Heterocyclic Derivatives of Naphthalene-1,8-dicarboxylic Anhydride. Part III. (1) Benzo[*k*,*l*]thioxanthene-3,4-dicarboximides.

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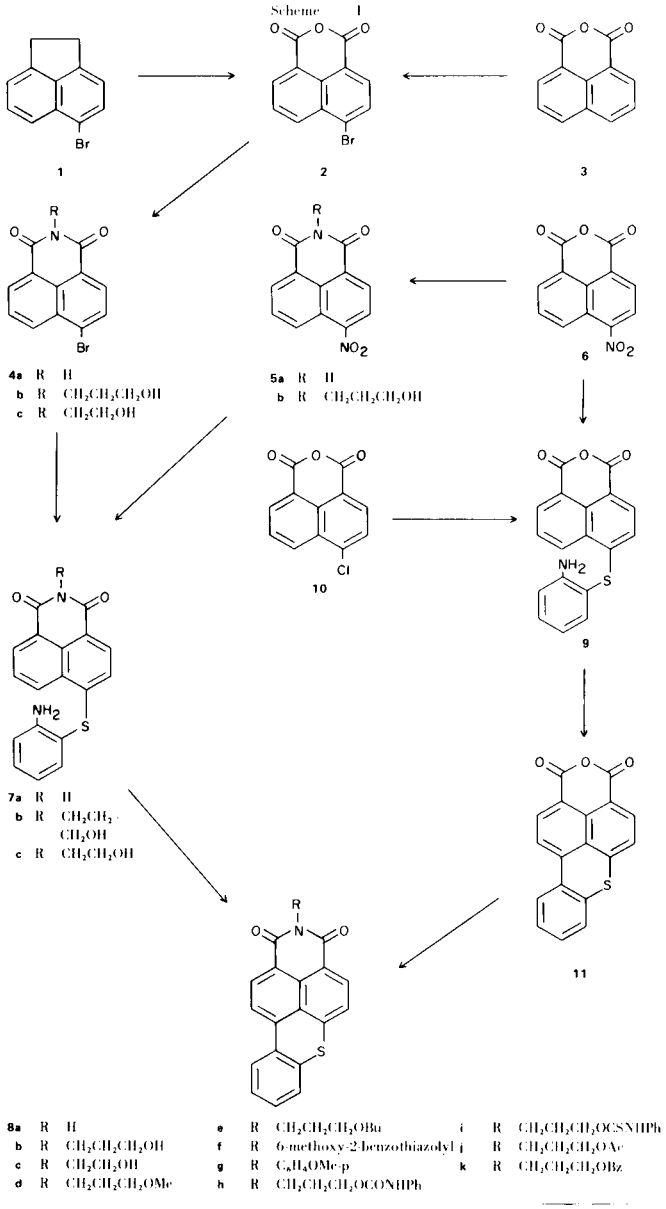
Condensation of 4-bromo- (**4**) and 4-nitro-1,8-naphthalimides (**5**) with 2-aminobenzenethiol gave 4-(2-aminophenylthio)-1,8-naphthalimides (**7**). Cyclisation of **7** by the Pschorr reaction afforded benzo[*k*,*l*]thioxanthene-3,4-dicarboximides (**8**), also obtained by reaction of amines with benzo[*k*,*l*]thioxanthene-3,4-dicarboxylic anhydride (**11**).

Whilst many substituted acenaphthenes and naphthalene-1,8-dicarboxylic anhydrides are well documented, few derivatives with fused sulphur heterocyclic rings have been described. The synthesis of some acenaphthobenzothiophenes (3), benzo[*d*]naphtho[1,2-*b*]thiophene (4), benzo[*k*,*l*]thioxanthene and 7,7-dioxobenzo[*k*,*l*]thioxanthenes (5,6) have been reported. Benzo[*k*,*l*]thioxanthene-3,4-dicarboximides (7) and their alkoxy (8) and nitro (9) derivatives have been claimed in patent specifications to be excellent dyes for synthetic fibres.

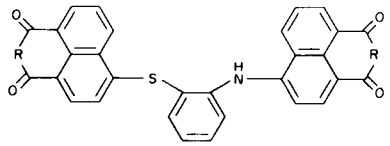
Benzo[*k*,*l*]thioxanthene-3,4-dicarboximides (**8**) may be synthesized by various routes (Scheme) and we report here comparative preparative methods and characterisation data for some new **8**.

