The Synthesis and Fluorescence of Novel *N*-Substituted-1,8-naphthylimides

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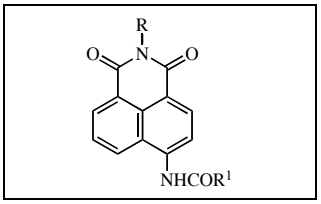

The synthesis and characterisation of a series of novel 4-acylamino and 4-alkylamino-*N*-1,8-naphthalimides is described. The UV-visible absorption and emission properties of the compounds are reported. Significant solvent effects are noted for 4-*n*-butyl-9-*n*-butyl-1,8-naphthylimide. The incorporation of acetyl and chloroacetyl groups into the 4-substituent markedly increases the fluorescence quantum yield compared with 4-alkylamino substituemnts.

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INTRODUCTION

The photochemistry and photophysics of the alkylaminonaphthalic-1,8-*N*-alkylimides continues to be of wide interest in technical, medical and electronic fields. In addition to their application in non-destructive testing (NDT) in metals and ceramics [1,2], laser applications [3,4], for sensors and switches [5-7], probes in cancer studies [8,9] and for their anti-viral activity [10-13], more recent research has highlighted their potential as electroluminescent materials [14-17] and as fluorescent sensors for metal ions [18-26].

The synthesis and fluorescence properties of a variety of N-alkylsubstituted-1,8-naphthalimides have been described [27,28] and one former aspect by others [7]. Methods of synthesis involving nucleophilic displacement of the nitro group [29] and developments with chloro and bromo analogues have been reported [30]. The role of structure has been fully examined in the case of monosubstituted [1] and extended to studies on disubstituted compounds [31,32].

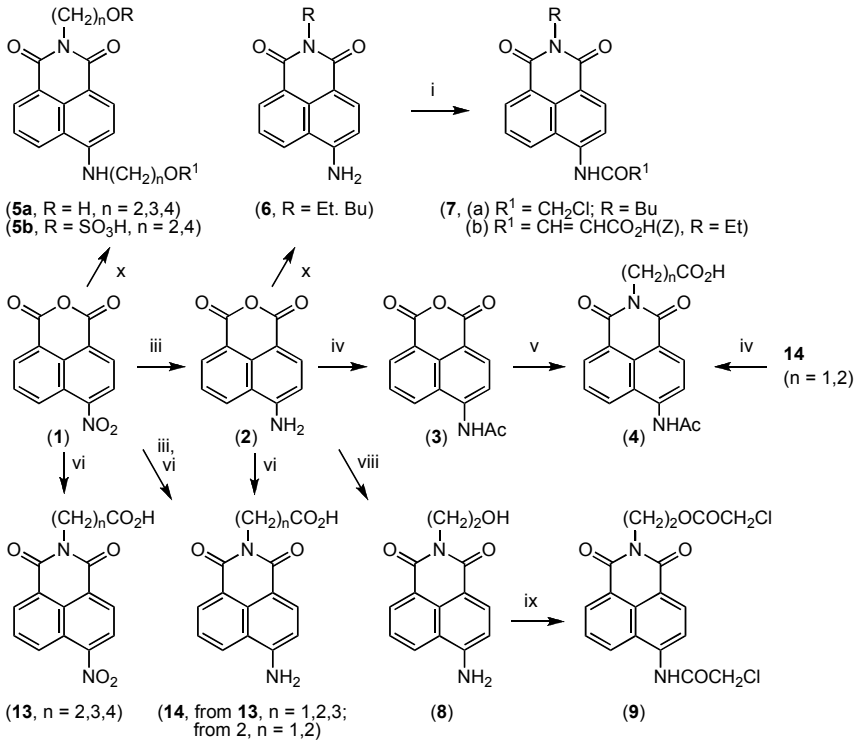
In the present investigation, directed partly to devising water-soluble compounds, a number of novel 4-alkyl-amino-*N*-alkylnaphthalimides (with similar 4- and 9-alkyl groups a series of 4-nitro-*N*-alkylaminonaphthalimides and a range of 4-amino-*N*-alkylnaphthalic-1,8-imides have been synthesized. Previously, substitution at the 4- and 9- positions by alkylamino groups has been investigated, but in the present work carboxyalkyl-, sulphoalkyl-, halogenoalkylcarboxy- and ethoxycarbonyl-alkylamino substituents have been introduced to study the role played by electron attracting groups. Fluorescence measurements have revealed novel properties.

RESULTS AND DISCUSSION

Substitution and Nucleophilic reactions. The reaction routes and compounds synthesised are depicted in Schemes 1 and 2. Scheme 1 gives the synthesis of compounds (**3**) and (**4**) from 4-nitronaphthalic anhydride **1** by way of reduction to 4-aminonapthalic anhydride (**2**). Compound (**5**) results from replacement both of the 4-nitro group and at the anhydride. Compound (**6**) is obtained from 4-aminonaphthalic anhydride by reaction first at the anhydride and then by acylation of the amino group. Compound (**8**) is also derived from 4-amino-naphthalic anhydride (**2**) by reaction first at the anhydride and (**9**) by acylation of the OH and the amino groups of (**8**). Compound (**13**) is formed from reaction of the anhydride group of (**1**), and (**14**) by reduction of (**13**). Dependent on the value of number of methylene groups, n, in the reactant, compound (**14**) can be obtained either directly from 4-aminonaphthalic anhydride (**2**) or from (**1**). Scheme 2 depicts the synthesis of compounds (**10**), (**11**), and (**12**) by reaction first at the anhydride group of **1** and then at the nitro group by nucleophilic displacement. Compounds (**15**) and (**16**) result from a similar procedure except that an amino acid intermediate is used instead of an amino alcohol. Hydrolysis of (**16** affords the acid (**17**).

