The UV–Visible Absorption and Fluorescence of some Substituted 1,8-Naphthalimides and Naphthalic Anhydrides

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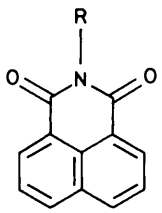
A number of substituted 1,8-naphthalimides and naphthalic anhydrides have been prepared and their absorption and fluorescence properties in absolute ethanol have been determined. In the absence of an alkylamino substituent in the naphthalene ring, the compounds are colourless and weakly fluorescent. In the presence of such a substituent they become yellow and frequently fluoresce strongly with quantum yields of the order of 0.8.

Organic fluorophores based on a naphthalene nucleus, usually with an amine substituent, have aroused the interest of photochemists and photobiologists because of their sensitivity to solvent effects.[1,2] Substantial changes in the fluorescence spectrum, quantum yield, and lifetime are often observed as the solvent is varied or as a result of binding to a substrate. A related group of compounds, based on the naphthalimide moiety (I), are used in the field of non-destructive testing for



(I)

crack detection. They have been proposed as potential fluorescent probes of hypoxic cells[3,4] and have also been investigated with a view to laser activity.[5,6] The presence of an amino substituent in the naphthalene ring can often give rise to very high fluorescence quantum yields, in the range 0.7–0.8. One of us has previously reported a general method for the preparation of substituted naphthalimides.[7] This method, and improvements upon it,[8] has been used to prepare a variety of *N*- and ring-substituted naphthalimides the fluorescence properties of which have been examined and described in this account. We also report on the preparation and fluorescence properties of some naphthalic anhydrides.

Results and Discussion

The compounds examined in this study are listed in Tables 1–4 and fall naturally into three groups: naphthalimides with bromo, cyano groups or without a substituent (**1**)–(**4**), naphthalimides with an amino or methoxy substituent on the napthalene ring (**5**)–(**25**) or naphthalic anhydrides with an amino substituent in the naphthalene ring (**26**)–(**30**). A number of methods of preparation were employed for the compounds shown in Tables 1–3 and the organic chemistry involved in these will be discussed more fully elsewhere. However, the methods are described briefly below.

Method A.—Interaction of 4-bromo-1,8-naphthalic anhydride and 4-nitro-1,8-naphthalic anhydride with primary amines in warm ethanol solution gave substitution only in the anhydride ring. To a lesser regiospecific extent the same compound resulted from the interaction of the same two anhydrides with primary amines in dimethylformamide or *N*-methylpyrrolidinone respectively kept at 0 °C for 24 h. Minor impurities were products of alkylamino substitution at the 4-position.[9]

Method B.—Interaction of 4-nitro-1,8-naphthalic anhydride with primary amines in dimethylformamide at 120 °C gave the *N*-alkyl-4-alkylamino-1,8-naphthalimide accompanied by small amounts of the *N*-alkyl-4-nitro-1,8-naphthalimide and the *N*-alkyl-4-dimethylamino-1,8-naphthalimide.[10]

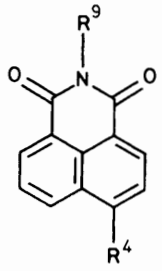
Method C.—Interaction of 4-chloro or 4-bromo-1,8-naphthalic anhydride with primary amines in *N*-methylpyrrolidinone at 55 °C and then 110 °C gave exclusively the *N*-alkyl-4-alkylamino-1,8-naphthalimide.[11]

Method D.—By the combined use of methods A and B, or C, unsymmetrical compounds were obtained from preliminary formation of the *N*-alkyl-4-bromo-1,8-naphthalimide followed by reaction in *N*-methylpyrrolidinone (or dimethylformamide) with another primary or secondary amine.

From method A products could be isolated by crystallisation. Direct crystallisation of crude products from method B was occasionally possible but invariably column chromatographic methods were necessary following initial monitoring by analytical thin layer chromatography. With method C the number of impurities was greatly reduced and, after removal of the excess amine and *N*-methylpyrrolidinone, the residual material in chloroform was washed with water to remove amine salt, the chloroform extract was dried, the chloroform recovered and the residual material crystallised. The melting points of the products are collated in Tables 1–4.