4-Bromonaphthalene-1,8-dicarboxylic anhydride (**2**) resulted from the oxidation of 5-bromoacenaphthene (**1**); the bromination of naphthalene-1,8-dicarboxylic anhydride (**3**) in sodium hydroxide, previously reported (10) to give 43% of **2** was modified to give considerably improved (80%) yields. Also formed during the bromination were 1,4,8-tribromonaphthalene (3%); mass spectrometry indicated the formation also of some tetrabromonaphthalene and a dibromonaphthalene-1,8-dicarboxylic anhydride. Similar replacement of the anhydride group by bromine occurs (11) on reaction of naphthalene-1,4,5,8-tetracarboxylic dianhydride with chlorine and with *N*-bromosuccinimide. The mechanism of this bromination in alkaline media has not been recorded; since substitution occurs at the more electron deficient 4-position, reaction involving a nucleophile is indicated. Substitution by the bromide ion is unlikely in view of its weak kinetic and thermodynamic nucleophilicity, particularly in presence of the strongly nucleophilic hydroxide ion. Reaction involving the hypobromite ion, present in solutions of bromine in sodium hydroxide, would require elimination of the oxygen atom and a more likely brominating species is the hydrated hypobromite ion.

Scheme I



The imides **4a,b,c** and **5a,b** condensed with 2-aminobenzenethiol in boiling *N,N*-dimethylformamide (DMF) giving 4-(2-aminophenylthio)-1,8-naphthalimides (**7a,b,c**). Ten percent excess of 2-aminobenzenethiol was necessary for complete reaction, use of larger amounts giving rise to resinous reaction products and formation of 2,2′-diaminodiphenyldisulphide, the latter also resulting with reaction conditions under which the required condensation proceeded slowly. Use of lower amounts of 2-aminobenzenethiol resulted in formation of insoluble yellow by-products,



12a R = NH
b R = O

including double linked molecules, *e.g.*, **12a**. In absence of potassium carbonate, **4** reacted slowly, but in presence of excess potassium carbonate, large amounts of purple and reddish-blue by-products of high molecular weight were formed. Optimum amounts of potassium carbonate were in the order of 0.5 mole per mole of hydrogen bromide evolved. The presence of potassium carbonate in the condensation of 2-aminobenzenethiol with **5** was, however, detrimental, leading predominantly to formation of resinous materials.

In general, the use of **4** was preferred to that of **5** in the synthesis of **7**; provided careful control was maintained over the amount of potassium carbonate used as acid binding agent, reaction products from **4** were isolated in good yield and in a degree of purity not requiring the chromatographic separations necessary with the crude reaction products derived from use of **5**.

Pschorr cyclisation (12) of **7a,b,c**, after diazotisation in either sulphuric acid with nitrosylsulphuric acid or in acetic acid with aqueous sodium nitrite, gave good yields of **8a,b,c**. In the preparation of **8b** by diazotisation of **7b** in acetic acid and subsequent cyclisation, some acetylation of the hydroxy group occurred, giving 6-7% of the *O*-acetyl derivative **8j**. During the cyclisation stage of the Pschorr synthesis, gradual addition of the diazonium liquor to the copper sulphate solution was necessary to prevent formation of 4-(2-hydroxyphenylthio)-1,8-naphthalimides and, to a lesser degree, of 4-phenylthio-1,8-naphthalimides.

In many respects a more convenient route to **8** is by condensation of amines with **11**, although synthesis of **11** also requires reaction of 4-substituted naphthalene-1,8-dicarboxylic anhydrides with 2-aminobenzenethiol, followed by Pschorr cyclisation of the resultant 4-(2-aminophenylthio)naphthalene-1,8-dicarboxylic anhydride **9**.

Reaction of 4-chloronaphthalene-1,8-dicarboxylic anhydride (**10**) with 2-aminobenzenethiol was generally unsatisfactory for formation of **9** without by-product formation. In hot DMF solution, **10** and **9** only were present in the initial stages of the reaction (10 minutes), but on continued refluxing, by-products were gradually formed as **10** reacted further. Compound **10** had completely disappeared from the reaction liquor after 45 minutes, but tlc showed **9** to be then very heavily contaminated with additional reaction products. The condensation was preferably stopped after 20-30 minutes; the resultant crude reaction product, after removal of alkali

TABLE I

Electronic Spectra Data (nm., log ε) for Benzo[*k,l*]thioxanthene-3,4-dicarboximides in (a) Ethanol or (b) Monochlorobenzene

