Preparation and Characterization of Bridged Naphthoxazinium Salts

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Dedicated to Professor Karl Heinz Drexhage on the accasion of his 65th birthday

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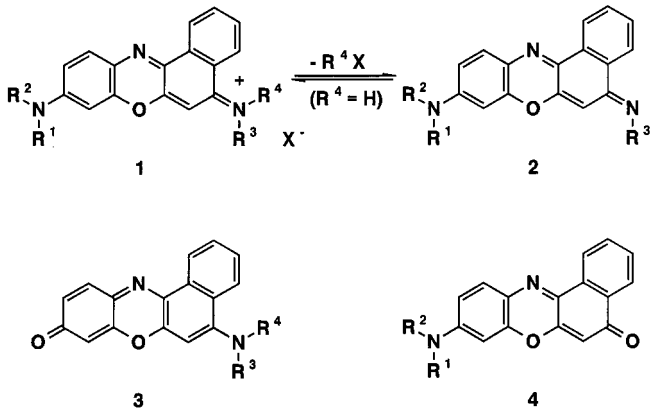
By condensation of bridged 4-arylazo-substituted 3-hydroxyanilines **18** and bridged or unbridged 4-arylazo-substituted 1-naphthylamines **19–23** with bridged 1-naphthylamines **15–17** and 3-aminophenols **14**, respectively, in the presence of perchloric acid, bridged naphthoxazinium perchlorates **24–30** have been prepared. The spectral properties of the products have been compared with those of the bridged phenoxazinium salt **31** as well as with data for some unbridged analogues.

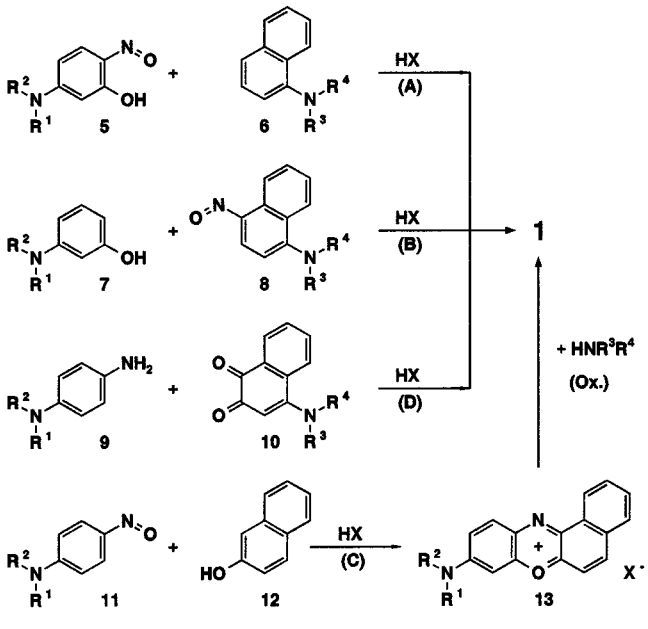
Introduction

Benzo[*a*]phenoxazinium salts (naphthoxazinium salts) of the general structure **1** possess several interesting properties. For example, they exhibit an intense long-wavelength absorption at about 650 nm and a strong red fluorescence.[1] Consequently, they have been utilized as dyestuffs for dyeing fibres and paper[2] and as laser dyes.[3] If one of their terminal amino groups bears a free proton and is also substituted by a long fatty acid residue, they can be used as sensor dyes in optodes for acid-base titrations.[4] This application relies on the fact that they can be transformed by the action of bases into naphthoxazine imines **2**, which absorb at considerably shorter wavelengths than their cationic counterparts **1**. Very recently, some naphthoxazinium dyes have been employed as ultrasensitive indicators for biomolecules.[5] Furthermore, it has also been reported that some naphthoxazinium salts **1** are potentially useful as photosensitizers in photodynamic cancer therapy[6] and as antituberculostatic or anticancerogenic agents.[7]