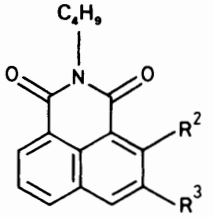
The absorption and fluorescence properties of all the compounds are presented in Tables 5 and 6. The absorption spectra of (**1**)–(**4**) are very similar to that of naphthalic anhydride[12] in exhibiting a peak at approximately 350 nm with an extinction coefficient in the region of 10 000. There is a small amount of

Table 1. Structures and properties of 4,*N*-disubstituted 1,8-naphthalimides.



Compound	R^4	R^9	M.p./°C
(1)	H	H	301–303
(2)	H	C_4H_9	97–98
(3)	Br	C_3H_7	129–130
(4)	CN	C_3H_7	178–179
(5)	NHC_3H_7	Ph	237–239
(6)	NHC_4H_9	H	237–239
(7)	$NHCH_3$	CH_3	261–262
(8)	NHC_2H_5	C_2H_5	189–190
(9)	NHC_3H_7	C_3H_7	150–151
(10)	NH-i-C_3H_7	i-C_3H_7	140–141
(11)	NHallyl	allyl	181–182
(12)	NHC_4H_9	C_4H_9	127–128
(13)	NHC_6H_{11}	C_6H_{11}	230–231
(14)	NHC_8H_{17}	C_8H_{17}	82–85
(15)	$NHC_{10}H_{21}$	$C_{10}H_{21}$	93–95
(16)	NH_2	C_4H_9	183–184
(17)	$N(CH_3)_2$	C_4H_9	114–115
(18)	$NHCOCH_3$	C_4H_9	233
(19)	NHC_4H_9	Ph	93–95
(20)	$NHNH_2$	NH_2	>360

Table 2. Structures and properties of isomeric *N*-butyl(alkylamino)-1,8-naphthalimides.

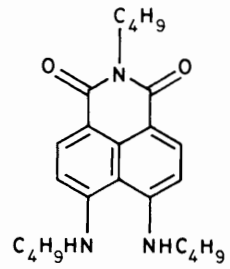


Compound	R^2	R^3	M.p./°C
(21)	NHC_4H_9	H	88–89
(22)	H	NH_2	170–171
(23)	H	NHC_4H_9	142–143

structure in the spectra as Figure 1 shows, the spectrum of (2) being identical with that of (1) except for a 1–2 nm red shift. The bromo and cyano substituents in (3) and (4) cause a further red shift of approximately 10 nm. All four compounds are only weakly fluorescent and (1) and (2) show slight structure in their spectra which are otherwise almost identical. The fluorescence decay times for these compounds are very short—too short for measurement with our equipment to any degree of certainty. We have, therefore, assigned to them an upper limit of 0.5 ns.

Substitution by an amino or alkoxy group in the naphthalene ring drastically alters both the absorption and fluorescence properties of (1) (Tables 5 and 6). The compounds become yellow due to the presence of an absorption band in the region

Table 3. Structures and properties of trisubstituted compounds.



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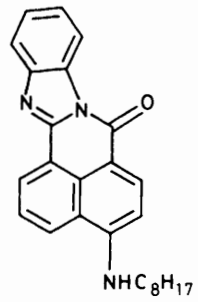

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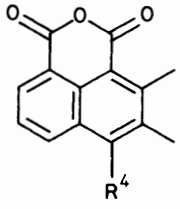
Compound	M.p./°C
(24)	184–185
(25)	153.5–154

Table 4. Structures and properties of 4-substituted 1,8-naphthalic anhydrides.



