Solid-state Fluorescent Photophysics of Some 2-Substituted Benzothiazoles

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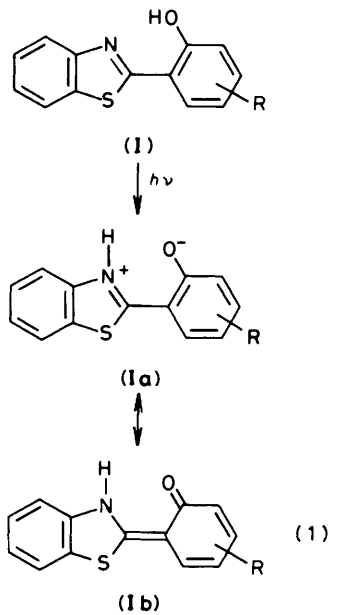
The solid-state fluorescence properties of a series of benzothiazoles with phenyl, naphthalene, and coumarin moieties substituted at the 2-position have been investigated. The necessity for a 2'-OH substituent for fluorescence has been confirmed and the effects of further substitution in the 2-phenyl ring are reported.

The photochemical properties of 2-aryl-substituted benzothiazoles (**I**) have aroused interest principally as a means of providing information about the photochromism of the salicylideneanilines.[1-3] The presence of the benzothiazole ring removes some rotational freedom from the molecule which might be expected to simplify the photochemical kinetics. As far as the emission is concerned, Barbara *et al.*[2] identify three processes which contribute to the decay. The first of these is intramolecular proton transfer [equation (1)] which occurs within 5 ps of excitation. This is followed by vibrational relaxation and finally by emission from (**Ia**) and/or (**Ib**) to return to the ground state. The same proton transfer is also observed in the excited state of solid benzothiazoles[4,5] and, as above, leads to fluorescence which has a Stokes shift of the order of 10 000 cm^{-1}. The quinonoid tautomer (**Ib**) presumably has a role to play in the photochemistry, but as yet its importance is unclear.

Our interest in colourless compounds which fluoresce towards the red region of the visible spectrum has led us to examine the emission properties of 2-aryl-substituted benzothiazoles of general structure (**I**). We have prepared a range of derivatives of (**I**) where R is NH_2, OH, OCH_3, CH_3, NO_2, or halogen with a view to shifting the fluorescence as far to the red as possible, whilst maintaining high fluorescence quantum yields. In addition, we have examined some compounds in which the 2-phenyl ring has been replaced by a naphthalene or coumarin moiety.



(1)

Results

Benzothiazoles were prepared either by the reaction of a salicylic acid derivative with 2-aminothiophenol in the presence of phosphorus trichloride[6] or from salicylaldehydes and 2-aminothiophenol in triethyl phosphate.[7] Preparative details are presented in the Experimental section and in Table 1.

The photophysical properties of the benzothiazoles are given in Table 2. The method employed for the determination of the quantum yields is similar to that suggested by Wrighton *et al.*,[8] except that all the emission was collected (using an integrating sphere) rather than just part of it. Our confidence in the quantum yields thus obtained is of the order of ±10%. The values of the quantum yields are compared with those available from the work of Williams and Heller.[4] There is usually reasonable agreement between the two sets of results, even though Williams and Heller used a slightly different excitation wavelength (365 nm) and appear to have made no correction for reflectance. Big discrepancies are noted for compounds (**5**), (**11**), (**32**), and (**33**). The nitro-derivatives (**32**)—(**34**) exhibit both thermo- and photo-chromism[4] and this may be the reason for the variation in quantum yields. Our value for compound (**11**) agrees with the values for the other bromo-derivatives, so the value of 0.022 quoted by Williams and Heller appears anomalous. A substantial portion of the fluorescence of compound (**5**) is outside the calibrated region of the spectrometer and hence the quoted quantum yield value of 0.04 (±0.02) is only an estimate. Nevertheless, this is insufficient to explain the discrepancy between this figure and that of Williams and Heller (0.376). Furthermore, the latter report fluorescence at 543 nm, whereas our compound (**5**) fluoresces at 640 nm. It is therefore possible that the two sets of data refer to different compounds. Quantum yields for some of the compounds reported here have also been measured by a photoacoustic method.[9]

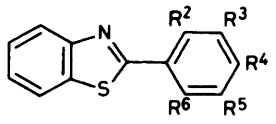
Combined with the fluorescence lifetimes (τ_f), the quantum yields (φ_f) have been used to calculate rate constants for radiative (k_R) and non-radiative (k_{NR}) decay by the relationships (2) and (3). Table 3 details the properties of the five

$$k_R = \varphi_f/\tau_f \quad (2)$$

$$k_{NR} = (1 - \varphi_f)/\tau_f \quad (3)$$

compounds (**35**)—(**37b**) with an aromatic system other than phenyl substituted at the 2-position of the benzothiazole ring.