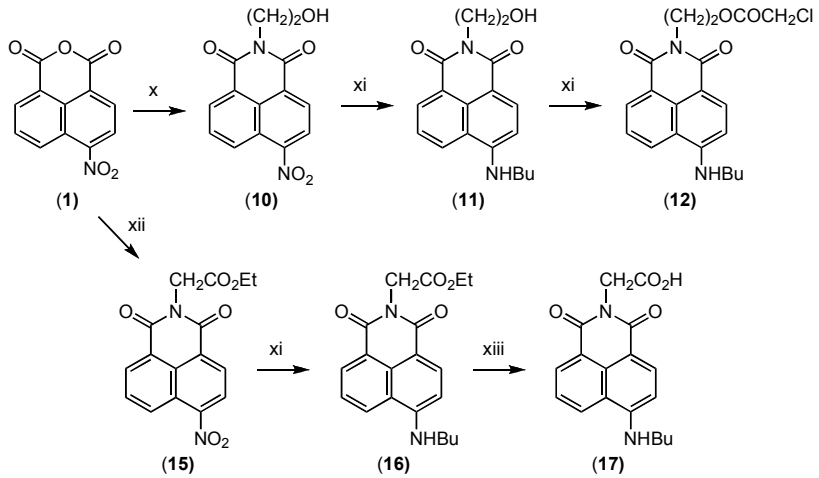
Reaction of 4-nitronaphthalic anhydride (**1**) and its 4-aminonaphthalic derivative (**2**) with amines occurred preferentially at the anhydride group to give 9-substituted 1,8-naphthalimides through a ring-opening and closing sequence. Displacement of a 4-nitro group by amines only occurs in aprotic solvents. DMF was employed in the present work although in later studies the use of N-methylpyrrolidinone [30] (NMP) is preferred since side-

Scheme 1



Reagents: (i)(a) $ClCH_2COCl$, DMF. (b) (COCH=CHCO)O. (ii) RNH_2,DMF. (iii) $SnCl_2$,MeOH, HCl. (iv) Ac_2O, Py. (v) $NH_2CH_2CO_2Na$, DMF; HCl. (vi) $NH_2(CH_2)_nCO_2H$, EtOH, (vii) n = 1, 2 $NH_2(CH_2)_nCO_2H$, DMF. (viii) $NH_2(CH_2)_2OH$, DMF. (ix) $ClCH_2COCl$, NEt_3. (x) (a) R = H, $NH_2(CH_2)_nOH$, DMF, heat; (b) n = 2; H_2SO_4; n = 4, H_2SO_4; KOH.

Scheme 2



Reagents: (ix), $ClCH_2COCl$, NEt_3, (x) $NH_2(CH_2)OH$, EtOH. (xi), $BuNH_2$,DMF, heat. (xii) $NH_2CH_2CO_2Et$, EtOH. (xiii) KOH; HCl.

reactions such as the formation of a 4-dimethylamino derivative are greatly reduced. Displacement of the halide ion from 4-halogenonaphthalic anhydrides can offer advantages over the 4-nitro compound in the work-up procedure [30] and enable products to be purified by crystallisation rather than chromatography. In the present work the formation of 4-dimethylamino impurities was minimal possibly because the reactions were carried out at 75-80°C rather than 100-120°C. These considerations do not apply to compounds having a 9-imidic function.

Attempts to use 4-nitronaphthalic anhydride in aprotic solvents (DMF, DMSO) with the weak nucleophile

sodium glycinate, *en route* to similar groups at the 4- and 9-positions led to complex mixtures. Glycine esters were little better and reminiscent of the behaviour of taurine [28]. Accordingly, for the introduction of electron-attracting groups at 4- and 9-positions, 4-amino-1,8-naphthalimide (**2**) was used as the substrate. Acetylation afforded the acetyl derivative (**3**) and reaction with sodium glycinate gave the carboxymethyl compound (**4,** n=1) in excellent yield, which possesses outstanding fluorescent properties. Compound (**4,** n=1) is also accessible from 4-aminonaphthalic-1,8-anhydride by direct reaction with glycine to give (**14**, n=1) followed by acetylation and from 4-nitronaphthalic-1,8-anhydride and glycine in ethanol to afford (**13**, n =1) followed by reduction with tin (II) chloride to (**14**, n =1) and acetylation.

Enhancement of the influence of electron-attracting properties of the substituents, involved the chloroacetylation of 4-amino-(9-n-butyl)-1,8-naphthalimide (**6**) and of 4-amino-(2-hydroxyethyl)-1,8-naphthalimide (**8**) to give compounds (**7a**) and (**9**) respectively. The major enhancement of fluorescence properties appears to come from the 4- rather than the 9-substituent, since compound (**16**) possessed only moderate properties. Increased aqueous solubility was conferred on the compounds by the introduction of a sulphonic group as in (**5b**, R = SO_3H, n = 2,4) although these were only obtained in low yield.

Fluorescence Properties of the 1,8-Naphthylimides. The incorporation of polar groups at the 4- and 9-positions of 1,8-naphthylimides not only resulted in increased water solubility but also produced compounds with high fluorescence intensities. This effect appears to be a consequence of the electron-withdrawing nature of the substituents. This behaviour contrasts with that of previously studied naphthalimides, notably 4-*n*-butylamino-9-(*n*-butyl)-1,8-naphthalimide (FBYR), in which the substituents possess electron-releasing character. Similar properties have been observed [8] in the compound (**7**, R = $(CH_2)_3Br$, R_1 =Me) in which however the halogen atom is remote from active electronic involvement. From our work with 4-chlorobenzoyl and 4-bromobenzoyl derivatives of a 4,4'-diaminostilbene compound [41], the presence of such halogen substituents in the conjugation depressed fluorescence intensity.

The fluorescence of FBYR is highly solvent dependent (Table1). Both the longest wavelength absorption band and the fluorescence emission maximum are shifted to longer wavelength with increasing solvent polarity, as anticipated for a charge-transfer transition. The absorption maxima of the second and third absorption transitions are relatively unaffected by the solvent. The highest fluorescence intensity is observed in ethyl acetate solution and the lowest in methanol although it dropped almost to zero in aqueous conditions. All of the fluorescence decays were clean single exponentials. Calculation of radiative (k_r) and non-radiative (k_{nr}) rate constants (Table 1) reveals that the decreased fluorescence intensity in polar solvents derives from both a decrease in the radiative rate constant and an increase in the non-radiative one. However, the large increase in k_{nr} for methanol compared to the other alcohols may also be a result of quenching of the excited state by solvent clusters as proposed previously for aqueous solutions of other amino-1,8-naphthalimides [43] and the role of hydrogen bonding. This last mechanism would also explain the virtually nil emission intensity for FBYR in water. By way of an alternative explanation [44], the formation of exciplexes between FBYR and protic solvents may account for both the decrease in k_r and the increase in k_{nr} in the three alcohols used here. It is interesting to note that Krystkowiak [44] also observed a decrease in k_r by a factor of 2.5 for 4-aminophthalimide in hexafluoroisopropanol, water and deuterated water.

Table 1

Effect of solvent on the fluorescence of 4-*n*-butylamino-9-*n*-butyl-1,8-naphthalimide.