8a	(a)	325 (3.63)	347 (3.66)	382 (3.48)	460 (4.34)	470s (4.30)
	(b)	327 (3.71)	348 (3.74)	382 (3.35)	467 (4.29)	474s (4.27)
8b	(a)	323 (3.61)	344 (3.65)	380 (3.42)	460 (4.29)	473s (4.27)
	(b)	326 (3.67)	346 (3.70)	382 (3.46)	463 (4.30)	475s (4.27)
8c	(a)	325 (3.66)	346 (3.69)	382 (3.45)	460 (4.31)	471s (4.29)
8d	(a)	322 (3.68)	343 (3.72)	379 (3.54)	459 (4.30)	468s (4.26)
	(b)	326 (3.70)	345 (3.61)	381 (3.44)	456 (4.27)	474s (4.20)
8e	(a)	323 (3.66)	344 (3.67)	379 (3.48)	459 (4.28)	472s (4.27)
	(b)	325 (3.64)	347 (3.64)	384 (3.41)	459 (4.25)	478s (4.21)
8f	(b)	324 (3.60)	346 (3.63)	383 (3.34)	459 (4.26)	480s (4.20)
8g	(b)	324 (3.58)	346 (3.61)	382 (3.47)	456 (4.31)	475s (4.28)
8h	(b)	324 (3.65)	345 (3.63)	381 (3.53)	458 (4.29)	477s (4.26)
8i	(b)	323 (3.60)	345 (3.64)	380 (3.44)	457 (4.27)	477s (4.20)
8j	(b)	325 (3.64)	346 (3.66)	382 (3.47)	463 (4.29)	477s (4.28)
8k	(b)	326 (3.68)	346 (3.69)	382 (3.48)	464 (4.28)	478s (4.27)

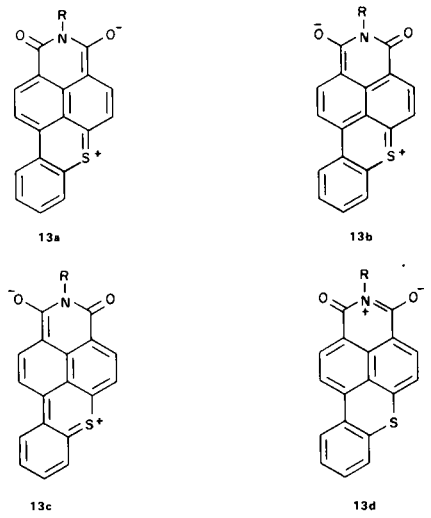
insoluble material followed by either repeated recrystallisation or by chromatographic purification, gave **9** in approximately 60% yield. No attempt was made to isolate any specific reaction by-products, but mass spectrometry studies of crude residues indicated progressive reaction of **9** with 2-aminobenzenethiol, giving *N*-(2-mercaptophenyl)-4-(2-aminophenylthio)-1,8-naphthalimide (P^+ at m/e 428, high resolution mass measurement $C_{24}H_{16}N_2O_2S$). Also indicated by mass spectra data was the formation of *N*-methyl-4-(2-aminophenylthio)-1,8-naphthalimide, P^+ at m/e 334, $C_{19}H_{14}N_2O_2S$ confirmed by high resolution mass measurement). The formation of the *N*-methylimide presumably arises from decomposition of DMF and liberation of a methylating species; similar formation of *N*-alkylamino compounds has been previously observed in reactions of halogenonitrobenzenes and halogenoanthraquinones using DMF (13,14) and other formamides (15) as reaction solvents. Mass spectrometry further indicated the formation of high molecular weight impurities (MW > 500), *e.g.*, **12b**, m/e 517; similar double linked molecules were also formed in reaction of 1,8-naphthalimides with 2-aminobenzenethiol. Use of excess of 2-aminobenzenethiol in attempts to facilate reaction with **10** led to additional formation of oxidation products of the thiol, particularly 2,2′-diaminodiphenyldisulphide.

Use of 2-methoxyethanol as alternative solvent to DMF gave similar results to the above, but without formation of the *N*-methylimides. In ethanol, reaction was much slower, *e.g.* after 2 hours refluxing, only partial reaction of **10** had occurred, but formation of large amounts of 2,2′-diaminodiphenyldisulphide was evident.

4-Nitronaphthalene-1,8-dicarboxylic anhydride (**6**) reacted more readily with 2-aminobenzenethiol. In boiling DMF, **9** was formed in good yield, but crude reaction products were in excess of quantitative yield due to contamination with 2,2′-diaminodiphenyldisulphide and of brown resinous materials. In presence of potassium carbonate, yields of **9** were very low, mass spectra of crude reaction products indicating preferential formation of high molecular weight derivatives (> 400) and of 4-(2-hydroxyphenylthio)naphthalene-1,8-dicarboxylic anhydride. Similar disadvantages occurred on reaction **5** with 2-aminobenzenethiol in presence of potassium carbonate. In ethanolic solution, by-product formation was minimal and **9** was obtained in excellent yield and purity by direct filtration from the cooled reaction liquor, followed by removal of 2,2′-diaminodiphenyldisulphide.