Table 1. Physical and analytical data for benzothiazoles (I)



(I)

Compd.	R^2	R^3	R^4	R^5	R^6	M.p. (°C)	Yield† (%)	Found (%) C	H	N	S	Halogen	Required (%) C	H	N	S	Halogen
(1)	OH	H	H	H	H	130—131[a]	65[f]										
(2)	OCH_3	H	H	H	H	90—91[b]	49[g]										
(3)	H	OH	H	H	H	172—173[c]	66[g]										
(4)	H	H	OH	H	H	223—224[d]	61[g]										
(5)	OH	H	H	NH_2	H	185—186	58[h]	64.5	4.1	11.7	12.8		64.5	4.1	11.6	13.2	
(6)	OH	H	H	$NHCOCH_3$	H	255—256	71[g]	63.0	4.1	9.9	10.9		63.4	4.2	9.9	11.3	
(7)	OH	H	H	NHCOPh	H	251—253	73[g]	69.5	4.0	7.9			69.4	4.1	8.1		
(8)	OH	H	H	NCHPh	H	128—129	75[i]	72.4	4.2	8.7	9.8		72.7	4.2	8.5	9.7	
(9)	OH	Br	H	H	H	190—191	43[j]	51.1	2.9	4.9	10.5	26.0	51.0	2.6	4.6	10.4	26.1
(10)	OH	H	Br	H	H	134—135	58[k]	51.3	2.8	4.3			51.0	2.6	4.6	10.4	26.1
(11)	OH	H	H	Br	H	165—166	82[l]	51.2	2.6	4.9	10.7	26.3	51.0	2.6	4.6	10.4	26.1
(12)	OH	Br	H	Br	H	179—180	62[f]	40.6	1.8	3.7	8.4	41.5	40.5	1.8	3.6	8.3	41.5
(13)	OH	Cl	H	H	H	83—84	94[m]	59.7	3.0	5.7	12.2	13.8	59.7	3.0	5.4	12.2	13.6
(14)	OH	H	Cl	H	H	146—147	81[l]	59.7	3.0	5.6	12.2	13.8	59.7	3.0	5.4	12.2	13.6
(15)	OH	H	H	Cl	H	149—150	64[m]	59.7	3.4	5.4	12.3	13.5	59.7	3.0	5.4	12.2	13.6
(16)	OH	Cl	H	Cl	H	178—179	87[m]	53.0	2.5	4.9	11.0	23.8	52.7	2.4	4.7	10.8	24.0
(17)	OH	H	NEt_2	H	H	167—168	83[j]	68.3	5.9	9.6	10.5		68.5	6.0	9.4	10.7	
(18)	OH	H	NMe_2	H	H	225—226	76[j]	66.7	5.2	10.6	11.8		66.7	5.2	10.4	11.8	
(19)	OH	H	H	F	H	162—164	92[j]	63.2	3.4	5.9	13.2	7.5	63.7	3.3	5.7	13.2	7.7
(20)	OH	OH	H	H	H	205—206	70[k]	63.9	3.8	6.0	13.4		64.2	3.7	5.8	13.2	
(21)	OH	H	OH	H	H	197—199[e]	70[k]	64.0	3.8	6.1	13.0		64.2	3.7	5.8	13.2	
(22)	OH	H	H	OH	H	198—199	68[n]	64.1	3.9	6.1	13.4		64.2	3.7	5.8	13.2	
(23)	OH	H	H	H	OH	264—266	70[k]	64.4	4.0	6.1	13.3		64.2	3.7	5.8	13.2	
(24)	OH	I	H	I	H	220—221	90[m]	32.8	1.7	3.2	6.4	52.7	32.6	1.5	2.9	6.7	53.0
(25)	OH	OCH_3	H	H	H	155—156	29[p]	65.0	4.1	5.7	12.3		65.4	4.3	5.5	12.4	
(26)	OH	H	OCH_3	H	H	136—137	94[m]	65.5	4.3	5.6	12.2		65.4	4.3	5.5	12.4	
(27)	OH	H	H	OCH_3	H	139—140	83[m]	65.4	4.3	5.6	12.2		65.4	4.3	5.5	12.4	
(28)	OH	CH_3	H	H	H	140—141	91[l]	69.6	4.5	6.0	13.4		69.7	4.6	5.8	13.3	
(29)	OH	H	CH_3	H	H	145—146	90[l]	69.5	4.5	6.1	13.2		69.7	4.6	5.8	13.3	
(30)	OH	H	H	CH_3	H	132—133	91[m]	69.6	4.7	5.9	13.1		69.7	4.6	5.8	13.3	
(31)	OH	CH_3	H	CH_3	H	162—163	55[l]	70.2	5.1	5.8	12.6		70.6	5.1	5.5	12.5	
(32)	OH	NO_2	H	H	H	191—193	30[k]	57.4	3.0	10.2	11.6		57.3	2.9	10.3	11.8	
(33)	OH	H	H	NO_2	H	212—214	53	57.3	3.1	10.5	12.0		57.3	2.9	10.3	11.8	
(34)	OH	NO_2	H	NO_2	H	243—245	61[q]	48.6	2.4	13.5	10.0		49.2	2.2	13.3	10.0	