Solvent	Absorption maxima (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϕ_f	τ_f (ns)	k_r x10^{-8} s^{-1}	K_{nr} X10^{-8} s^{-1}
Methylcyclohexane	264, 272, 410	410	470	0.83	9.40	1.09	0.22
Toluene	263, 286, 420	420	479	0.84	8.85	1.00	0.19
Ethyl acetate	260, 280, 428	428	500	0.93	9.50	0.98	0.07
Acetonitrile	260, 280, 432	432	512	0.84	10.57	0.82	0.16
2-Propanol	260, 284, 440	442	522	0.66	9.63	0.69	0.35
Ethanol	260, 284, 442	442	523	0.66	8.95	0.67	0.38
Methanol	260, 284, 442	442	523	0.38	8.24	0.46	0.75

λ_{ex} and λ_{em} are the excitation wavelength and the maximum of the fluorescence emission respectively.

The fluorescence properties of the synthesised and novel 1,8-naphthalimides in ethanol solution are shown in Table 2 along with data for FBYR. The absorption and fluorescence properties of the compounds reported in Table 2 divide naturally into two groups. Compounds (**5**), (**14**) and (**16**) are similar to FBYR in their properties while compounds (**4**), (**7**) and (**9**), despite the presence of the amino function at the 4-position, resemble the properties of naphthalimides lacking a 4-amino substituent [27].

Table 2

Fluorescence properties of 4,9-disubstituted-1,8-naphthalimides (in ethanol).

Compound	Absorption maxima(nm) Extinction Coefft. ($log_{10}\varepsilon$)	λ_{ex} (nm)	λ_{em} (nm)	ϕ_f	τ_f (ns)	k_r $x10^{-8}$ s^{-1}	k_{nr} $x10^{-8}$ s^{-1}
FBYR	260(4.29) 284(4.25) 442(4.20)	442	523	0.66	8.95	0.67	0.38
5a, n=3	262(4.61) 284(4.31) 444(4.46)	444	526	0.55	8.76	0.63	0.51
5a, n=4	262(4.31) 284(4.31) 444(4.22)	444	525	0.62	9.00	0.69	0.42
5b, n=2	258(3.86) 282(3.83) 436(3.94)	436	525	0.69	7.13	0.97	0.43
14, n=1	260(4.21) 274(sh) 434(4.09)	434	540	0.46	8.88	0.52	0.61
14, n=2	258(4.28) 274(sh) 434(4.09)	434	537	0.50	8.88	0.58	0.58
14, n=3	258(4.30) 274(sh) 434(4.25)	434	537	0.54	8.78	0.62	0.52
16	256(3.97) 284(4.07) 442(4.11)	442	543	0.64	8.94	0.72	0.40
4	238(4.45) 364(4.19)	364	454	0.94	7.03	1.34	0.09
7a	238(4.41) 360(4.14)	360	454	0.91	6.59	1.38	0.14
7b	242(4.46) 382(4.21)	382	518	0.01	1.49 / 8.12	-	-
9	238(4.38) 360(4.08)	360	454	0.88	6.67	1.32	0.18

λ_{ex} and λ_{em} are the excitation wavelength and the maximum of the fluorescence emission respectively; sh, shoulder.

Distal hydroxy groups as in compounds (**5a**, n = 3 and 4), have little effect on fluorescence intensity relative to that of FBYR. This is in contrast to the quenching effect of distal nitrogen atoms at the 4- position [18] and the 9-position [45] (although the quenching effect is much smaller in the latter). The ethoxycarbonyl group in compound (**16**) also has similar properties to FBYR as does (**5b**, n=2), although the terminal sulphonic group greatly increases solubility in water with little effect on the absorption and fluorescence properties. By contrast, acetyl and chloroacetyl groups as in compounds (**4**), (**7a**) and (**9**) enhance the fluorescence intensity and also alter the colour of the emission relative to FBYR. A primary amino group as in (**14**), although assisting fluorescence is much less effective than an alkylamino group as in compound **16**.

Thus, the major influence on increase of the fluorescence intensity arises from incorporation of acetyl and chloroacetyl groups into the 4-amino substituent, These two electron-withdrawing groups alter the behaviour of the 4-amino function as observed in FBYR. Although we have no supporting evidence, it is possible that the carbonyl group of the acetyl function forms a hydrogen-bond to the 3-H atom creating a new stabilising six-membered ring which may partially increase the conjugation of the whole system. The hydrogen atoms of the NH and at the *peri*-position do not sterically interact and obstruct coplanarity.

The negligible fluorescence of (**7b**) could be ascribed to loss of coplanarity as for a 4-dimethylamino substituent [27], which is twisted out of plane, or due to an electronic effect of the $CH{=}CHCO_2H$ group which may exert a negative effect as found with 4-phenylamino and 4-nitro substituents; and linear conjugation with the naphthalimide ring then results in a major loss of fluorescence. It would be of interest to examine the succinoyl analogue having a $CH_2CH_2CO_2H$ group lacking conjugation, but this opportunity was not available.

It is noticeable that although the lowest energy absorption maximum of (**7b**) in ethanol is similar to that of naphthalimides which do not have a 4-amino substituent [27], the emission maximum is close to that of FBYR. This observation suggests that in the emissive excited state the 4-amino substituent is conjugated with the ring. The double exponential fluorescence kinetics therefore reflect the twisting process necessary to convert the initially excited state into the emissive state.

EXPERIMENTAL

UV/visible absorption spectra were measured on a Perkin-Elmer Lambda 3 spectrophotometer and a Hewlett Packard 8452A diode array instrument in 1 cm quartz cells at ambient temperature with concentrations 10^{-4}-10^{-5} mol dm^{-3}. Fluorescence spectra were recorded on a Perkin-Elmer LS-5 Luminescence spectrometer and a SPEX Fluoromax spectrofluorimeter in corrected mode. Quantum yield measurements were made on optically dilute samples which were deoxygenated by bubbling with oxygen-free nitrogen for 30 min. Fluorescein in 0.1 mol dm^{-3} sodium hydroxide (ϕ_f = 0.90) [33] or quinine sulphate in 0.1 mol dm^{-3} perchloric acid (ϕ_f = 0.55) [34] were used as quantum yield standards. Fluorescence lifetimes were measured by the technique of time-correlated single-photon counting [35] at the Synchroton Radiation source in the SERC Daresbury

laboratory [36]. Infrared spectra were recorded on a Galaxy series FTIR 3000, Mattson Polaris FTIR and Perkin-Elmer 1310 spectrometers. Proton nuclear magnetic resonance spectra were obtained on a Bruker WM250 cryospectrometer and on a Hitachi R-1100 instrument. Mass spectra were determined on a modified AEI MS902 instrument. Accurate masses were determined by the EPSRC centre at the Chemistry Department, University of Wales at Swansea. Thin layer chromatography (TLC) was carried out on silica gel GF254. High performance liquid chromatography (HPLC) was affected with the aid of a Perkin Elmer UV variable wavelength spectrometer (LC55) equipped with a flow through cell. Microanalyses were carried out in the Microanalytical Department, University of Manchester. Commercial compounds used for absorption and fluorescence measurements were obtained from Molecular Probes Inc., and chemicals for organic synthesis from the Aldrich Chemical Co.