Compound	R^4	M.p./°C
(26)	NH_2	>360
(27)	$NHCOCH_3$	282–283
(28)	$N(CH_3)_2$	204–205
(29)	piperidyl	179–180
(30)	morpholine	205–206

of 450 nm. For the majority of compounds this band is broad and structureless with a suggestion of asymmetry on the long wavelength edge (Figure 2). Compounds (24) and (25) differ in exhibiting definite structure in their absorption spectra (Figure 3); resulting from a change in the molecular structure from the general pattern.

As this absorption band is not observed in either (1) or the naphthylamines[12] it may be assigned to a charge-transfer (CT) transition since the criteria for a CT transition, the presence of electron-donating and accepting groups, are fulfilled. Spectral measurements for (12) in solvents of varying polarity show[13] that the positions of both the absorption and fluoresence peaks correlate well with solvent polarity parameters such as Z and E_T, as would be expected for a CT transition.[14]

Although the absorption properties of these molecules are fairly similar, there are big differences in the emission properties which may be traced to changes in the substituent at a particular ring position [compounds (5)–(20)] and to alteration in the position of substitution [(12), (16), (21)–(23)]. A number of the compounds studied have substituents with identical hydrocarbon chains at the 4- and at the imide positions in the naphthalimide as a result of the preparative method [compounds (7)–(15)]. The effects of changing the length and/or nature of this group are small enough to be accounted for by the experimental uncertainty in the values of the quantum yield and lifetime, although substantial differences might be expected in other solvents. Replacement of the hydrocarbon group at the

Table 5. UV–VIS absorption properties of naphthalimides.

Compound	Wavelength/nm; (extinction coefficient/dm^3 mol^{-1} cm^{-1}); (sh = shoulder)
(1)	339 (1.14×10^4), 330 (1.18×10^4), 318 (sh)
(2)	341 (1.14×10^4), 331 (1.18×10^4), 320 (sh), 296 (sh), 284 (sh)
(3)	354 (1.16×10^4), 341 (1.33×10^4), 325 (sh), 300 (sh)
(4)	350 (1.31×10^4), 334 (1.41×10^4), 320 (sh), 305 (sh)
(5)	441 (1.58×10^4), 280 (1.80×10^4), 255 (sh)
(6)	440 (1.29×10^4), 281 (1.65×10^4), 253 (1.26×10^4)
(7)	437 (1.45×10^4), 281 (1.84×10^4), 257 (1.91×10^4)
(8)	440 (1.48×10^4), 280 (1.80×10^4), 257 (1.83×10^4)
(9)	440 (1.27×10^4), 281 (1.50×10^4), 257 (1.16×10^4)
(10)	439 (1.25×10^4), 282 (1.46×10^4), 259 (1.57×10^4)
(11)	436 (1.39×10^4), 281 (1.70×10^4), 257 (1.64×10^4)
(12)	440 (1.48×10^4), 282 (1.79×10^4), 259 (1.88×10^4)
(13)	439 (1.15×10^4), 284 (1.24×10^4), 261 (1.38×10^4)
(14)	441 (1.57×10^4), 282 (1.49×10^4), 258 (1.74×10^4)
(15)	442 (1.52×10^4), 283 (1.94×10^4), 260 (2.21×10^4)
(16)	434 (6.33×10^3), 274 (sh, 8.40×10^3), 259 (1.09×10^4)
(17)	418 (1.14×10^4), 277 (sh), 259 (1.68×10^4), 225 (sh)
(18)	363 (1.62×10^4), 247 (2.69×10^4)
(19)	440 (1.56×10^4), 283 (1.77×10^4), 272 (sh), 257 (sh)
(20)	439 (9.26×10^3), 271 (1.92×10^4), 228 (1.48×10^4)
(21)	439 (1.62×10^4), 417 (1.37×10^4), 325 (7.16×10^3), 264 (3.92×10^4)
(22)	425 (4.06×10^3), 342 (7.70×10^3), 252 (2.49×10^4)
(23)	448 (4.04×10^3), 353 (7.05×10^3), 259 (2.42×10^4)
(24)	447 (2.35×10^4), 430 (sh), 250 (3.30×10^4)
(25)	464 (2.50×10^4), 450 (sh), 270 (3.67×10^4)
(26)	427 (1.08×10^4), 300 (9.01×10^3), 270 (1.97×10^4)
(27)	361 (9.80×10^3), 255 (sh), 240 (2.18×10^4)
(28)	420 (9.15×10^3), 306 (sh), 272 (1.43×10^4)
(29)	409 (1.03×10^4), 267 (1.67×10^4)
(30)	420 (9.57×10^3), 300 (sh), 272 (1.73×10^4)