[a] Ref. 18, m.p. 131—132 °C. [b] Ref. 19, m.p. 91—92 °C. [c] Ref. 20, m.p. 169—170 °C. [d] Ref. 20, m.p. 225 °C. [e] Ref. 20, m.p. 194—195 °C. † Compounds crystallised from: [f] butan-1-ol, [g] chloroform, [h] carbon tetrachloride, [i] light petroleum (b.p. 80—100 °C), [j] ethyl acetate, [k] aqueous ethanol, [l] methanol, [m] ethanol, [n] toluene, [p] propan-2-ol, [q] dimethylformamide.

Discussion

As may be seen from Table 2, only those benzothiazoles with a hydroxy group at the 2′-position fluoresce in the solid phase. Compounds with a 2′-methoxy or with a 3′- or 4′-hydroxy substituent (**2**)—(**4**) are non-fluorescent. All the other benzothiazoles reported here fluoresce to some extent. In most cases, the compounds are colourless or cream solids, yet the fluorescence which is observed is usually green or green-yellow, indicating a large Stokes shift. Previous workers[1,4] have attributed this property to the intramolecular hydrogen transfer shown in the Scheme, and this is confirmed by solution-phase studies[10] where fluorescence is observed from the excited benzothiazole prior to hydrogen transfer. This 'normal' fluorescence occurs at *ca.* 400 nm for (**1**), a shift of *ca.* 3 000—4 000 cm^{-1} from the first peak in the absorption spectrum.