5-Nitroacenaphthene mp 101-102 °C and 3-nitroacenaphthene, mp 147-148 °C were prepared in 72% and 20% yields respectively as previously described [37,38]. 4-Nitronaphthalic anhydride (**1**), mp 227-228 °C in 33% yield was obtained by oxidation of 5-nitroacenaphthene [39]. 4-Aminonaphthalic-1,8-anhydride (**2**), mp > 360 °C was prepared from the nitro compound by reduction with stannous chloride [27]. 4-Acetylaminonaphthalic-1,8-anhydride (**3**), mp 283-285 °C was obtained by acetylation of the amino compound [40]. The compounds synthesis are depicted in Schemes 1 and 2.

4-Acetamido-1,8-naphthalic anhydride (3), (spectral properties not previously decribed). A mixture of 4-aminonaphthalic anhydride (0.50 g, 2.3 mmol), glacial acetic acid (1 mL, 17.0 mmol), and pyridine (4 mL, 50.0 mmol) was refluxed for 1 h. After the addition of acetic anhydride (8 mL, 84.0 mmol) the yellow mixture became brown and refluxing was continued for 3 h. The cooled mixture was diluted with water (100 mL) and the grey precipitate filtered and the product crystallised (acetic acid) to give the acetate, (yield, 43%), mp 283-285 °C (lit., [30] 282-283 °C); ir, (nujol), 3574,3380 (NH), 1773, 1711 (C=O), 1586 (C=C), 777, 751 (ArCH bend) cm^{-1}; ^1H nmr, (DMSO-d_6),δ, 2.27 (3H, s, Me), 7.89-7.95 (1H, t, *J* 8.0Hz, 6-H), 8.27-8.30 (1H, d, *J* 8.1Hz, 3-H), 8.48-8.79 (3H, m, 2-H, 5-H and 7-H).

Synthesis of 4,9-Disubstituted 1,8-Naphthalimides. 4-(3-Hydroxypropylamino)-9-(3-hydroxypropyl)-1,8-naphthalimide (5a, n = 3; R = H). A solution of 4-nitronaphthalic anhydride, **1** (2.43 g, 10.0 mmol) and 3-hydroxypropylamine (3.375 g, 45.0 mmol) in dimethylformamide (40 mL) was stirred and heated under nitrogen until TLC indicated complete reaction. The reaction mixture was cooled and diluted with water. The precipitate was collected by filtration and crystallised from ethanol and obtained as yellow needles, (yield, 70%), mp 210-211 °C.; ir: (nujol), 3340 (NH), 1675, 1630, 1580 (C=C), 775, 760 cm^{-1}; ^1H nmr: (DMSO-d_6), δ, 1.70-1.92 (4H, m, $NHCH_2CH_2$ and NCH_2CH_2), 3.14-3.61 (6H, m, $NHCH_2CH_2CH_2$ and $NCH_2CH_2CH_2$), 4.03-4.09, (2H, t, *J* 7.2Hz, NCH_2), 4.46-4.66 (2H, m, 2O*H*, exch.), 6.75-6.79 (1H, d, *J* 9Hz, 3-H), 7.63-7.69, (1H, t, *J* 7.6Hz, 6-H), 7.73-7.78 (1H, br., N*H*, exch.), 8.23-8.27, (1H, d, *J* 9Hz, 2-H), 8.40-8.68 (2H, m, 5-H and 7-H). *Anal.* Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.8; H, 6.2; N, 8.5..Found: C, 65.4; H, 6.4; N, 8.3.

4-(4-Hydroxybutylamino)-9-(4-hydroxybutyl)-1,8-naphthalimide (5a, n = 4; R = H). This compound was prepared in a similar way from 4-nitronaphthalic anhydride and 4-hydroxybutylamine to give, yellow needles, (yield, 54%), mp 203-204°C; ir: (nujol), 3340 (NH), 1675, 1625 (C=O), 1580 (C=C), 775, 755 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 1.45-1.74 (8H, m, 2x $(CH_2)_2CH_2OH$), 3.36-3.46 (6H, m, $NHCH_2(CH_2)_2CH_2$ and $NCH_2(CH_2)_2CH_2$), 3.98-4.04 (2H, t, *J* 6.9Hz, NCH_2), 4.39-4.51 (2H, dt, 2xO*H*,.*exch*.), 6.75-6.78 (1H, d, *J* 8.7Hz, 3-H), 7.63-7.69 (1H, t, *J* 7.9Hz, 6-H), 7.79 (1H, br., N*H*, exch.), 8.23-8.26 (1H, d, *J* 8.5Hz, 2-H), 8.38-8.70 (2H, m, 5-H and 7-H). *Anal.* Calcd.for $C_{20}H_{24}N_2O_4$: C, 67.3; H, 6.8; N, 7.8%. Found: C, 66.9; H, 6.8; N. 7.8.

4-(2-Sulphatoxyethylamino-9-(2-sulphatoxyethyl)-1,8-naphthalimide (5b, n = 2;R = SO_3H). 4-(2-Hydroxyethylamino)-9-(2-hydroxyethyl)-1,8-naphthalimide, (prepared as described [28]) (0.50 g, 1.7 mmol), was stirred with 98% conc. sulphuric acid (20 mL) at 2-4°C for 18 h. The solution was diluted with water at 0° and kept at that temperature for 3 h when a precipitate formed which was filtered and the solid washed with isopropanol and methanol. The solid was dissolved in hot water and ethanol, cooled to 4°C, and isopropanol added to give a precipitate which was collected by filtration to give orange crystals of the product (0.43g, 55%), mp > 300°C (decomp); ir: (nujol), 3389 (NH), 1680,1640 (C=O), 1575 (C=C), 1211, 1017 (S=O), 780, 782 (ArCH bend).cm^{-1}; ^1H nmr (D_2O): δ, 3.36-3.85 (6H, tt, NCH_2CH_2 and $NHCH_2CH_2$), 4.23-4.28 (2H, t, *J* 4.6Hz, NCH_2CH_2), 5.94-5.98 (1H, d, *J* 8Hz, 3-H), 6.83-6.86 (1H, t, *J* 7.8Hz, 6-H), 7.17-7.20 (1H, d, *J* 8Hz, 2-H), 7.25-7.29 (2H, dd, 5-H and 7-H).