Table 6. Fluorescence properties of napthalimides and naphthalic anhydrides.

Compound	φ_f	τ_f/ns	λ_{max}/nm
(1)	0.029	<0.5	370
(2)	0.040	<0.5	370
(3)	0.003	<0.5	380
(4)	0.007	<0.5	380
(5)	0.700	8.9	530
(6)	0.680	9.3	527
(7)	0.760	10.2	523
(8)	0.740	10.1	540
(9)	0.720	9.9	540
(10)	0.790	10.5	520
(11)	0.805	10.3	535
(12)	0.810	10.5	525
(13)	0.670	10.2	525
(14)	0.720	9.7	540
(15)	0.710	9.9	530
(16)	0.640	9.3	522
(17)	0.034	10.2	535
(18)	0.750	7.5	465
(19)	0.700	9.3	530
(20)	0.160	1.5/7.6	522
(21)	0.405	2.9	460, 480 (sh)
(22)	0.460	20.1	540
(23)	0.230	15.3	560
(24)	0.430	5.6	465 (sh), 520
(25)	0.720	6.9	503, 530 (sh)
(26)	0.140	3.5	550
(27)	0.007	—	485
(28)	0.007	5.3	535
(29)	0.012	6.5	540
(30)	0.009	5.2	525

imide position [compounds (**5**) and (**6**)] or at the nitrogen in position 4 (**16**) also have little or no effect.

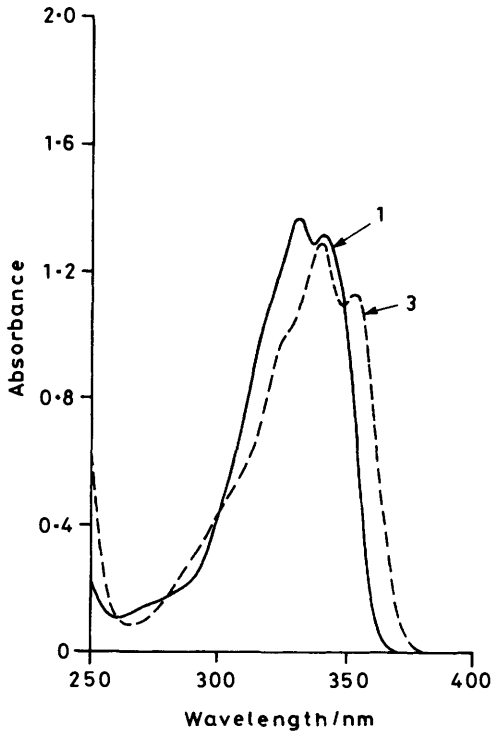


Figure 1. Absorption spectra of compounds (**1**) (1.15×10^{-4} mol dm^{-3}) and (**3**) (0.97×10^{-4} mol dm^{-3}) in absolute ethanol.