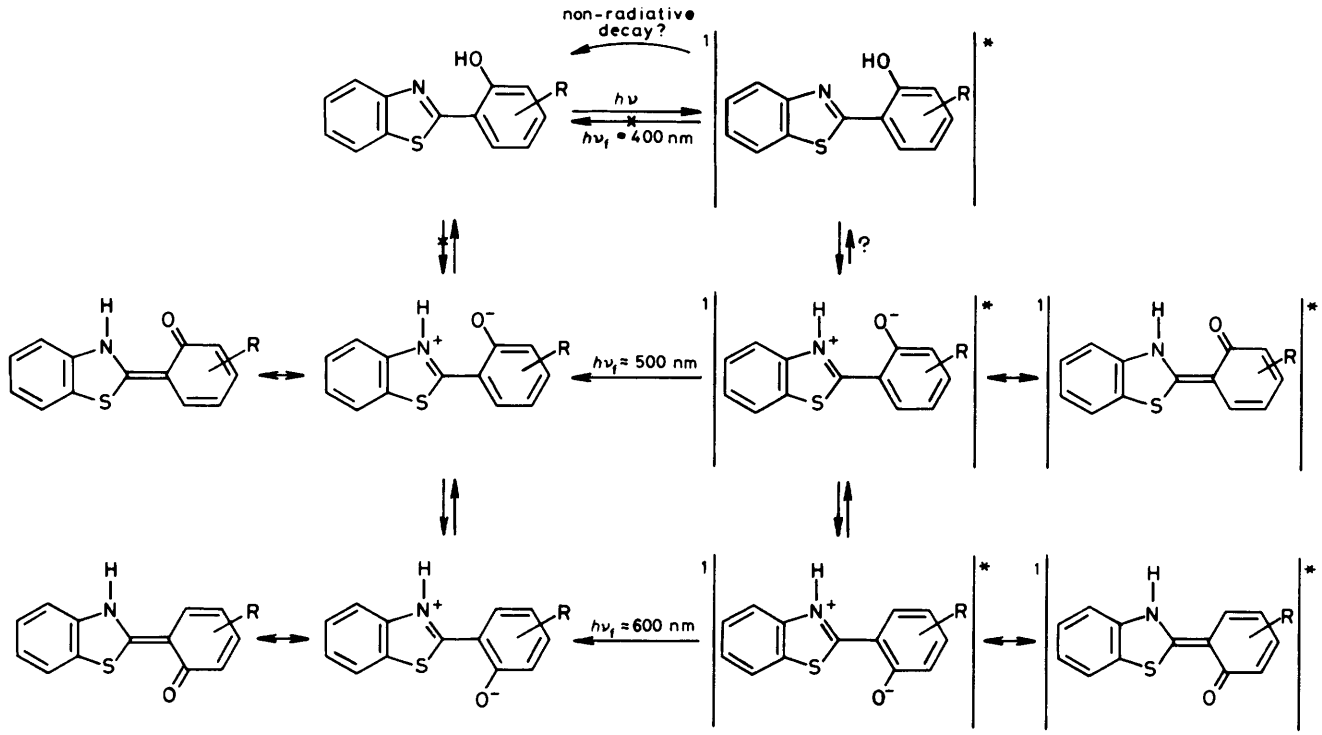
The Scheme shows the sequence of events which occurs on absorption of a photon by the solid benzothiazole. Excitation produces the non-fluorescent first excited singlet state of the benzothiazole which yields the 'ionic' form following intramolecular hydrogen transfer. We have not observed any multi-exponential character in the fluorescence decays of these compounds and therefore conclude that the hydrogen transfer takes place with a rate constant $> 10^{10}$ s^{-1}. Barbara *et al.*[2] place a lower limit of 2×10^{11} s^{-1} on this rate constant in their solution-phase work, but the time resolution of our lifetime spectrometer is inferior to theirs. Intramolecular hydrogen transfer rates in excess of 10^{11} s^{-1} have also been measured for 2-(2-hydroxy-5-methylphenyl)benzotriazole,[11] although once again those measurements were performed in solution.

The energy difference between (**Ia**) and its prescursor is *ca.* 5 000—6 000 cm^{-1} making the reverse hydrogen transfer extremely unlikely. Species (**Ia**) may be stabilised by resonance so the species formed as a result of the hydrogen-transfer step should more correctly be written as (**Ic**) and the ionic (**Ia**) and

Table 2. Photophysical properties of the 2-phenyl-substituted benzothiazoles

Compound	λ_{em}[a]/nm	φ_f	φ_f[b]	τ_f/ns	$10^{-8}k_R/s^{-1}$	$10^{-8}k_{NR}/s^{-1}$
(1)	510, 535 (sh)	0.380	0.310	4.7	0.809	1.319
(2)	No fluorescence					
(3)	No fluorescence					
(4)	No fluorescence					
(5)	640	0.040	0.376	1.3	0.308	7.385
(6)	535	0.180		5.6	0.321	1.460
(7)	540	0.250		5.9	0.424	1.271
(8)	570, 620 (sh)	0.160		3.7	0.432	2.270
(9)	526	0.250		3.0	0.833	2.500
(10)	510	0.210		2.9	0.724	2.724
(11)	520, 550 (sh)	0.270	0.022	3.5	0.771	2.086
(12)	535, 570 (sh)	0.320		2.5	1.280	2.720
(13)	522	0.470		6.0	0.783	0.883
(14)	508, 540 (sh)	0.330		4.8	0.688	1.396
(15)	525, 550 (sh)	0.250	0.254	5.5	0.455	1.364
(16)	530, 570 (sh)	0.370	0.365	6.6	0.561	0.955
(17)	440, 460, 490, 520	0.038		0.4	0.950	24.050
(18)	440, 460, 490, 520	0.048		0.4	1.200	23.800
(19)	537, 555 (sh)	0.280		4.6	0.609	1.566
(20)	550, 575 (sh)	0.066		1.8	0.367	5.189
(21)	500, 525 (sh)	0.390		3.1	1.258	1.968
(22)	535, 565 (sh)	0.250		5.4	0.463	1.389
(23)	500 (sh), 526 (sh)	0.018		0.85	0.212	11.553
(24)	530	0.041		0.4	1.025	23.975
(25)	527, 560 (sh)	0.220	0.218	4.8	0.458	1.625
(26)	492, 520 (sh)	0.460		4.3	1.070	1.256
(27)	570, 610 (sh)	0.070	0.135	4.4	0.159	2.114
(28)	523, 550 (sh)	0.360		4.7	0.766	1.362
(29)	512, 540 (sh)	0.39		3.2	1.219	1.906
(30)	525, 570 (sh)	0.35	0.57	5.9	0.593	1.102
(31)	540	0.23		5.1	0.451	1.510
(32)	526	0.05	0.01	1.7	0.294	5.588
(33)	510 (sh), 523	0.02	0.065	2.0	0.100	4.900
(34)	500 (sh), 526	0.009		0.6	0.150	15.167