Dipotassium 4-(Sulphatoxybutylamino-9-(4-sulphatoxybutyl)-1,8-naphthalimide (5b, n=4, R = SO_3K). 4-(4-Hydroxybutylamino)-9-(4-hydroxybutyl)-1,8-naphthalimide (0.5 g, 1.4 mmol) in 98% concentrated sulphuric acid (10 mL) was stirred at 2-4°C for 24 h, then diluted with water (250 cm^3), neutralised with potassium hydroxide, and kept at 2-4°C for 12 h, when the salt was precipitated. The precipitate was collected by filtration, extracted with ethanol and the extract dried to give orange crystals of the product (0.04 g, 6%), mp 178-184°C which contained traces of inorganic salts; ir (nujol): 3441, 3319 (NH), 1678, 1631 (C=O), 1581 (C=C), 1361, 1190 (S=O), 774, 757 (ArCH bend). cm^{-1}; ^1H nmr (DMSO-d_6/$CDCl_3$): δ 1.48-1.85 (8H, m, $CH_2CH_2CH_2CH_2CH_2$), 3.26-3.57 (6H, m, NCH_2 $CH_2CH_2CH_2$ and $NHCH_2CH_2CH_2CH_2$), 4.00-4.05 (2H, t, *J* 7.1Hz, NCH_2), 6.53-6.56 (1H, d, *J* 8.4Hz, 3-H), 7.41-7.47 (1H, t, *J* 7.6Hz, 6-H), 8.23-8.41 (3H, m, 2-H, 5-H and 7-H).

4-Acetamido-9-carboxymethyl-1,8-naphthalimide (4; n =1). 4-Acetamido-1,8-naphthalic anhydride (0.2 g, 0.8 mmol) and sodium glycinate (0.4 g, 0.8 mmol) in dimethylformamide (10 mL) were heated at 80°C for 3 h under a nitrogen atmosphere at which point TLC indicated that no reaction had taken place. The heating was continued at 120°C for 2 h and finally, to complete reaction, at 140°C for 13 h. The cooled mixture was diluted with water and acidified to afford a precipitate which was collected by filtration and crystallised (ethanol), to give yellow crystals (0.16 g, 64%), mp > 315°C (decomp.); ir (nujol): 3389, 3260 (NH), 1725, 1669 (C=O), 1598 (C=C),788,761 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.26 (3H, s, Me), 4.69 (2H, s, CH_2), 7.83-7.89 (1H, t, *J* 7.9Hz, 6-H), 8.19-8.23 (1H, d, *J* 8.1Hz, 3-H), 8.42-8.64 (3H, m, 2-H, 5-H and 7-H). *Anal.* Calcd. for $C_{16}H_{12}N_2O_5$: C, 61.5; H, 3.9; N, 9.0. Found: C, 61.7; H, 4.0; N, 9.0.

4-Chloroacetamido-9-(n-butyl)-1,8-naphthalimide (7a, R = Bu, R_1 = CH_2Cl). Chloroacetyl chloride (0.13 g, 1.12 mmol) in dimethylformamide (2 mL) was added dropwise to 4-amino-9-(*n*-butyl)-1,8-naphthalimide (0.15 g, 0.56 mmol) in dimethyl-

formamide (10 mL) containing triethylamine (0.11 g, 1.12 mmol) cooled in an ice/water bath. The reaction mixture was stirred at ambient temperature for 10 h when TLC indicated partial reaction. Further chloroacetyl chloride (0.26 g, 2.24 mmol), and triethylamine (0.22 g, 2.24 mmol) in DMF (5 mL) were then added at 2-4°C. The mixture was left at ambient temperature for 20 h (TLC monitoring), and finally heated at 60°C for 5 h, to complete reaction. The mixture was diluted with water (100 mL), the precipitate was collected by filtration and crystallised (acetic acid), to give the product (0.14 g, 73%), as cream crystals, mp 244-246°C; ir(nujol): 3257 (NH), 1696, 1650 (C=O), 1593 (C=C), 783, 750 (ArCH bend) cm^{-1}; ^{1}H nmr (DMSO-d_6/$CDCl_3$): δ, 0.85-0.91 (3H, t, *J* 7.5Hz, Me), 1.30-1.39 (2H, m, CH_2CH$_3$), 1.55-1.64 (2H, m, CH_2CH$_2$CH$_3$), 4.04-4.10 (2H, t, *J* 7.5Hz, NCH_2), 4.29 (2H, s, CH_2Cl), 7.66-7.73 (1H, t, *J* 8.8Hz, 6-H), 8.25-8.28 (1H, d, *J* 7.5Hz, 3-H), 8.33-8.54 (3H, m, 2-H, 5-H and 7-H), 9.95 (1H, s, N*H*). *Anal*. Calcd.for $C_{18}H_{17}ClN_2O_3$: C, 62.7; H, 5.0: Cl, 10,3; N, 8.1. Found: C, 62.7; H, 5.2; Cl, 10.3; N, 8.3.

4-(Maleiamido-9-ethyl-1,8-naphthalimide (7b, R = Et, R^1 = carboxyethenyl). A mixture of 4-amino-9-ethyl-1,8-naphthalimide (**6**), (0.50 g, 2.1 mmol) and maleic anhydride (0.60 g, 6.3 mmol) in chloroform (50 mL) was refluxed for 20 h and the solvent then removed *in vacuo*. The residue was stirred with water, then filtered and the solid crystallised (ethanol/DMF) to give yellow crystals, (0.38 g, 53%), mp 222-224°C; ir (nujol): 3275 (NH), 3132 (OH), 1717 (C=O, COOH), 1697, 1653 (C=O), 1591 (C=C), 783, 757 (ArCH bend) cm^{-1}; ^{1}H nmr (DMSO-d/$CDCl_3$): δ, 0.83-0.88 (3H, t, *J* 6.3Hz, Me), 3.70-3.79 (2H, q, *J* 7.5Hz, CH_2Me, 5.92-5.97 (1H, d, *J* 12.5Hz, C*H*COOH), 6.26-6.31(1H, d, *J* 12.5Hz, NHCOC*H*), 7.31-7.37 (1H, t, *J* 7.0Hz, 6-H), 7.94-7.97 (1H, d, *J* 7.0Hz, 3-H), 8.08-8.22 (3H, td, 2-H, 5-H and 7-H), 11.0 (1H, s, N*H*). *Anal* Calcd. for $C_{18}H_{14}N_2O_5$: C, 63.9; H, 4.2; N, 8.3. Found: C, 63.6; H, 4.3; N, 8.3.