However, if the 4-amino substituent has two alkyl groups attached, the effect is quite dramatic, as evidenced by compound (**17**). The hypsochromic shift of the absorption maximum for this compound and its somewhat weaker intensity might have

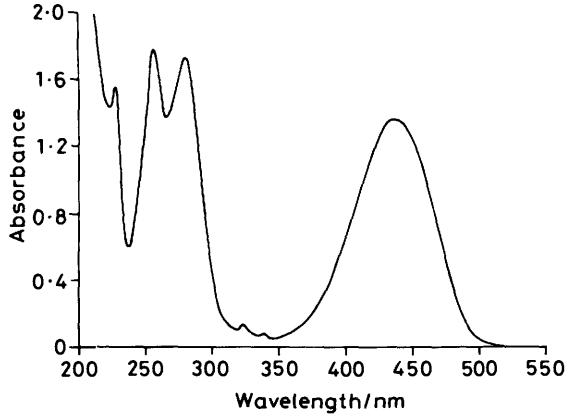


Figure 2. Absorption spectrum of compound (7) (0.93×10^{-4} mol dm^{-3}) in absolute ethanol.

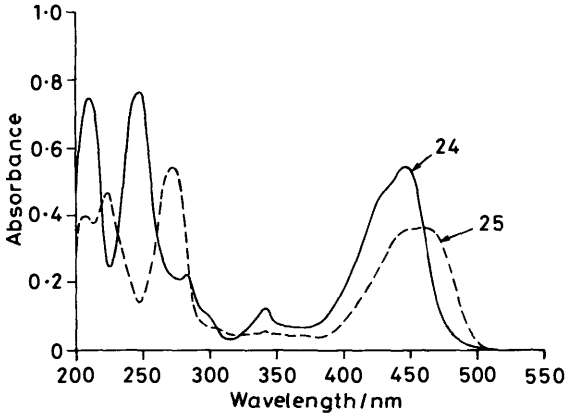
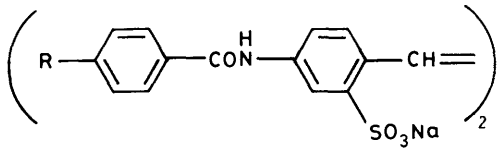


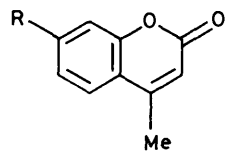
Figure 3. Absorption spectra of compounds (**24**) (2.3×10^{-5} mol dm^{-3}) and (**25**) (1.36×10^{-5} mol dm^{-3}) in absolute ethanol.

been anticipated, but the diminution of the fluorescence is very marked. This is presumably due to steric interaction between one of the methyl groups of the 4-dimethylamino substituent and the hydrogen at the 5-position (the *peri* effect). For 4-alkylamino substituents with a hydrogen attached to the nitrogen this effect is minimised by the alignment of the substituent so that the *peri* hydrogen and that of the alkylamino group are close together and the alkyl group points away. It is also of interest that the isopropylamino group [compound (**10**)] is sufficiently removed from the *peri* H atom to show no diminution of fluorescence and little steric interaction seems evident. Since the excited state for these molecules involves charge transfer from the nitrogen at the 4-position to the carbonyl group(s), any steric interaction which causes lack of planarity of the 4-amino substituent with the ring will inhibit the charge transfer and destabilise the excited state. This is manifested as a simultaneous decrease in the radiative rate constant for (**17**) and an increase in the non-radiative rate constant.

Attempts to extend the conjugated π-system with an aromatic ring at position 9 [compound (**19**)] are without any effect, and it is interesting to note that an acetamido group at 4 also has little additional effect [compound (**18**)]. Similar strong fluorescence ($\varphi_f = 0.77$) from the analogue 4-acetamido-*N*-(3-bromopropyl)-1,8-naphthalimide has been noted.[4] Given that the acetamido group is a much weaker electron donor than a plain amino or alkylamino group these results are surprising. The absorption peak for (**18**) has been shifted to higher energy by *ca.* 5 000 cm^{-1}, as has the fluorescence maximum, although the fluorescence yield is unchanged with a shortening of the lifetime. The fluorescence yields for the 4-butylamino and 4-acetylamino [Table 1, $R^4 = NHC_4H_9$ (**12**), $NHCOCH_3$ (**18**), and $R^9 = NHC_4H_9$ respectively] are all similar although the wavelengths of emission are different in each case. In these compounds the steric influence of the *peri* H is probably minimal and similar. In other series particularly in the *p*-derivatives of 4,4′-dibenzoylaminostilbene-2,2′-disulphonic acid (**31**)[15,16] somewhat greater differences were observed for *p*-NH_2, $NHCOCH_3$, and OCH_3 substituents in the benzoyl ring. In these compounds, no steric factor is operative. A similar situation applies in the 7-substituted 4-methyl coumarins (**32**) where the 7-dialkylamino and 7-hydroxy (as the anion) compounds have intense fluorescence.[17]