Scheme 1

Few simple routes exist for the preparation of naphthoxazinium salts **1**. The majority of these starts from nitrosoanilines **5** or **11** or from nitrosonaphthylamines **8**, which are condensed with appropriate 1-naphthylamines **6** (route A), 3-aminophenols **7** (route B), or 2-naphthol **12** (route C), respectively, in the presence of a strong mineral acid such as perchloric acid.[8] In the last case, monoamino-substituted naphthoxazinium salts **13** are the initial products.[9] Subsequently, these compounds may be transformed



1, 6, 8, 10 22 - 25	R 3	R 4
a	H	H
b	CH_3	H
c	C_2H_5	H
d	CH_3	CH_3
e	$(CH_2)_2CN$	H
f	$(CH_2)_5COOH$	H
g	$(CH_2)_5COOC_2H_5$	H

Scheme 2

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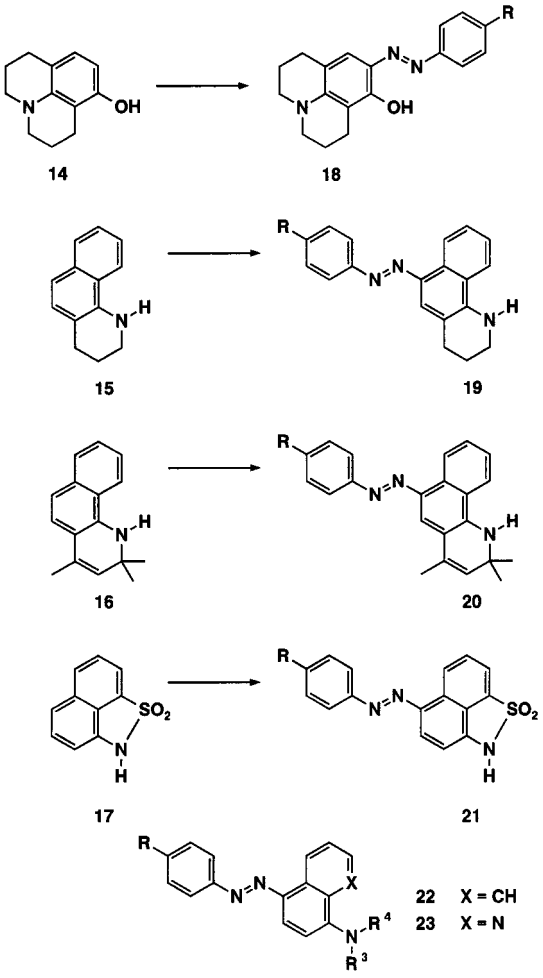
into the naphthoxazinium salts **1** by reaction with amines under the influence of an oxidizing agent. A further route D starts from *para*-phenylenediamines **9**, which are condensed with 4-amino-substituted 1,2-naphthoquinones **10**.[10]

The applicability of naphthoxazinium salts **1** is somewhat restricted, however, owing to their sensitivity towards hydrolysis, which results in their conversion either to nonionic naphthoxazinones of structure **3**, or, more probably, to naphthoxazinones of structure **4**.[11] Therefore, the synthesis of naphthoxazinium salts that are more resistant to hydrolysis would seem to be a worthwhile goal. In this regard, anilines and 1-naphthylamines that have their amino moieties incorporated into bridged structures should be suitable starting compounds. The bridged amines **14**–**17** are examples of such compounds. However, these secondary and tertiary amines cannot be transformed into the corresponding nitroso derivatives by reaction with nitrous acid under standard conditions. As we reported recently,[12] in order to obtain the desired nitroso derivatives the starting amines have to be transformed into various oxidation products, which cannot be used as building blocks for the synthesis of naphthoxazinium salts. Hence, other routes of preparing naphthoxazinium salts from the bridged anilines or 1-naphthylamines **14**–**17** would be desirable.