[a] λ_{em} = emission maximum; sh = shoulder. [b] Literature values from ref. 4.

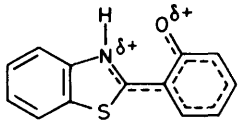


Scheme.

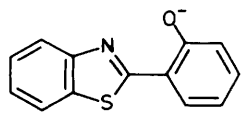
Table 3. Physical and analytical data and physical properties of benzothiazoles substituted with coumarin and naphthalene moieties at the 2-position

Compd.	M.p. (°C)	Yield† (%)	Found (%) C	H	N	S	Required (%) C	H	N	S	λ_{em}*/nm	φ_f	τ_f/ns	$10^{-8}k_R/s^{-1}$	$10^{-8}k_{NR}/s^{-1}$
(35)	241—242	74[a]	65.9	3.7	4.9	10.6	66.0	3.6	4.5	10.4	510	0.39	5.5	0.709	1.111
(36a)	178—180	61[b]	73.3	3.8	5.2	11.4	73.6	4.0	5.1	11.6	508, 530 (sh)	0.48	3.9	1.231	1.333
(36b)	222—224	89[c]	57.3	2.8	3.9	9.0	56.9	2.9	3.9	8.9	508, 535 (sh)	0.2	1.5	1.333	5.333
(37a)	182—183	65[b]	73.5	4.3	5.2	11.7	73.6	4.0	5.1	11.6	490 (sh), 525	0.111	0.52	0.212	19.02
(37b)	253—254	88[c]	46.8	2.0	3.2	7.5	46.9	2.1	3.2	7.4	490 (sh), 525	0.111	0.41	0.268	24.12

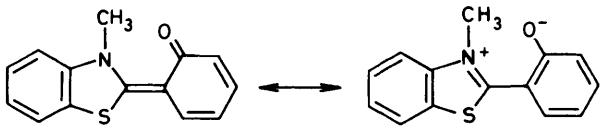
†Compounds crystallised from: [a]dimethylformamide, [b]aqueous acetone, [c]toluene.
*λ_{em} = emission maximum; sh = shoulder.



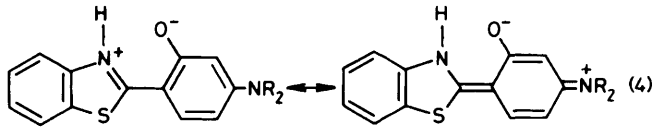
(Ic)



(III)



(II)



(4)

quinonoid (**Ib**) forms considered as two extreme contributors to this species.

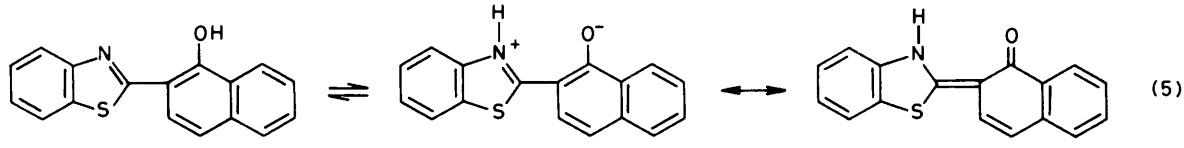
Rotation about the C(2)–C(1′) bond will lead to a *trans*-conformation. Williams and Heller[4] suggest that the *trans*-form fluoresces to the red of the *cis*-form and that this could account for the shoulder observed on many of the spectra. If this is the case, then the *cis*-species predominates over its *trans*-counterparts in the excited state, but whether the ionic or quinonoid form is the more significant contributor to the overall structure is not known.