(**31**)



(**32**)

Substitution with an $NHNH_2$ at position 4 and NH_2 at the imide [compound (**20**)] causes the fluorescence quantum yield to decrease by a factor of five and the fluorescence decay kinetics to become complex. The double exponential decay profile (Figure 4) has been confirmed by other workers and we are currently investigating the reasons for this behaviour.

If the position of substitution is changed from the 4-position, the fluorescence spectrum shifts in wavelength and decreases in intensity. This is the observed behaviour for compounds (**21**), (**23**), and (**12**) which have NHBu in the 2-, 3-, and 4- positions respectively and for (**22**) and (**16**) which have NH_2 in the 3- and 4-positions. The substituent can interact inductively with a carbonyl moiety in all relative orientations, but can only have a mesomeric interaction in the 2- and 4-positions relative to the carbonyl group(s). These two effects are reflected in the higher values for the radiative rate constant for (**21**), (**16**), and (**12**) relative to (**22**) and (**23**) and in (**21**) having a larger value than (**12**). Unfortunately, the non-radiative rate constant for (**21**) is also considerably increased (conceivably due to a hydrogen bonding interaction) and there is an overall decrease in fluorescence efficiency for (**21**) relative to (**12**).

Disubstitution in the naphthalene ring (**24**) does not improve the fluorescence yield. The radiative rate constant remains the same as for (**12**) but the non-radiative rate increases fivefold. Steric interaction between the two large groups will tend to result in both being out of the plane of the ring and on the basis of the results observed for (**17**) an increase in non-radiative modes would be predicted together with a decrease in radiative ones. That the latter is not observed is presumably due to the predicted decrease, due to steric effects, being balanced out by an increase from the presence of the second substituent.

The fluorescence properties of the substituted naphthalic anhydrides are generally much poorer than those of the naphthalimides. A charge-transfer interaction still appears to account for the longest wavelength absorption band in these molecules, but the transition is weaker and of higher energy than for the corresponding naphthalimide. To obtain even a relatively modest fluorescence yield, the substituent at the