4-(Maleimido-9-ethyl-1,8-naphthylimide. A mixture of the preceding maleiamido compound (0.30 g, 0.9 mmol) and sodium acetate trihydrate (0.50 g, 3.6 mmol) was refluxed in acetic anhydride for 1 h, and then cooled to give the imide by dehydration. The reaction mixture was diluted with water, stirred for 7 h at 2-4°C and then filtered. The washed solid was crystallised from acetic acid to give brown crystals of the naphthalimide, (0.10 g, 35%), mp 219-221°C; ir (nujol): 1720 (C=O), 1699, 1659 (C=O), 1589 (C=C), 784, 757 (ArCH bend) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ, 1.32-1.38 (3H, t, *J* 7.5Hz, Me), 4.23-4.32 (2H, q, *J* 7.5Hz, CH_2CH$_3$), 7.06 (2H, s, COC*H*=C*H*CO), 7.62-7.66 (1H, d, *J* 10.0Hz, 3-H), 7.76-7.82 (1H, t, *J* 7.5Hz, 6-H), 7.90-7.94 (1H, d, *J* 10.0Hz, 2-H), 8.66-8.71(2H, m, 5-H and 7-H). *Anal*. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.8; H, 3.8; N, 8.8. Found: C, 68.0; H, 3.7; N, 8.7.

4-Amino-9-(2-hydroxyethyl)-1,8-naphthalimide (8). 4-Amino-naphthalic-1,8-anhydride (2.0 mmol) and 2-hydroxyethylamine (6.0 mmol) in DMF (25 mL) were stirred at 90°C and heated under nitrogen until TLC indicated complete reaction (2 h). The reaction mixture was cooled, diluted with water and the precipitated solid was filtered and crystallised (ethanol) to afford dark yellow prisms (50% yield), of **8**, mp 261-263°C; ir (nujol): 3525 (OH), 3363, 3224 (NH), 1658, 1631 (C=O), 1576 (C=C), 778, 759 (ArCH bend).cm^{-1}; ^{1}H nmr (DMSO-d_6/$CDCl_3$): δ, 3.47-3.56 (2H, q, *J* 5.9Hz, CH_2OH), 3.74-3.80 (1H, t, *J* 5.9Hz, O*H*), 4.00-4.05 (2H, t, *J* 5.9Hz, NCH_2), 6.19 (2H,br., NH_2, exch.), 6.52-6.56 (1H, d, *J* 8.5Hz, 3-H), 7.24-7.30 (1H, t, *J* 7.8Hz, 6-H), 7.97-8.00 (1H, d, *J* 8.5Hz, 2-H), 8.11-8.23 (2H, dd, 5-H and 7-H). *Anal*. Calcd. for $C_{14}H_{12}N_2O_3$:C, 65.6; H, 4.7; N, 10.9. Found: C, 66.0; H, 5.0; N, 11.1.

4-Chloroacetamido-9-(2-chloroacetoxyethyl)-1,8-naphthalimide (9). An ice-cold solution of 4-amino-9-(2-hydroxyethyl)-1,8-naphthalimide (**8**) (0.34 g, 1.3 mmol) in DMF (5 mL) containing triethylamine (0.20 g, 2.0 mmol), was stirred and treated dropwise with chloroacetyl chloride (0.22 g, 2.0 mmol) in DMF (2 mL). Since reaction (TLC monitoring) was slow (after 4 h) more chloroacetyl chloride (0.22 g, 2.0 mmol) and triethylamine (0.20 g, 2.0 mmol) were added dropwise to the mixture, which was reacted at ambient temperature for 1 h. TLC then indicated complete reaction and the mixture was diluted with water (150 cm^3) and the precipitate filtered and crystallised (ethanol) to afford brown-yellow crystals (0.32 g, 60%), mp 211-214°C; ir (nujol): 3274 (NH), 1753 (C=O, COOR), 1697, 1659, 1593 (C=C), 784, 755 (ArCH bend) cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 4.28 (2H, s, OCOCH_2Cl), 4.29-4.45 (4H, m, CH_2CH_2), 4.55 (2H, s, NHCOCH_2Cl), 7.86-7.92 (1H, t, *J* 7.9Hz, 6-H), 8.21-8.25 (1H, d, *J* 8.2Hz, 3-H), 8.46-8.65 (3H, m, 2-H, 5-H and 7-H), 10.27 (1H, s, N*H*). *Ana*l. Calcd. for $C_{18}H_{14}Cl_2N_2O_5$: C, 52.8; H, 3.5; Cl, 17.3. N, 6.8. Found: C, 52.6; H, 3.6; Cl,17.2; N, 6.8.

4-n-Butylamino-9-(2-hydroxyethyl)-1,8-naphthalimide (11). 4-Nitro-9-(2-hydroxyethyl)-1,8-naphthalimide (**10**) was prepared as described previously [28]. To 4-nitro-9-(2-hydroxyethyl)-1,8-naphthalimide (0.50 g, 1.5 mmol) in dry DMF (25 mL), *n*-butylamine (0.50 g, 6.0 mmol) was added and the mixture heated at 105-110°C for 1.5 h under nitrogen (TLC monitoring). After work-up by dilution with water and filtration, yellow-green crystals (0.20 g, 43%) were obtained and crystallised (ethanol), mp 190-192°C; ir(nujol): 3471 (OH), 3392 (NH), 1672, 1641 (C=O), 1588 (C=C), 767, 757 (ArCH bend) cm^{-1}; ^{1}H nmr (DMSO-d_6/$CDCl_3$): δ, 0.56-0.62 (3H, t, *J* 7.5Hz, Me), 1.01-1.16 (2H, m, CH_2 CH$_3$), 1.30-1.45 (2H, q, *J* 7.5Hz, CH_2CH$_2$CH$_3$), 2.97-3.00 (2H, q, *J* 7.1Hz, NHCH_2), 3.37-3.40 (2H, q, *J* 7.8Hz, CH_2OH), 3.81-3.87 (1H, t, *J* 6.8Hz, O*H*), 3.88-3.93 (2H, t, *J* 6.3Hz, NCH_2), 6.24-6.27 (1H, d, *J* 7.9Hz, 3-H), 6.60-6.69 (1H, br., N*H*, exch.), 7.13-7.20 (1H, t, *J* 8.8Hz, 6-H), 7.93-7.96 (1H, d, *J* 7.5Hz, 2-H) 8.07-8.16 (2H, dd, 5-H and 7-H). *Anal*. Calcd.for $C_{18}H_{20}N_2O_3$: C, 69.2; H, 6.5; N, 9.0. Found: C, 69.1; H, 6.4; N, 9.1.

