m.p. 316–8°. Calculated for $C_{20}H_{15}N_3O_4$: C, 66·5; H, 4·2; N, 11·6. Found: C, 68·9; H, 4·2; N, 11·0%.

3.7. Ethyl 1-*N*-(1-*N*-phenylphthalimid-4-yl)amino-2-acetoethylene-2-carboxylate (9c)

Recrystallized from DMF as bright yellow crystals (66%), m.p. >340°. Calculated for $C_{21}H_{18}N_2O_5$: C, 66·7; H, 4·8; N, 7·4. Found: C, 66·6; H, 4·7; N, 7·1%.

3.8. 1-*N*-(1-*N*-Phenylphthalimid-3-yl)amino-2-phenylethylene-2-carbonitrile (8d)

To a stirred solution of 3-amino-1-*N*-phenylphthalimide (**5**) (2·38 g, 0·01 mol) in dry xylene (25 ml) was added ethyl orthoformate (2·22 g, 0·015 mol) and the solution refluxed for 3 h. A change in colour of the solution was observed and the formation of the intermediate ethoxymethylene amino compound was detected on TLC. The solution was

cooled to 80–90° and diethyl malonic diester (1·60 g, 0·01 mol) was added. The reaction mixture was refluxed until the reaction was complete (5 h) (monitored by TLC). It was filtered hot and the filtrate cooled to give compound **8d** as a yellow crystalline solid. This was recrystallized from DMF to give bright yellow crystals (72%), m.p. 286–8°. Calculated for $C_{23}H_{15}N_3O_2$: C, 75·6; H, 4·1; N, 11·5. Found: C, 75·2; H, 3·9; N, 11·4%.

The compounds **8e–8f** and **9d–9f** were synthesized following the above typical procedure.

3.9. 1-*N*-(1-*N*-Phenylphthalimid-3-yl)amino-2-(benzimidazol-2-yl)-ethylene (8e)

Recrystallized from DMF as bright yellow crystals (77%), m.p. 302–6°. Calculated for $C_{23}H_{16}N_4O_2$: C, 72·6; H, 4·2; N, 14·7. Found: C, 72·3; H, 4·1; N, 14·6%.

3.10. 1-*N*-(1-*N*-Phenylphthalimid-3-yl)amino-2-(benzimidazol-2-yl)-ethylene-2-carbonitrile (8f)

Recrystallized from DMF as bright yellow crystals (67%), m.p. >340°. Calculated for $C_{24}H_{16}N_5O_2$: C, 71·1; H, 3·7; N, 17·3. Found: C, 71·0; H, 3·7; N, 18·0%.

3.11. 1-*N*-(1-*N*-Phenylphthalimid-4-yl)amino-2-phenylethylene-2-carbonitrile (9d)

Recrystallized from DMF–ethanol (1:1) as bright yellow crystals (79%), m.p. 327–9°. Calculated for $C_{23}H_{15}N_3O_2$: C, 75·6; H, 4·1; N, 11·5. Found: C, 76·2; H, 3·95; N, 11·7%.

3.12. 1-*N*-(1-*N*-Phenylphthalimid-4-yl)amino-2-(benzimidazol-2-yl)-ethylene (9e)

Recrystallized from acetic acid as bright yellow crystals (86%), m.p. >340°. Calculated for $C_{23}H_{16}N_4O_2$: C, 72·6; H, 4·2; N, 14·7. Found: C, 72·0; H, 3·9; N, 14·2%.

3.13. 1-*N*-(1-*N*-Phenylphthalimid-4-yl)amino-2-(benzimidazol-2-yl)-ethylene-2-carbonitrile (9f)

Recrystallized from DMF as bright yellow crystals (77%), m.p. >340°.

Calculated for $C_{24}H_{16}N_5O_2$: C, 71·1; H, 3·7; N, 17·3. Found: C, 70·7; H, 3·8; N, 18·0%.

3.14. Ethyl 4-hydroxy-8-*N*-phenyl pyrrolo[3,4-*h*]quinoline-7,9-dione-3-carboxylate (10a)

The compound **8a** (4·08 g, 0·01 mol) was added to Dowtherm A (25 ml) at 200° under stirring. It was refluxed until the reaction was complete (7–10 h) (monitored by TLC). The reaction mixture was cooled and added to petroleum ether (30–40 ml), when a dark coloured solid separated. This was filtered, washed with petroleum ether, dried and crystallized from acetic acid to give yellow crystals (75%), m.p. >340°. Calculated for $C_{20}H_{14}N_2O_5$: C, 66·3; H, 3·9; N, 7·7. Found: C, 65·9; H, 3·9; N, 7·7%.

The compounds **10b–10c** and **11a–11c** were synthesized following the above typical procedure.

3.15. 4-Hydroxy-8-*N*-phenylpyrrolo[3,4-*h*]quinoline-7,9-dione-3-carbonitrile (10b)

Crystallized from acetic acid as yellow crystals (77%), m.p. >340°. Calculated for $C_{18}H_9N_3O_3$: C, 71·8; H, 3·0; N, 9·3. Found: C, 72·1; H, 2·9; N, 9·2%.

3.16. 3-Aceto-4-hydroxy-8-*N*-phenylpyrrolo[3,4-*h*]quinoline-7,9-dione (10c)

Crystallized from acetic acid as yellow crystals (80%), m.p. >340°. Calculated for $C_{19}H_{12}N_2O_4$: C, 68·7; H, 3·6; N, 8·4. Found: C, 68·3; H, 3·5; N, 8·4%.

3.17. 4-Hydroxy-7-*N*-phenylpyrrolo[3,4-*g*]quinoline-6,8-dione-3-carboxylate (11a)

Crystallized from DMF as yellow crystals (79%), m.p. >340°. Calculated for $C_{20}H_{14}N_2O_5$: C, 66·3; H, 3·9; N, 7·7. Found: C, 65·0; H, 3·8; N, 7·8%.

3.18. 4-Hydroxy-7-*N*-phenylpyrrolo[3,4-*g*]quinoline-6,8-dione-3-carbonitrile (11b)

Crystallized from DMF as yellow crystals (72%), m.p. >340°. Calculated for $C_{18}H_9N_3O_3$: C, 71·8; H, 3·0; N, 9·3. Found: C, 71·15; H, 2·9; N, 9·2%.

3.19. 3-Aceto-4-hydroxy-7-*N*-phenylpyrrolo[3,4-*g*]quinoline-6,8-dione (11c)

Crystallized from DMF as yellow crystals (76%), m.p. $>340°$. Calculated for $C_{19}H_{12}N_2O_4$: C, 68·7; H, 3·6; N, 8·4. Found: C, 68·7; H, 3·5; N, 8·4%.

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