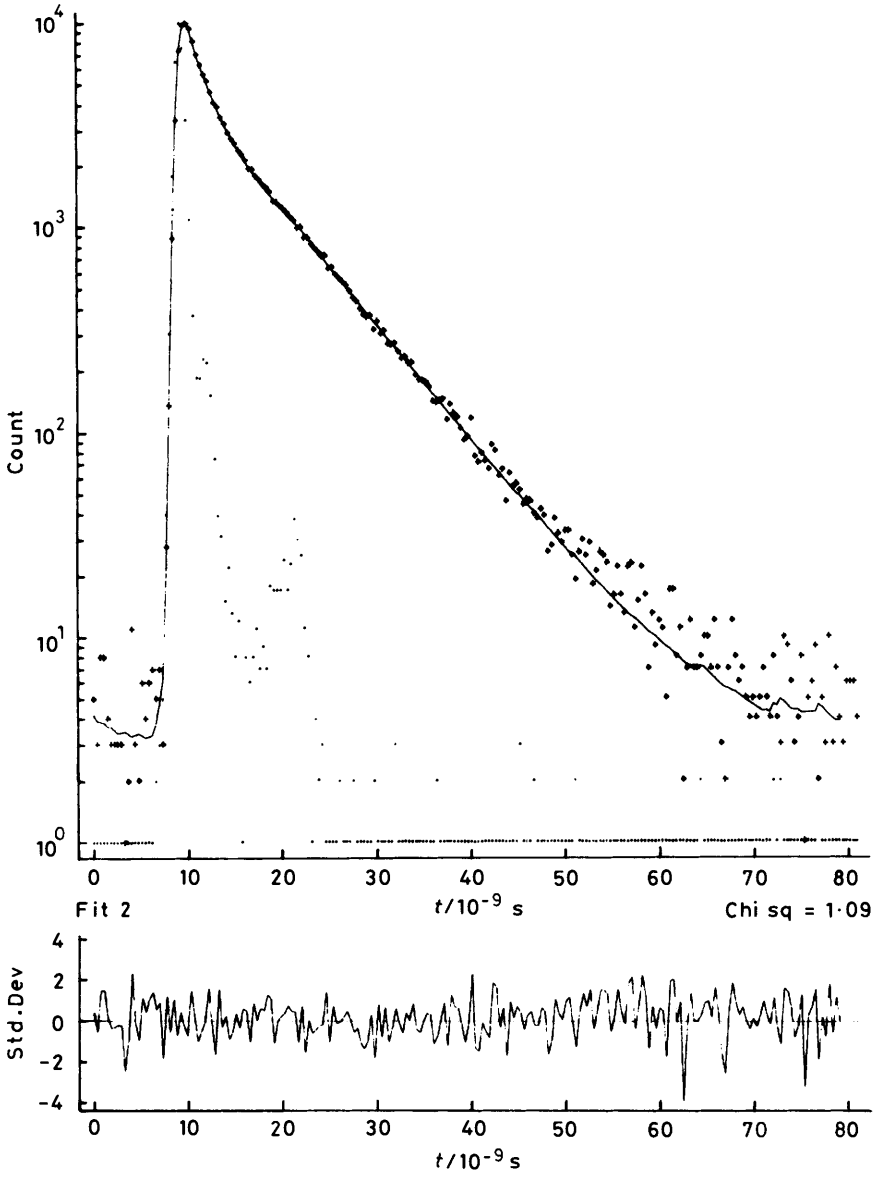


Figure 4. Fluorescence decay profile of compound (**20**) (excitation wavelength 300 nm, emission wavelength 530 nm) in absolute ethanol.

4-position appears to require optimal donor properties. We have not yet prepared 4-alkylaminonaphthalic anhydrides to absolutely confirm this, but the effects of decreasing the substituent donor properties in compounds (**27**)–(**30**) is very clear.

Experimental

Materials.—4-Bromo-1,8-naphthalic anhydride was obtained by bromination of 1,8-naphthalic anhydride[18] in improved yield. 4-Nitro-1,8-naphthalic anhydride was obtained by the nitration of acenaphthene to give 5-nitroacenaphthene[19] followed by oxidation with sodium dichromate in acetic acid solution.

3-Nitro-1,8-naphthalic anhydride was obtained[20] by nitration of 1,8-naphthalic anhydride. Chemical or catalytic reduction gave the corresponding 3-amino compound. 4,5-Dinitro-1,8-naphthalic anhydride was obtained by nitration of 4-nitro-1,8-naphthalic anhydride.[21]

The compounds listed in Table 1 were synthesised in the following ways. Compound (**1**) was obtained from 1,8-naphthalic anhydride with concentrated ammonia solution and compound (**2**) by the action of butylamine on 1,8-naphthalic anhydride in hot ethanol solution. Compound (**3**) resulted from the reaction of 4-bromo-1,8-naphthalic anhydride with butylamine in hot ethanol. Compound (**4**), *N*-butyl 4-cyano-1,8-naphthalimide was formed from the 4-bromo analogue by heating with copper cyanide in hot quinoline solution. Compound (**5**) was obtained by the interaction of 4-bromo-1,8-naphthalic anhydride with aniline in hot ethanol and treatment of the purified product with propylamine in hot *N*-methylpyrrolidinone. Compound (**6**) resulted from treatment of 4-nitro-1,8-naphthalimide with butylamine in hot dimethylformamide and from 4-bromo-1,8-naphthalimide with butylamine in hot *N*-methylpyrrolidinone. Compounds (**7**)–(**15**) were all produced from the respective primary amine by methods B and C. Compound (**16**) was produced by chemical and by catalytic reduction of *N*-butyl-4-nitro-1,8-naphthalimide. Compound (**17**) was synthesised (method D) from *N*-butyl-4-nitro-1,8-naphthalimide and dimethylamine in hot dimethylformamide solution. Compound (**18**) was prepared by