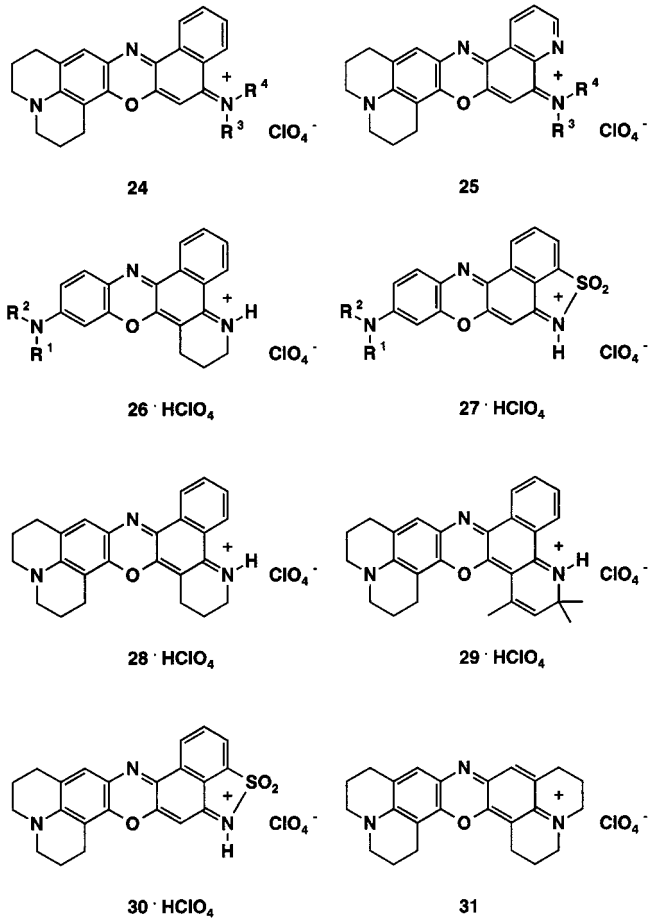
Results and Discussion

In 1890, procedures were developed at Bayer AG for preparing naphthoxazinium salts **1** by heating arylazo-substituted aminophenols or naphthylamines with appropriate 1-naphthylamines or aminophenols in high-boiling solvents.[13] This reaction corresponds to routes A and B above. Although this procedure, which starts from arylazo-substituted precursors rather than the corresponding nitroso derivatives, has seemingly not been mentioned since the 1890s, neither in the patent nor the scientific literature,[14] nor in textbooks,[15] we have found it to be well-suited for transforming the bridged aniline and 1-naphthylamine derivatives **14**–**17** into the corresponding bridged naphthoxazine dyes. In order to carry out this reaction, some modifications of the published methods[13] were, however, necessary. Thus, we used a dipolar aprotic solvent, such as DMF, in place of the reported solvents (ethylene glycol or glycerol); we used arylazo compounds substituted with electron-accepting substituents on the arylazo moiety, and added a strong mineral acid to the reaction mixture.

The desired arylazo compounds **18**–**23** were obtained from the bridged aniline and 1-naphthylamine derivatives **14**–**17** as well as from unbridged 1-naphthylamine and 8-



Scheme 3



Scheme 4

aminoquinoline by coupling these aromatic amines with an aryl diazonium salt in the standard manner.[16] Details of all the azo compounds prepared in this way are presented in Table 1. Their structures were unambiguously confirmed on the basis of their analytical and some of their characteristic spectroscopic data.

Somewhat surprisingly, these azo compounds were readily protonated in acidic solution and the absorption maxima of the resulting species proved to be strongly structure-dependent. Thus, on going from neutral to acidic solutions, hypsochromic as well as bathochromic shifts were observed, as is apparent from Table 1.

By treating the arylazo compounds **18**−**23** with the corresponding co-reagents lacking an azo group, **5**, **6**, **8**, **14**, **15**, and **17**, in the presence of perchloric acid, the bridged naphthoxazinium perchlorates **24**−**30** were prepared, in most cases in satisfactory yields. The sulfamido-bridged naphthoxazinium salts **27** could only be isolated as the free bases. The results achieved are presented in Table 2.