Substituent effects will be important at various points in the Scheme. Electron-withdrawing substituents in the 2-phenyl ring will enhance the probability of the hydrogen-transfer process by making the 2′-hydroxy group more acidic. However, given that the rate constant for this process is already extremely large [2×10^{11} s^{-1} for compound (**1**)][2] there may be little or no overall effect on the fluorescence yield. Electron-donating substituents will reduce the acidity of 2′-OH and may decrease the rate constant for hydrogen transfer sufficiently to enable other processes to compete, with a consequent decrease in the observed fluorescence quantum yield. This effect would be particularly marked for $+M$ substituents in the 3′- and 5′-positions and may partially account for the decrease in quantum yield observed for compounds with amino, hydroxy, or methoxy groups in these positions. Picosecond fluorescence decay time measurements may be able to detect a rise-time for the fluorescence and thus provide information on substituent effects on the hydrogen-transfer process.

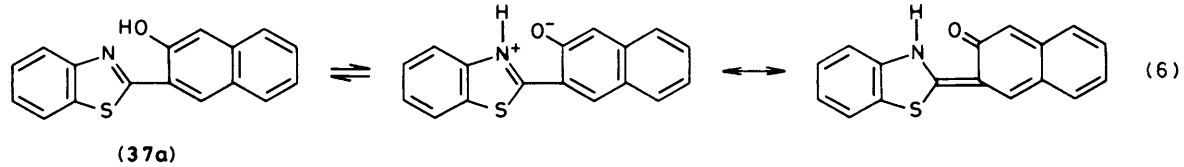
In an attempt to quantify substituent effects on the emission process, values of radiative and non-radiative rate constants have been calculated. Unfortunately, the quantum yields which are measured may lead to k_R and k_{NR} values which are distorted by the substituent effects on the hydrogen-transfer step. In particular, if a strongly electron-donating substituent causes a significant fraction of the excited benzothiazole molecules to decay by a process or processes other than hydrogen transfer, the measured quantum yield will be less than the quantum yield which would be obtained if (**Ic**) could be excited directly. This would lead to values of k_R and k_{NR} which would be respectively lower and higher than the true values. For all the compounds in Tables 2 and 3, the calculated k_R values represent the minimum value for this rate constant and the k_{NR} values the maximum for this rate constant.

The substituent effects on the radiative and non-radiative decay processes of (**Ic**) may be discussed in terms of the electronic properties of the substituent and of the position of substitution. In addition, the heavy atom effect must be considered for the four bromo-derivatives (**9**)—(**12**) and the di-iodo-compound (**24**). The heavy atom effect is clearly the reason for the low fluorescence quantum yield from (**24**), since the non-radiative rate constant has increased by a factor of 20 over the unsubstituted compound. k_{NR} is also increased for the bromo-derivatives, but only by a factor of two, and in the case of the dibromo-compound (**12**), the radiative rate constant increases slightly, so that the overall fluorescence quantum yield is reduced only slightly from that of the parent. The lack of a substantial heavy atom effect for the bromine atom may imply that intersystem crossing is negligible in (**Ic**) in the absence of a heavy atom.

With the exception of the two dialkylamino-compounds (**17**) and (**18**), substituents in the 4′-position have little effect. A similar situation obtains for 3′- and 5′-substituents which are unable to interact mesomerically with the π-electron system. Apart from the slight heavy atom effect already noted for the bromo-substituted derivatives, these and the methyl and chloro-derivatives have similar emission properties and rate constants to the parent compound. The two 4′-dialkylamino-compounds not only exhibit a big reduction in quantum yield and lifetime, but their fluorescence emission is shifted to the blue. The 4′-hydroxy and 4′-alkoxy derivatives are also slightly blue-shifted in their fluorescence spectra. A $+M$ substituent in the 4′-position, although unable to interact mesomerically with the 2′-



(36a) (5)



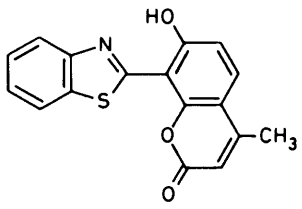
(37a) (6)

position, appears to reduce the likelihood of fluorescence through a large increase in non-radiative decay.