Compound **9** cyclised by the Pschorr reaction giving **11** in excellent yield. Preferred reaction conditions include relatively prolonged diazotisation conditions (above 10 hours) and slow addition of the diazonium liquor to copper sulphate solution. Rapid addition in the latter stage resulted in heavy contamination of **11** with 4-(2-hydroxyphenylthio)naphthalene-1,8-dicarboxylic anhydride; presence of small amounts of the latter in **11** leads to a reduced fastness to light and sublimation of derived dyestuffs. Compound **11** condensed with the appropriate amines to give **8b-g**; **8b** reacted with phenylisocyanate or phenylisothiocyanate, afforded **8h** and **8i**, respectively. While reaction of **11** with the strongly basic alkylamines occurred quantatively, the less basic *p*-anisidine, and especially, 6-methoxy-2-aminobenzothiazole, were less reactive.

Principal electronic spectra data of **8** (Table I) indicate the bathochromicity of these dyes compared with many 1,8-naphthalimides (16), colour and constitution aspects of which we have recently (1) discussed. The deeper colour of the benzo[*k*,*l*]thioxanthene-3,4-dicarboximides arises from additional resonance possibilities due to the increased conjugation through the phenyl ring, *e.g.*, **13c**.



13a 13b

13c 13d

The nature of the substituent R has, in this present series of dyes, limited effect on the colour, the weakly inductive alkylene group insulating any significant polar contribution (**13d**) from terminal hydroxy and derived substituents. All compounds **8** dyed polyester and cellulose triacetate fibres in deep yellow shades showing excellent fastness to light and sublimation.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 by the potassium bromide technique, electronic spectra on a Unicam SP800, and mass spectra on an AEI MS-902 at 70 eV using a direct insertion probe. Elemental analysis were performed by the Division of Chemical Standards, National Physical Laboratory, Teddington.

4-Bromonaphthalene-1,8-dicarboxylic Anhydride (**2**).

(a) Compound **1** (2 g.) was oxidized (17) by refluxing for 30

minutes with sodium dichromate (7.6 g.) in glacial acetic acid (200 ml.). Solvent was removed *in vacuo*, chromium salt removed from the residue with boiling water, leaving a white insoluble residue (1.52 g., 64%), which crystallized from glacial acetic acid in white needles, m.p. 224° (lit. (10) 222°).

(b) Compound **3** (20 g.) was dissolved in potassium hydroxide (28 g.), and water (120 ml.) at 70° and the solution cooled to room temperature with vigorous stirring to precipitate the dipotassium salt in finely divided form. Bromine (48 g.) was run in over 2.5 hours at room temperature, the liquor then heated at 60° for 30 minutes, cooled and acidified with hydrochloric acid. After warming at 60° to expel bromine, a white residue (24.4 g., 87%), was collected. The mass spectrum of this showed the presence of three minor impurities, showing bromine isotope clusters at masses corresponding to a tribromonaphthalene, a tetrabromonaphthalene and a dibromonaphthalene-1,8-dicarboxylic anhydride. The crude reaction product was warmed at 70-80° in 5% aqueous sodium hydroxide (600 ml.) for 20 minutes and cooled; insoluble material (0.84 g. 3%) crystallized from ethanol in white needles of 1,4,5-tribromonaphthalene, m.p. 84°. The alkaline filtrate, acidified with hydrochloric acid, gave 22.94 g. (82%) of a white solid, which recrystallised from concentrated nitric acid in white needles, m.p. 224°, identical to the product prepared as in (a) above.

Anal. Calcd. for $C_{12}H_5BrO_3$: C, 52.0; H, 1.8; Br, 28.9. Found: C, 51.8; H, 1.7; Br, 28.7.

4-Nitro-1,8-naphthalimide (**5a**).

Compound **6** (5 g.), prepared as previously described (18), was refluxed for 3 hours in aqueous ammonia d. 0.880 (200 ml.). A pale yellow solid (4.08 g., 98%), m.p. 288°, was collected; recrystallisation from concentrated nitric acid gave pale yellow neeldes, m.p. 295° (lit. (19) 287-288°; (20) 289-290°).

Anal. Calcd. for $C_{12}H_6N_2O_4$: C, 59.5; H, 2.5; N, 11.6; Found: C, 59.3; H, 2.3; N, 11.4.

N-(3-Hydroxypropyl)-4-nitro-1,8-naphthalimide (**5b**).

Compound **6** (4 g.) and 3-aminopropan-1-ol (2 ml.) were refluxed for 10 minutes in ethanol (100 ml.), the hot solution treated with activated charcoal and filtered. The filtrate was concentrated to 50 ml. and a brownish yellow solid (4.74 g., 96%) collected; this recrystallised from ethanol in pale yellow needles, m.p. 167°.

Anal. Calcd. for $C_{15}H_{12}N_2O_5$: C, 60.0; H, 4.0; N, 9.3. Found: C, 60.0; H, 3.9; N, 9.3.

4-Bromo-1,8-naphthalimide (**4a**).

By the procedure adopted for **5a**, **2** gave an 87% yield of a white solid, which recrystallised from concentrated nitric acid in white needles, m.p. 298° (lit. 20) 296-297°).