In order to differentiate the route starting from the bridged arylazophenol derivative **18** from those starting from the nitroso precursors **5**, **8** and **11**, the former is designated as route E, while the route starting from the bridged and unbridged 4-arylazo-1-naphthylamine derivatives **19**−**22** or from the 8-amino-5-arylazoquinoline **23** is designated as route F.

The successful use of arylazo compounds as starting materials for preparing unbridged and bridged naphthoxazinium dyes **1** and **24**−**30** can be rationalized by viewing the azo moiety as an azomethine analogue of a nitroso group. Hence, instead of the elimination of water that occurs during the condensation of nitroso compounds, a substituted aniline group, which serves as a precursor of the azo compound, is eliminated in the course of the naphthoxazinium salt formation. This aromatic amine could be detected in the reaction mixture by chromatography or isolated from it by adding aqueous base and extracting the resulting mixture with diethyl ether.

To allow comparison of the properties of bridged naphthoxazinium salts **24**−**30** with those of their unbridged analogues **1**, several such compounds were also prepared using methods A or B. Data relating to these are also collected in Table 2.

Table 1. Characterization of the diarylazo starting compounds **18**−**22**

Compd.	R	R^3	R^4	Yield [%]	M.p. [°C] (ref. m.p.)	λ_{max} (log ε)[a]	λ_{max} (log ε)[b]	Emp. formula (mol. mass)	calcd. C found	H	N	S
18	NO_2	−	−	78	268−269	494 (4.74)	470 (4.71)	$C_{18}H_{18}N_4O_3$ (338.4)	63.89 63.65	5.36 5.72	16.56 16.27	
19a	NO_2	−	−	92	247−249	525 (4.65)	558 (4.35)	$C_{19}H_{16}N_4O_2$ (332.4)	68.66 68.99	4.85 5.22	16.86 16.73	
19b	Cl	−	−	88	259−260	545 (4.64)	500 (4.46)	$C_{19}H_{16}N_3Cl$ (321.8)	70.91 71.16	5.01 5.53	13.06 13.38	
20a	NO_2	−	−	92	173−177	544 (4.50)	577 (4.24)	$C_{22}H_{20}N_4O_2$ (372.4)	70.95 71.19	5.41 5.81	15.04 14.86	
20b	Cl	−	−	84	155−157	558 (4.65)	512 (4.42)	$C_{22}H_{20}N_3Cl$ (361.9)	73.02 73.02	5.57 5.97	11.61 11.63	
21b	Cl	−	−	80	197−200	399 (4.27)	490 (4.33)	$C_{16}H_{10}N_3O_2SCl$ (343.8)	55.90 56.11	2.93 3.41	12.22 12.19	9.33 9.17
22a	NO_2	H	H	95	253−255 (252)[21]	522 (4.75)	520 (4.52)	$C_{16}H_{12}N_4O_2$ (292.3)	65.75 65.53	4.14 4.42	19.17 18.86	
22b	Cl	H	H	92	183−184 (187−188)[22]	539 (4.81)	458 (4.28)	$C_{16}H_{12}N_3Cl$ (281.7)	68.21 68.56	4.29 4.51	14.91 15.03	
22c	NO_2	CH_3	H	84	180−182	539 (4.63)	517 (4.34)	$C_{17}H_{14}N_4O_2$ (306.3)	66.66 66.52	4.61 5.05	18.29 17.86	
22d	Cl	CH_3	H	80	160−163	544 (4.67)	469 (4.42)	$C_{17}H_{14}N_3Cl$ (295.8)	69.04 68.98	4.77 5.08	14.21 13.95	
22e	NO_2	C_2H_5	H	90	225−227	531 (4.59)	530 (4.36)	$C_{18}H_{16}N_4O_2$ (320.4)	67.49 67.29	5.03 5.40	17.49 17.20	
22f	Cl	C_2H_5	H	85	118−119	547 (4.74)	475 (4.52)	$C_{18}H_{16}N_3Cl$ (309.8)	69.79 69.76	5.21 5.73	13.56 13.44	
22g	NO_2	CH_3	CH_3	82	148−150 (156−157)[23]	528 (4.61)	473 (4.24)	$C_{18}H_{16}N_4O_2$ (320.3)	67.49 67.86	5.03 5.50	17.49 17.46	
22h	NO_2	$(CH_2)_2CN$	H	85	213−213	528 (4.61)	509 (4.43)	$C_{19}H_{15}N_5O_2$ (345.4)	66.08 66.04	4.38 4.78	20.28 20.54	
22i	NO_2	$(CH_2)_5COOH$	H	80	204−206	532 (4.79)	536 (4.49)	$C_{22}H_{22}N_4O_4$ (406.4)	65.01 65.02	5.46 5.83	13.78 13.95	
22j	NO_2	$4\text{-}SO_2C_6H_5CH_3$	H	82	208−209	410 (4.02)	542 (4.00)	$C_{23}H_{18}N_4O_4S$ (446.5)	61.87 61.54	4.06 3.96	12.55 12.73	7.81 7.41
22k	Cl	$4\text{-}SO_2C_6H_5CH_3$	H	78	191−192	393 (4.21)	477 (4.36)	$C_{23}H_{18}N_3O_2S$ (435.9)	63.37 63.52	4.16 4.50	9.64 9.89	7.35 7.59
23a	NO_2	H	H	94	198−200	512 (4.61)	489 (4.37)	$C_{15}H_{11}N_5O_2$ (293.3)	61.43 61.57	3.78 4.27	23.88 23.53	
23b	Cl	H	H	80	180−182	524 (4.49)	437 (4.33)	$C_{15}H_{11}N_4Cl$ (282.7)	63.72 64.05	3.92 4.41	19.82 19.59	