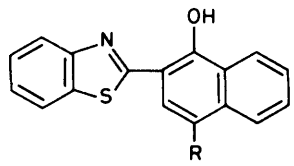
We have already noted the effect of $+M$ substituents at the 5′-position in a preliminary publication.[5] The fluorescence red-shifts, but the quantum yields decrease and the solids become cream or yellow. Comparison of the solution-phase absorption spectra[10] of these compounds with that of the parent (**1**) indicates that all the change in emission wavelength may be accounted for by the bathochromic shift in absorption, *i.e.* the Stokes shift is essentially unchanged. Dearden and Forbes[12] have observed a similar shift in the absorption spectra of *para*-substituted phenols when a $+M$ substituent is introduced. Furthermore, it is known that introduction of amino[13] and hydroxy and methoxy groups[14] shifts the absorption of quinones substantially to the red. Unfortunately, we have been unable to prepare 2-(3-amino-2-hydroxyphenyl)benzothiazole to complete the comparison of the 3′-substituted compounds with the 5′-series. However, the trends appear to be similar for the two series, but the proximity of the 3′-substituents to the 2′-position introduces steric effects and care is needed in the interpretation of the results.

Williams and Heller[4] assign the fluorescence of solid benzothiazoles to a predominantly ionic form of (**Ic**), but appear to have no evidence to support this assignment. In the ground state of 6-(3-methyl-2,3-dihydro-2-benzothiazoylidene)cyclohexa-2,4-dienone (**II**) the compound appears to favour the ionic species in the *cis*-conformation, whilst the reverse is the case for the *trans*-conformation.[4] This situation is unlikely to remain true following excitation and, given that the electron distribution can change rapidly in the excited state, these ground-state studies can provide little information about the excited state. We have attempted to prepare (**II**) by deprotonating 2-(2-hydroxyphenyl)benzothiazolium iodide in base solution. Unfortunately, the benzothiazolium ring is very sensitive to basic cleavage and even when an equivalent amount of base is used, a mixture of products is obtained. Deprotonation of (**I**) in basic solution yields the anion (**III**) which fluoresces at 460—470 nm.[10] As this is only 2 000 cm^{-1} higher in energy than the fluorescence from (**Ic**), an energy difference which could be accounted for by protonation of the benzothiazole nitrogen, this is of no help in assigning the exact nature of (**Ic**).

For 2-(2-hydroxyphenyl)benzothiazole in both rigid and fluid solution[1,3] and for the salicylideneanilines in solution and the solid phase,[1,15,16] the evidence points to the emitting species being essentially quinonoid in character. It seems reasonable to assume that this is also the case for solid benzothiazoles. The effect of the 4-dialkylamino-substituents might therefore be

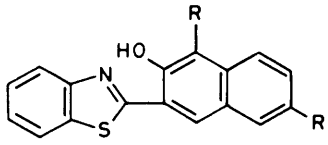


(35)



(36)

a; R = H
b; R = Br



(37)

a; R = H
b; R = Br

explained on the basis of their 'interception' of (**Ic**) before it can attain the quinonoid form [equation (4)].

As may be seen from Table 3, replacement of the 2-phenyl ring by a naphthalene or coumarin has little effect on the fluorescence spectra except for a slight blue-shift for (**37a** and **b**). These compounds also exhibit much reduced values for their fluorescence quantum yield and lifetime. Initially, this appears to be a surprising observation since (**36a** and **b**) are still highly fluorescent. However, if the ionic and quinonoid forms for (**36**) and (**37**) are examined [equations (5) and (6)], it can be seen that the quinonoid form of the latter cannot be formed without the disruption of the second aromatic ring of the naphthalene group. This will be unfavourable on energetic grounds, so that if the emission originates from a quinonoid form of (**Ic**), it would be expected to be weaker because this form will not be

populated. However, using this argument it would be anticipated that the fluorescence quantum yields from 1-phenylazo-2-naphthol and 2-phenylazo-1-naphthol would be similar, whereas they differ by a factor of 9.[17]

Compounds (**35**)—(**37**) are coloured. The coumarin is cream-yellow, whilst the naphthalene derivatives are an intense yellow. One might have anticipated the fluorescence to be further to the red than is actually observed, so in fact the Stokes shifts for these compounds are less than for the 2-(2-hydroxyphenyl)-benzothiazoles. Clearly, extension of the aromatic system holds no benefits and can be a definite retrograde step, as in the case of (**37**). The photophysical properties of (**35**) and (**36a**) are similar to those of (**1**), although the heavy atom effect of bromine is more pronounced than in the simple phenyl analogues. The four-fold increase in k_{NR} for (**36b**) compared to (**36a**) is particularly noteworthy. k_{NR} for (**37a**) is already high and hence the effect is not so marked for (**37b**).