4-*n*-Butylamino-9-(2-chloroacetoxyethyl)-1,8-naphthalimide (12). To 4-*n*-butylamino-9-(2-hydroxyethyl)-1,8-naphthalimide (0.6 g, 1.9 mmol), in DMF (10 mL), containing triethylamine (0.3 g, 2.9 mmol), chloroacetyl chloride (0.32 g, 2.9 mmol) in DMF (5 mL) was added dropwise to the ice-cold solution. TLC indicated after 4 h that reaction was still incomplete, and chloroacetyl chloride (0.54 g, 4.75 mmol) in DMF (5 mL) containing triethylamine (0.48 g, 4.75 mmol) was added to the reaction mixture, which was stirred for a further 6 h at ambient temperature. TLC indicated complete reaction and the mixture was concentrated, and diluted with water to afford a yellow emulsion, which solidified after stirring for 2 h at 2-4°C. The solid was collected by filtration and crystallised (ethanol/acetone) to give dark yellow crystals (0.20g, 27%), mp 113-116°C; ir (nujol): 3442, 3432 (NH), 1750 (COOR), 1685, 1642 (C=O) ,1546 (C=C), 773, 755 (ArCH bend) cm^{-1}; ^{1}H nmr ($CDCl_3$): δ, 1.01-1.07 (3H, t, *J* 7.5Hz, Me), 1.48-1.63 (2H, m, CH_2CH$_3$), 1.76-1.88 (2H, q, *J* 7.2Hz, CH_2CH$_2$CH$_3$), 3.39-3.46 (2H, q, *J* 5.8Hz, NHCH_2), 4.07 (2H, s, CH_2Cl), 4.49-4.69 (4H, m, NCH_2CH_2), 5.32 (1H, br., N*H*, exch.), 6.71-6.74 (1H, d, *J* 7.5Hz, 3-H), 7.58-7.66 (1H, t, *J* 8.8Hz, 6-H), 8.08-8.11 (1H, d, *J* 7.9Hz, 2-H), 8.44-8.59 (2H, dd, 5-H and 7-H).. *Anal*. Calcd. for

$C_{20}H_{21}ClN_2O_4$: C, 61.8; H, 5.5; Cl, 9.1:, N, 7.2. Found: C, 62.1; H, 5.8; Cl, 9.0; N, 6.8.

4-Amino-9-(carboxymethyl)-1,8-naphthalimide (14; n=1).

(a) 4-Nitronaphthalic anhydride (1.94 g, 8.0 mmol) and glycine (0.75 g, 10.0 mmol) in ethanol (40 mL) were stirred and refluxed until TLC indicated complete reaction. The cooled mixture was diluted with water and the precipitated solid filtered and crystallised (ethanol), to give pale yellow needles of the nitro compound (**13**, n = 1) (yield 35%), mp 266-267°C; ir (nujol)::3080 (CH), 1715 (C=O, COOH), 1675, 1630 (C=O), 1587 (C=C), 1535, 1360 (NO_2), 788, 759 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6/$CDCl_3$): δ, 4.69 (2H, s, CH_2), 7.77-7.84 (1H, t, *J* 8.0Hz, 6-H), 8.20-8.24 (1H, d, *J* 8.0Hz, 3-H), 8.23-8.65 (3H, m, 2-H, 5-H and 7-H). *Anal*. Calcd.for $C_{14}H_8N_2O_6$: C, 56.0; H, 2.7: N, 9.3. Found: C, 56.4; H, 3.0; N, 9.6. The nitro compound (1.2 g, 4.0 mmol) and stannous chloride (3.80 g, 20.0 mmol) in methanol (20 mL) containing conc. hydrochloric acid (5 mL) were refluxed for 1.5 h, concentrated *in vacuo*, then cooled and diluted with water. The precipitated solid was filtered and crystallised (ethanol) to give yellow microcrystals (yield 44%), mp 263-266°C; ir (nujol): 3483, 3430, 3354, 3260 (NH), 1745 (C=O, COOH), 1670, 1646, (C=O), 1581 (C=C), 785, 763, (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 4.64 (2H, s, CH_2), 6.81-6.85 (1H, d, *J* 8.4Hz, 3-H), 7.59-7.66 (1H, t, *J* 8.0Hz, 6-H), 8.12-8.15 (1H, d, *J* 8.4Hz, 2-H), 8.37-8.58 (2H, dd, 5-H and 7-H). *Anal*. Calcd. for $C_{14}H_{10}N_2O_4$:C, 61,7; H, 3.7; N, 10.4.. Found: C, 61.7; H, 4.0; N, 10.1.

(b) 4-Aminonaphthalic-1,8-anhydride (**2**) (2.0 mmol) and glycine (6.0 mmol) in DMF (25 mL) were heated at 120°C for 8 h under nitrogen when TLC indicated complete reaction. The cooled mixture was diluted with water and the precipitated solid filtered and crystallised (ethanol) to give yellow microcrystals, (yield 47%), mp 263-266°C.

The products from methods (a) and (b) were identical. Acetylation of the amino compound gave the acetyl derivative which was identical with compound (**4**).

4-Amino-9-(2-carboxyethyl)-1,8-naphthalimide (14; n = 2). 4-Nitro-1,8-naphthalic anhydride (8.0 mmol) and 3-amino-propionic acid (10.0 mmol) were refluxed in ethanol (40 mL) for 3 h when TLC showed reaction was completed. The cooled mixture was diluted with water and the precipitated solid was collected by filtration and crystallised (ethanol) to afford white microcrystals (yield 65%), mp 198-200°C of the nitro compound, (**13,** n = 2); ir (nujol): 3080 (CH), 1705 (COOH), 1675, 1628 (C=O), 1587 (C=C), 1535, 1352 (NO_2), 788, 732 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ, 2.37-2.44 (2H, t, *J* 7.6Hz, NCH_2), 4.10-4.16 (2H, t, *J* 7.6Hz, NCH_2CH_2), 7.67-7.74 (1H, t, *J* 8.0Hz, 6-H), 8.10-8.14 (1H, d, *J* 8.0Hz, 3-H), 8.35-8.56 (3H, m, 2-H, 5-H and 7-H). *Anal*. Calcd. for $C_{15}H_{10}N_2O_6$: C, 57.3; H, 3.2; N, 8.9. Found: C, 57.4; H, 3.1; N, 9.0. The nitro compound (1.26 g, 4.0 mmol) was reduced by the general method with stannous chloride and the precipitated solid was collected by filtration and crystallised (ethanol) to give pale yellow needles, mp 226-228°C; ir (nujol): 3471, 3362, 3258 (NH), 1724 (C=O, COOH), 1675, 1642 (C=O), 1581 (C=C), 778, 757 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ 2.34-2.40 (2H, t, *J* 7.5Hz, NCH_2), 4.04-4.10 (2H, t, *J* 7.5Hz, NCH_2CH_2), 6.28 (2H, br., NH_2, exch.), 6.50-6.53 (1H, d. *J* 7.1Hz, 3-H), 7.20-7.27 (1H, t, *J* 8.8Hz, 6-H), 7.92-7.95 (1H, d, *J* 7.5Hz, 2-H), 8.10-8.17 (2H, m, 5-H and 7-H). *Anal.* Calcd. for $C_{15}H_{12}N_2O_4$: C, 63.4; H, 4.3: N, 9.9. Found: C, 63.7; H, 4.7: N, 9.4.