Anal. Calcd. for $C_{12}H_6BrNO_2$: C, 51.5; H, 2.2; N, 5.1; Br, 29.0. Found: C, 51.4; H, 5.0; Br, 28.8.

4-Bromo-*N*-(2-hydroxyethyl)-1,8-naphthalimide (**4c**).

2-Aminoethanol (2 ml.) and **2** (4 g.) were refluxed for 30 minutes in ethanol (80 ml.). The reaction liquor, treated as for **5b**, gave an off-white solid (4.4 g., 96%), which recrystallised from ethanol in white needles, m.p. 146-147°; ir 1700 and 1660 cm^{-1} (C=O).

Anal. Calcd. for $C_{14}H_{10}BrNO_3$: C, 52.5; H, 3.1; N, 4.4; Br, 25.0. Found: C, 52.1; H, 3.0; N, 4.2; Br, 24.7.

4-Bromo-*N*-(3-hydroxypropyl)-1,8-naphthalimide (**4b**).

By the procedure used for **4c**, **2** and 3-aminopropan-1-ol gave a pale yellow solid (4.5 g., 94%), which recrystallised from ethanol in cream colored needles, m.p. 127-128°; ir 1705 and 1665 cm^{-1} (C=O).

Anal. Calcd. for $C_{15}H_{12}NO_3Br$: C, 53.9; H, 3.6; N, 4.2; Br, 23.95. Found: C, 53.6; H, 3.4; N, 4.0; Br, 23.8.

4-(2-Aminophenylthio)naphthalene-1,8-dicarboxylic Anhydride (**9**).

(a) Compound **10** (20 g.) was refluxed in DMF (200 ml.) for 30 minutes with 2-aminobenzenethiol (16.2 g., 50% excess) in presence of anhydrous potassium carbonate (5 g.). The reaction liquor was cooled, added to water (500 ml.) and a greenish-yellow solid (24.3 g., 88.1%) collected. This product was heated at 90° for 10 minutes in 5% aqueous sodium hydroxide; insoluble material (4 g.), containing predominantly 2,2′-diaminodiphenyldisulphide and some *N*-(2-mercaptophenyl)-4-(2-aminophenylthio)-1,8-naphthalimide was discarded. The alkaline solution was acidified, and the greenish-yellow solid collected; tlc showed it to contain several components, removed by preparative layer chromatography on silica gel, or be repeated crystallisation from dimethylformamide giving greenish-yellow needles (17.7 g., 64%), m.p. 200-201°; ir 3450, 3360 (NH), 1770 and 1735 cm^{-1} (C=O); uv max, log ϵ (ethanol) 382 nm (4.11).

Anal. Calcd. for $C_{18}H_{11}NO_3S$: C, 67.3; H, 3.4; N, 4.4; S, 10.0. Found: C, 67.2; H, 3.2; N, 4.2; S, 9.7.

(b) Compound **6** (2.43 g.) was refluxed for 30 minutes with 2-aminobenzenethiol (1.2 g.) in DMF (20 ml.). The reaction liquor was added to water (200 ml.) and a brown solid (4 g.) collected. Alkali insoluble material was removed as in (a) above, and the residue, tlc of which showed it to contain an orange impurity at high Rf and brown impurities at low Rf, was purified by preparative layer chromatography or by repeated recrystallisation from monochlorobenzene to give greenish-yellow needles (1.80 g., 56%), m.p. 201°, identical to the compound as synthesized in Method (a).

(c) 2-Aminobenzenethiol (0.8 g.) and **6** (1.6 g.) were refluxed for 45 minutes in ethanol (15 ml.). The liquor was cooled, filtered and a brownish-yellow solid collected; 2,2′-diaminodiphenyldisulphide was removed by boiling for 20 minutes in 5% aqueous sodium hydroxide and filtering hot. Acidification of the alkaline filtrate gave a yellow-solid (1.88 g., 89%), m.p. 199-201°, identical to the compound synthesised as in (a) above.

4-(2-Aminophenylthio)-1,8-naphthalimide (**7a**).

(a) Compound **4a** (8.9 g.) and 2-aminobenzenthiol (4.4 g., 10% excess) were refluxed for 30 minutes in DMF (250 ml.) in presence of anhydrous potassium carbonate (2.2 g.). The liquor was added to 20% aqueous hydrochloride acid (1500 ml.) and, after standing overnight, filtered to give a yellow solid (10.3 g., 100%), m.p. 259°. Digestion with warm glacial acetic acid left 30 mgm. insoluble yellow residue, m.p. >360°, the mass spectrum of which showed P^+ at m/e 515; high resolution mass measurement indicated a molecular formula $C_{30}H_{17}N_3O_4S$, compatible with **12a**. The acetic acid liquor gave, on concentration, a yellow solid (9.9 g., 96%), which recrystallised from glacial acetic acid in yellow needles, m.p. 261°.