the acetylation of compound (**16**) with acetic anhydride in pyridine solution. Compound (**19**), like compound (**5**), was prepared from 4-bromo-*N*-phenyl-1,8-naphthalimide or the corresponding 4-nitro compound with butylamine in *N*-methylpyrrolidinone or dimethylformamide respectively. The action of 90% hydrazine hydrate on 4-nitro-1,8-naphthalic anhydride gave compound (**20**). The isomers (**21**) and (**23**) of compound (**12**) shown in Table 2 were synthesised by similar routes. Thus, by the interaction of 2-chloro- or 2-bromo-1,8-naphthalic anhydride with butylamine (method C) or from 2-nitro-1,8-naphthalic anhydride. Similar (method B) gave compound (**21**). Compound (**22**) was obtained from 3-nitro-1,8-naphthalic anhydride and butylamine (method A). Catalytic reductive alkylation with butyraldehyde gave compound (**23**).

The disubstituted compound (**24**) in Table 3 was obtained from 4,5-dinitro-1,8-naphthalic anhydride and butylamine (method A) followed by method B with butylamine treatment of the product. Compound (**25**) was prepared from 4-nitro-1,8-naphthalic anhydride and *o*-phenylenediamine[22] followed by treatment of the purified product with octylamine according to method B.

For the compounds (**28**)–(**30**) shown in Table 4, 4-nitro-1,8-naphthalic anhydride was used in dimethylformamide with the corresponding secondary amine and the products were crystallised after chromatography.[23] Compound (**26**) was obtained by reduction of 4-nitro-1,8-naphthalic anhydride chemically with stannous chloride or catalytically (Pd/C, H_2). Acetylation with acetic anhydride in hot pyridine solution gave the 4-acetylamino compound (**27**).

Methods.—(*i*) Absorption spectra were measured in absolute ethanol on a Pye-Unicam SP8-100 or a Perkin-Elmer Lambda 3 spectrophotometer in 1 cm pathlength quartz cells. The accuracy of the peak wavelengths is estimated at ± 1 nm and the extinction coefficients at $\pm 5\%$. (*ii*) Fluorescence spectra were measured either on Perkin-Elmer LS5 and MPF44 spectrofluorimeters in the fully corrected mode or on a modular spectrofluorimeter designed and built by Applied Photophysics Ltd.[24] Spectra obtained on the latter instrument were corrected for the wavelength response of the fluorimeter by using quinine sulphate in perchloric acid as the standard.[25] Quantum yields were measured on optically dilute samples (absorbance <0.05) which were degassed either by bubbling with oxygen-free nitrogen or by freeze–thaw degassing both of which gave the same result. Fluorescein in 0.1 mol dm^{-3} sodium hydroxide ($\varphi_f = 0.90$)[26] purified by the method of Orndorff and Hemmer,[27] disulphonated perylene ($\varphi_f = 0.92$)[28] and quinine sulphate in aqueous perchloric acid ($\varphi_f = 0.55$)[24] were used as quantum yield standards. The confidence placed in the quantum yields is ± 5–10%. (*iii*) Fluorescence decay profiles were measured by the technique of time-correlated single-photon counting. Measurements were undertaken either at the Synchrotron Radiation Source at Daresbury or on an Edinburgh Instruments Model 199 Fluorescence Decay Time Spectrometer. The decay profiles were analysed by computer convolution using χ^2 values and a random distribution of residuals as the 'goodness of fit criteria'.

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