Experimental

Reflectance and fluorescence spectra were recorded on the solid samples using an Applied Photophysics optical integrating spectrometer. Corrected fluorescence spectra were obtained by calibrating the wavelength response of the spectrometer with quinine sulphate. Fluorescence decay profiles were measured by the technique of time-correlated, single-photon counting on an Edinburgh Instruments model 199 fluorescence decay time spectrometer. The profiles were analysed by computer convolution and goodness of fit judged on the basis of χ^2 values and a random distribution of residuals.

Fluorescence spectrum yields (φ) were determined by comparing the area underneath the corrected fluorescence spectrum of an unknown material (A_u) with the area underneath the corrected fluorescence spectrum of a standard compound (A_s) using equation (7). This ratio was corrected for the

$$\frac{\varphi_u}{\varphi_s} = \frac{A_u}{A_s}\frac{(100 - R_s)}{(100 - R_u)} \qquad (7)$$

reflectance of each material (R) expressed as a percentage relative to the amount of light reflected by a barium sulphate plate at the excitation wavelength (380 nm). The standards used were sodium salicylate (Aldrich Gold Label) and 1,1,4,4-tetraphenylbuta-1,3-diene (Aldrich Gold Label), the quantum yields for which were taken to be 0.55 and 0.90, respectively.

Materials.—3-Bromo-[21] and 3-chloro-salicylic acid[21] were prepared by the carboxylation of the sodium salts of the *m*-substituted phenols, whilst the corresponding 3,5-dihalogeno-compounds were obtained by halogenation of salicylic acid.[22,23] The latter method was used to synthesise the bromohydroxynaphthoic acids. 7-Hydroxy-4-methylcoumarin-8-carboxylic acid was prepared from the reaction of 2,6-dihydroxybenzoic acid and ethyl acetoacetate in sulphuric acid.[24]

General Method of Preparation of Benzothiazoles.—Phosphorus trichloride (0.03 mol) was added dropwise to a solution of the substituted carboxylic acid (0.33 mol) and 2-aminothiophenol (0.036 mol) in toluene (50 cm^3), maintaining the temperature at 40—45 °C. The mixture was boiled vigorously under reflux for 4 h, whereupon the cooled solution was made alkaline to phenolphthalein with aqueous sodium carbonate solution (20% w/v). Toluene was removed by distillation in steam and the solid which remained was collected and purified.

2-(2-*Hydroxy*-5-*nitrophenyl*)*benzothiazole.*—5-Nitrosalicylaldehyde (5.0 g) was stirred into a solution of 2-aminothiophenol (3.13 g) in triethyl phosphate (25.0 g). After 10 min, acetic acid (25.0 g) was added and the solution was stirred for a further 15 min. Whilst maintaining the temperature below 60 °C, lead(IV) acetate (15.0 g) was added and stirring was continued for a further 15 min. Ethane-1,2-diol (2.5 g) was added and the solid which formed on cooling was collected and crystallised from aqueous ethanol and then from aqueous dimethylformamide to give 2-(2-*hydroxy*-5-*nitrophenyl*)*benzothiazole* (53%), m.p. 212—214 °C, as a yellow solid (Found: C, 57.3; H, 3.0; N, 10.5; S, 12.0. $C_{13}H_8N_2O_3S$ requires C, 57.3; H, 2.9; N, 10.3; S, 11.8%).

2-(5-*Acetamido*-2-*hydroxyphenyl*)*benzothiazole.*—Acetyl chloride (0.98 g) and 2-(5-amino-2-hydroxyphenyl)benzothiazole (3.0 g) reacted at 75 °C in pyridine (2.8 g) during 15 min. Addition of water precipitated the *acetyl derivative* (71%), m.p. 255—256 °C (from chloroform). The *benzoyl derivative*, m.p. 251—253 °C, was obtained in a similar manner.

2-(5-*Benzylideneamino*-2-*hydroxyphenyl*)*benzothiazole.*—A solution of 2-(5-amino-2-hydroxyphenyl)benzothiazole (2.0 g) and benzaldehyde (1.15 g) in ethanol (25 cm^3) was refluxed for 30 min. The solid which formed when the solution was poured onto ice was recrystallised from light petroleum (b.p. 80—100 °C) to give the *Schiff's base* (75%), m.p. 128—129 °C (Found: C, 72.4; H, 4.2; N, 8.8; S, 9.8. $C_{20}H_{14}N_2OS$ requires C, 72.7; H, 4.3; N, 8.5; S, 9.7%).

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