The product was identical to that obtained in 51% yield from reaction of 4-aminonaphthalic-1,8-anhydride with β-alanine in DMF.

4-Amino-9-(3-carboxypropyl)-1,8-naphthalimide (14; n = 3). 4-Nitronaphthalic anhydride (8.0 mmol) and 4-aminobutanoic acid (10.0 mmol) were refluxed in ethanol (40 mL) for 4 h. Work up as for the previous compound afforded creamy white needles of the nitro compound (**13**, n = 3), from ethanol (yield 67%), mp 182-184°C; ir (nujol): 3084(CH), 1705 (C=O, COOH), 1658, 1628 (C=O), 1587 (C=C), 1540, 1346 (NO_2), 785, 770 (ArCH bend) cm^{-1}; ^1H (DMSO-d_6): δ 1.59-1.71 (2H, q, *J* 7.2Hz, $NCH_2CH_2CH_2$), 1.96-2.03 (2H, t, *J* 7.4Hz, NCH_2), 3.81-3.87 (2H, t, *J* 7.0Hz, $NCH_2CH_2CH_2$), 7.59-7.66 (1H, t, *J* 8.0Hz, 6-H), 8.03-8.06 (1H, d, *J* 8.0Hz, 3-H), 8.27-8.42, (3H, m, 3-H, 5-H and 7-H). *Anal*. Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.5; H, 3.7; N, 8.5. Found: C, 58.5; H, 3.7: N, 8.5. The nitro compound was reduced by the general method with stannous chloride and gave the same compound as that formed in 11% yield from the reaction of 4-aminonaphthalic-1,8-anhydride with 4-aminobutanoic acid, namely, 4-amino-9-(3-carboxypropyl)-1,8-naphthalimide, orange needles mp 163-165°C; ir (nujol): 3457, 3356, 3258 (NH), 1721 (C=O, COOH), 1678, 1652 (C=O), 1574 (C=C), 772, 755 (ArCH bend) cm^{-1}; ^1H nmr (DMSO-d_6): δ 1.90-2.02 (2H, q, *J* 7.5Hz, $NCH_2CH_2CH_2$), 2.30-2,36 (2H, t, *J* 7.5Hz, NCH_2), 4.07-4.13 (2H, t, *J* 7.5Hz, CH_2COOH), 5.82 (2H, br., NH_2, exch.), 6.74-6.78 (1H, d, *J* 8.1Hz, 3-H), 7.47-7.53 (1H, t, *J* 8.5Hz, 6-H), 8.20-8.46 (3H, m, 2-H, 5-H and 7-H). *Anal*. Calcd for $C_{16}H_{14}N_2O_4$: C, 64.4; H, 4.7; N, 9.4. Found: C, 64.3; H, 4.5; N, 9.8..

4-Butylamino-(9-ethoxycarbonylmethyl)-1,8-naphthalimide (16). 4-Nitro-1,8-naphthalic anhydride (8 mmol) and ethyl glycinate (11 mmol) in ethanol were refluxed for 10 h when TLC indicated complete reaction. The cooled mixture was diluted with water and the precipitated solid collected by filtration and crystallised (ethanol) to give orange-yellow needles (yield 55%), mp 154-155°C, consisting of 4-nitro-(9-ethoxycarbonylmethyl)-1,8-naphthalimide (**15**); ir (nujol): 3085 (ArCH), 1743, (C=O, COOEt), 1707, 1670 (C=O), 1590 (C=C), 1570, 1377 (NO_2), 781, 752 (ArCH bend) cm^{-1}; ^1H nmr ($CDCl_3$): δ 1.26-1.32 (3H, t, *J* 7.0Hz, Me), 4.19-4.28 (2H, q, *J* 7.1Hz, CH_2CH_3), 4.91 (2H, s, NCH_2), 7.79-7.87 (2H, m, 3-H and 6-H), 8.47-8.66 (3H, m, 2-H, 5-H and 7-H). *Anal*. Calcd. for $C_{16}H_{12}N_2O_6$: C, 58.5; H, 3.7; N, 8.5.. Found: C, 58.4; H, 3.9; N, 8.8. 4-Nitro-(9-ethoxycarbonylmethyl)-1,8-naphthalimide (15) (0.33 g, 1.0 mmol) and *n*-butylamine (0.22 g, 3.0 mmol) were heated at 80°C in DMF (15 mL) under nitrogen for 2 h and then at 100°C when TLC indicated complete reaction. The cooled mixture was diluted with water and the precipitated solid collected by filtration and crystallised (ethanol) to afford dark yellow crystals (0.12 g, 35% yield), mp 170-171°C; ir (nujol): 3407 (NH), 1733 (C=O, COOR), 1686, 1646 (C=O), 1593 (C=C), 781, 760 (ArCH bend) cm^{-1}; ^1H nmr ($CDCl_3$): δ 0.98-1.05 (3H, t, *J* 7.3Hz, CH_2CH_2 Me), 1.29-1.35 (3H, t, *J* 7.1Hz, OCH_2CH_3), 1.42-1.59 (4H, m, $CH_2CH_2CH_3$), 3.33-3.39 (2H, s, NHCH_2), 4.22-4.31 (2H, q, *J* 7.1Hz, OCH_2CH_3), 4.91(2H, s, NCH_2), 6.59-6.63 (1H, d, *J* 8.4Hz, 3-H), 7.43-7.50 (1H, t, *J* 7.9Hz, 6-H), 8.04-8.08 (1H, d, *J* 8.2Hz, 2-H), 8.33-8.47 (2H, dd, 5-H and 7-H). *Anal*. Calcd.for $C_{20}H_{22}N_2O_4$: C, 67.8; H, 6.3; N, 7.9. Found: C, 68.0; H, 6.6; N, 7.9.

Hydrolysis and acidification gave the acidic product believed to be (**17**), 4-*n*-butylamino-9-carboxymethyl-1,8-naphthalimide the nmr spectrum of which showed the presence of a carboxyl and lacked an ethyl group.

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