Anal. Calcd. for $C_{18}H_{12}N_2O_2S$: C, 67.5; H, 3.8; N, 8.8; S, 10.0. Found: C, 67.4; H, 3.6; N, 8.8; S, 10.3.

Similar reactions in absence of, or smaller amounts of, potassium carbonate, resulted in slower formation of **7a** and formation of large amounts of resinous material, including 2,2′-diaminodiphenyldisulphide. Presence of larger amounts of potassium carbonate (above 3 g.) resulted in contamination of **7a** with relatively large amounts of purple to reddish-blue compounds. From a thick

layer chromatographic separation of these was isolated deep purple-blue prisms, m.p. above 360°. The compound did not give a satisfactory mass spectrum; it had low solubility in pyridine (red solution) and acetic acid (purple solution), these solutions rapidly degenerating to dark brown on exposure to light.

(b) Compound **5a** (2.42 g.) and 2-aminobenzenethiol (1.4 g.) were refluxed for 30 minutes in DMF (50 ml.). The reaction liquor, treated as in method (a) above, gave a brown product (2.88 g., 90%), m.p. 251-252°; Tlc indicated absence of the yellow component (m/e 515) obtained in (a), but presence of brown impurities of low Rf value. Two recrystallisations from glacial acetic acid gave yellow needles (2.37 g., 74%), m.p. 260-261°, identical with the compound synthesised as in (a) above. The presence of potassium carbonate in this reaction led to considerably reduced yields of **7a** and the formation of large amounts of resinous material.

4-(2-Aminophenylthio)-*N*-(3-hydroxypropyl)-1,8-naphthalimide (**7b**).

(a) Compound **4b** (10.8 g.) was condensed with 2-aminobenzenethiol in a manner identical with the synthesis of **7a** from **4a** to give a yellow-brown solid (10.2 g., 83%), which recrystallised from ethanol in golden-yellow leaflets, m.p. 176°; ir 3435, 3340, 3320 (NH); 1695 and 1632 cm^{-1} (C=O).

Anal. Calcd. for $C_{21}H_{18}N_2O_3S$: C, 66.6; H, 4.8; N, 7.4; S, 8.5. Found: C, 66.8; H, 4.9; N, 7.3; S, 8.4.

(b) 2-Aminobenzenethiol (1.6 g., 25% excess) and **5b** (3 g.) were refluxed for 1 hour in DMF (75 ml.). The reaction liquor on addition to 20% aqueous hydrochloric acid (250 ml.) gave a dark brown resinous precipitate which was filtered after standing for 1 hour, during which time it solidified (yield above 100% of theory). Chromatography on activated alumina from chlorobenzene solution, eluting initially with benzene-acetone (90:10) and finally with acetone, gave high Rf minor yellow brown, blue and pink zones (eluted without investigation), and strongly absorbed brown zones (Rf = 0), which were not investigated.

A major yellow zone, on extraction with ethanol, afforded deep yellow needles (2.68 g. 71%), m.p. 174-176°, identical with the product obtained by method (a) above.

4-(2-Aminophenylthio)-*N*-(2-hydroxyethyl)-1,8-naphthalimide (**7c**).

In a manner identical to the synthesis of **7a** from **4a**, **4c** (10.3 g.) gave a yellow solid (11.48 g., 98%), which recrystallised from ethanol in yellow needles, m.p. 186-187°; ir 3435, 3335, 3215 (NH); 1695 and 1630 cm^{-1} (C=O).

Anal. Calcd. for $C_{20}H_{16}N_2O_3S$: C, 65.9; H, 4.4; N, 7.8; S, 8.8. Found: C, 65.7; H, 4.2; N, 7.6; S, 8.4.

Benzo[*k,l*]thioxanthene-3,4-dicarboxylic Anhydride (**11**).

A vigorously stirred suspension of **9** (16 g.) in glacial acetic acid (120 ml.), water (20 ml.) and concentrated hydrochloric acid (12.5 ml.) at 0-5° was diazotised by addition over 10 minutes of a solution of sodium nitrite (36 g.) in water (35 ml.). After stirring overnight, initially at 0-5° and allowing the temperature to rise to 20-25°, the diazonium liquor was added over 1.5 hours to a boiling solution of hydrated copper sulphate (35 g.) in water (500 ml.) and glacial acetic acid (30 ml.). After the addition was complete, the liquor was boiled for a further 30 minutes, cooled, and an orange-red solid (14.8 g., 98%) m.p. 320-322°, collected. Recrystallisation from dimethylformamide gave deep orange-red needles, m.p. 332-333° (lit. (7) 330-331°); ir 1765 and 1725 cm^{-1} (C=O); uv max nm (log ε), 460 (4.10) and 481 (4.00) in monochlorobenzene.