[a] Protonated species. − [b] Unprotonated species.

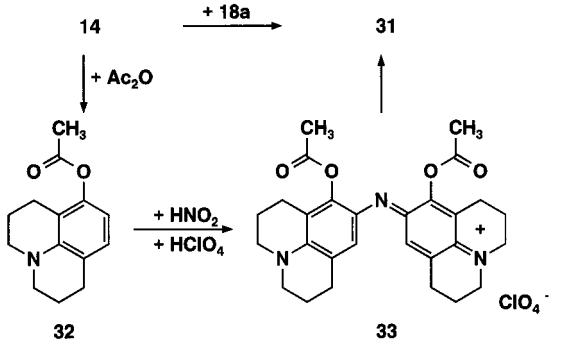
Table 2. Characterization of the bridged phenoxazinium perchlorates **1** and **24–31**

Compd.	R^1	R^2	R^3	R^4	Yield [%] (method)	Starting compd.	M. p. [°C]	Emp. formula (mol. mass)	calcd. C found	H	N	S
1a	C_2H_5	C_2H_5	H	H	31 (A)	**5 + 6**	> 360	$C_{20}H_{20}N_3O_5Cl$	57.49	4.82	10.06	
								(417.9)	57.78	5.07	10.10	
1b	C_2H_5	C_2H_5	CH_3	H	40 (A)	**5 + 6**	265–268	$C_{21}H_{22}N_3O_5Cl$	58.40	5.13	9.73	
								(431.9)	58.51	5.10	9.50	
1c	C_2H_5	C_2H_5	C_2H_5	H	42 (A)	**5 + 6**	287–289	$C_{22}H_{24}N_3O_5Cl$	59.26	5.43	9.42	
								(445.9)	59.16	5.41	9.25	
1d	C_2H_5	C_2H_5	CH_3	CH_3	32 (A)	**5 + 6**	240–243	$C_{22}H_{24}N_3O_5Cl$	59.26	5.43	9.42	
								(445.9)	59.48	5.66	9.19	
24a	–	–	H	H	27 (F)	**14 + 22a**, **22b**	335 (dec.)	$C_{22}H_{20}N_3O_5Cl$	59.80	4.56	9.51	
					35 (F)	**14 + 22j**, **22k**		(441.9)	60.04	4.58	9.67	
24b	–	–	CH_3	H	28 (F)	**14 + 22c**, **22d**	233–235	$C_{23}H_{22}N_3O_5Cl$	60.60	4.86	9.22	
								(455.9)	60.43	4.93	8.95	
24c	–	–	C_2H_5	H	42 (F)	**14 + 22e**, **22f**	> 360	$C_{24}H_{24}N_3O_5Cl$	61.34	5.15	8.94	
					53 (B)	**14 + 8c**		(462.9)	61.12	5.04	9.09	
24d	–	–	CH_3	CH_3	32 (F)	**14 + 22g**	> 360	$C_{24}H_{24}N_3O_5Cl$	61.34	5.15	8.94	
								(462.9)	61.04	4.98	9.20	
24e	–	–	$(CH_2)_2CN$	H	59 (F)	**14 + 22h**	>360	$C_{25}H_{23}N_4O_5Cl$	60.67	4.68	11.32	
								(494.9)	60.36	4.98	11.53	
24f	–	–	$(CH_2)_5COOH$	H	25 (F)	**14 + 22i**	180–184	$C_{28}H_{30}N_3O_7Cl$	60.49	5.44	7.56	
					28 (B)	**14 + 8f**		(556.0)	60.16	5.67	7.43	
24g	–	–	$(CH_2)_5COOC_2H_5$	H	45 (B)	**14 + 8g**	223–224	$C_{30}H_{34}N_3O_7Cl$	61.69	5.87	7.19	
								(584.1)	61.40	5.97	6.94	