Anal. Calcd. for $C_{18}H_8O_3S$: C, 71.05; H, 2.6; S, 10.5. Found: C, 70.8; H, 2.4; S, 10.4.

Benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8a**).

Compound **7a** (5 g.) was stirred into concentrated sulphuric acid (50 ml.) at 0° and nitrosylsulphuric acid (prepared from 1.2 g. sodium nitrite and 20 ml. concentrated sulphuric acid) added over 30 minutes at 0-5°. After diazotising for 1.5 hours at 0-5°, the liquor was added to crushed ice (300 g.) and the resultant lemon yellow suspension added over 1.5 hours to a boiling solution of hydrated copper sulphate (20 g.) in water (200 ml.). After stirring at boiling for 45 minutes, the liquor was cooled and a rust-brown solid (4.7 g., 100%) m.p. 321-324° filtered; three recrystallisations from pyridine or dimethylformamide gave bright orange needles, m.p. 331°; ir 3170 (NH); 1681 and 1665 cm^{-1} (C=O).

Anal. Calcd. for $C_{18}H_9NO_2S$: C, 71.3; H, 3.0; N, 4.6; S, 10.5. Found: C, 71.0; H, 3.0; N, 4.7; S, 10.5.

N-(3-Hydroxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8b**).

(a) Compound **7b** (2 g.) was dissolved in warm glacial acetic acid (20 ml.) and concentrated hydrochloric acid (2 ml.) added to give a fine suspension of the amine hydrochloride. The suspension was stirred while cooling to 0° and a solution of sodium nitrite (0.4 g.) in water (6 ml.) added and diazotisation continued for 2 hours. The diazonium liquor was added over 1.5 hours with good stirring to a boiling solution of hydrated copper sulphate (4 g.) in water (100 ml.). After boiling a further 40 minutes, the liquor was cooled and a brown-orange residue, (2.08 g.) m.p. 155-159° filtered. Column chromatography on activated alumina from chlorobenzene solution, using benzene-acetone (75:25) as eluant gave two principal yellow zones. Minor deep colored zones were not investigated. A higher Rf yellow zone was eluted to give 0.21 g. of orange plates, identical to **8j** (see below). The lower Rf orange-yellow zone on extraction with ethanol gave an orange product (1.4 g., 73.3%); three recrystallisations from monochlorobenzene gave orange needles, (0.87 g., 45.6%), m.p. 202-203°; ir 1681 and 1645 cm^{-1} (C=O).

Anal. Calcd. for $C_{21}H_{15}NO_3S$: C, 69.8; H, 4.2; N, 3.9; S, 8.9. Found: C, 69.7; H, 4.0; N, 3.8; S, 8.5.

(b) Compound **11** (3 g.) was refluxed for 3 hours in ethanol (30 ml.) with 3-aminopropan-1-ol (1.2 g.). Addition of the reaction liquor to water (150 ml.) gave an orange solid, (3.5 g., 96%), m.p. 193-195°. This was collected and recrystallised from ethanol in orange needles, m.p. 204-205°, identical with the product obtained by method (a) above.

N-(2-Hydroxyethyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8c**).

Compound **7c** (2 g.) was diazotised in glacial acetic acid and cyclised by the method (a) for **8b** to give a brownish-orange solid (1.47 g., 77%). Two recrystallisations from ethanol gave yellow needles (1.0 g., 52.6%) m.p. 224-225°; ir 1682 and 1640 cm^{-1} (C=O).

Anal. Calcd. for $C_{20}H_{13}NO_3S$: C, 65.9; H, 4.4; N, 7.7; S, 8.8. Found: C, 65.8; H, 4.4; N, 7.8; S, 8.9.

N-(3-Methoxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8d**).

In a manner identical with the synthesis of **8b** by method (b), **11** (3 g.) and 3-methoxypropylamine (1.4 g.) gave a brown solid (3.2 g., 86%); recrystallisation from dimethylformamide afforded orange-brown needles, m.p. 178-179°; ir 1607 and 1655

cm^{-1} (C=O).

Anal. Calcd. for $C_{22}H_{17}NO_3S$: C, 70.4; H, 4.5; N, 3.7; S, 8.5. Found: C, 70.3; H, 4.2; N, 3.5; S, 8.2.

N-(3-Butoxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8e**).

In a similar manner to the synthesis of **8d**, **11** (3 g.) and 3-butoxypropylamine (2 g.) gave an orange-brown product (3.2 g., 78%), which recrystallised from monochlorobenzene in orange needles, m.p. 155-156°; ir 1690 and 1645 cm^{-1} (C=O).

Anal. Calcd. for $C_{25}H_{23}NO_3S$: C, 71.9; H, 5.5; N, 3.35; S, 7.7. Found: C, 71.8; H, 5.3; N, 3.4; S, 7.5.

N-(4-Methoxyphenyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8f**).

4-Methoxyaniline (0.5 g.) and **11** (1 g.) were refluxed for 10 hours in diethyleneglycoldimethylether (20 ml.). The reaction liquor was added to cold water (200 ml.) and an orange-brown solid (1.2 g., 89.5%) filtered. Two recrystallisations from monochlorobenzene gave deep orange needles (0.9 g., 66%), m.p. 300-301°; ir 1660 and 1698 cm^{-1} (C=O).

Anal. Calcd. for $C_{25}H_{15}NO_3S$: C, 73.3; H, 3.7; N, 3.4; S, 7.8. Found: C, 73.1; H, 3.6; N, 3.3; S, 7.5.

N-(6-Methoxy-2-benzothiazolyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8g**).

6-Methoxy-2-aminobenzothiazole (1.3 g.) and **11** (1.5 g.) were refluxed in diethyleneglycoldimethylether (25 ml.) for 15 hours. Tlc showed reaction to be incomplete and the formation of several minor by-products. The crude reaction product, isolated as **8f**, was extracted with warm 5% aqueous sodium hydroxide to remove unreacted **11**. Insoluble material (1.5 g., 65.2%) was recrystallised twice from mono-chlorobenzene and once from DMF to give brownish-orange needles, m.p. 334-335°; ir 1705 and 1675 cm^{-1} (C=O).

Anal. Calcd. for $C_{26}H_{14}N_2O_3S_2$: C, 66.95; H, 3.0; N, 6.0; S, 13.7. Found: C, 66.8; H, 2.8; N, 5.8; S, 13.6.

N-(3-Acetoxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8j**).

Compound **8b** (1 g.) was refluxed for 20 minutes in acetic anhydride (2 ml.) and glacial acetic acid (8 ml.) and the liquor added to cold water (50 ml.). An orange solid (1.08 g., 97%) was collected; recrystallisation from ethanol gave orange needles, m.p. 208-209°; ir 1738, 1681 and 1642 cm^{-1} (C=O).

Anal. Calcd. for $C_{23}H_{17}NO_4S$: C, 68.5; H, 4.2; N, 3.5; S, 7.9. Found: C, 68.6; H, 4.1; N, 3.5; S, 7.7.

The by-product isolated during the synthesis of **8b** by method (a) was identical in all respects to this compound.

N-(3-Benzoyloxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8k**).

Compound **8b** (1 g.) was refluxed in pyridine (6 ml.) with benzoyl chloride (1 ml.) for 2 hours. Addition of the liquor to water, filtering and washing the residue with cold 5% aqueous sodium hydroxide to remove traces of benzoic acid, gave an orange solid (1.09 g., 85%); recrystallisation from ethanol afforded orange needles, m.p. 178-179°; ir 1725, 1685 and 1641 cm^{-1} (C=O).

Anal. Calcd. for $C_{28}H_{19}NO_4S$: C, 72.7; H, 4.1; N, 3.0; S, 6.9. Found: C, 72.7; H, 4.0; N, 3.1; S, 7.0.

N-(3-*N*-Phenylcarbamoyloxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8h**).

Compound **8b** (1.5 g.) was heated at 80° in anhydrous pyridine (15 ml.) and a solution of phenylisocyanate (0.6 g.) in anhydrous pyridine (15 ml.) added dropwise over 40 minutes. After heating at 80° for 3 hours, the liquor was added to water and filtered. Yield was in excess of theory due to formation of *sym*-diphenylthiourea by reaction of unreacted phenylisocyanate with water. Three recrystallisations from monochlorobenzene gave (1.7 g., 85.4%) deep orange needles, m.p. 204-205°; ir 3325 (NH); 1735, 1684 and 1645 cm^{-1} (C=O).

Anal. Calcd. for $C_{28}H_{20}N_2O_4S$: C, 70.0; H, 4.2; N, 5.8; S, 6.7. Found: C, 69.8; H, 4.1; N, 5.6; S, 6.4.

N-(3-*N*-Phenylthiocarbamoyloxypropyl)benzo[*k,l*]thioxanthene-3,4-dicarboximide (**8i**).

Compound **8b** (1.5 g.) was stirred with phenylisothiocyanate (0.6 g.) in anhydrous pyridine (20 ml.) for 5 hours at 80-85°. The product, isolated as **8h**, gave, after three recrystallisations from monochlorobenzene, orange needles (0.9 g., 43.7%), m.p. 198-199°; ir 3320 (NH); 1690 and 1650 cm^{-1} (C=O).

Anal. Calcd. for $C_{28}H_{20}N_2O_3S_2$: C, 67.7; H, 4.0; N, 5.6; S, 12.9. Found: C, 67.6; H, 3.8; N, 5.4; S, 12.7.

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