25	–	–	H	H	12 (F)	**14 + 23a**, **23b**	> 280 (dec.)	$C_{21}H_{19}N_4O_5Cl$	56.96	4.32	12.56	
								(442.9)	56.53	4.42	12.41	
26	C_2H_5	C_2H_5	–	–	16 (A)	**5 + 15**	315–318	$C_{20}H_{17}N_3O_3S$	63.31	4.52	11.07	8.45
								(379.4)	62.87	4.85	10.96	8.30
27	C_2H_5	C_2H_5	–	–	45 (A)	**5 + 17**	298–301	$C_{23}H_{24}N_3O_5Cl$	60.33	5.28	9.16	
								(457.9)	60.50	5.53	9.16	
28	–	–	–	–	57 (F)	**14 + 19a**, **19b**	> 360	$C_{25}H_{24}N_3O_5Cl$	62.31	5.02	8.72	
								(481.9)	62.20	5.30	8.79	
29	–	–	–	–	10 (F)	**14 + 20a**, **20b**	> 360	$C_{28}H_{28}N_3O_5Cl$	64.43	5.41	8.05	
								(522.0)	64.96	5.70	7.80	
30	–	–	–	–	10 (F)	**14 + 21b**	> 360	$C_{22}H_{18}N_3O_7SCl$	52.44	3.60	8.34	6.36
								(503.9)	52.11	3.89	8.54	6.51
31	–	–	–	–	1 (E)	**14 + 18**	> 360	$C_{24}H_{26}N_3O_5Cl$	61.08	5.55	8.90	
					80 (G)	**32**		(471.9)	60.86	5.92	8.86	

Remarkably, method E also proved successful for the preparation of the simply bridged phenoxazinium perchlorate **31**. This compound was obtained by heating an equimolar amount of 8-hydroxyjulolidine **14** with its nitrophenylazo derivative **18a** in ethanolic solution containing some perchloric acid.

An alternative route G for preparing the phenoxazinium perchlorate **31** was found by allowing 8-hydroxyjulolidine (**14**) to react with nitrous acid in acetic anhydride at room temperature rather than in the usually used acetic acid. In the course of this procedure, the indaminium salt **33** was produced, which could be isolated in satisfactory yield as the perchlorate by adding diethyl ether to the reaction mixture. Nevertheless, refluxing of the resulting mixture for a few minutes also led to formation of the bridged phenoxazine perchlorate **31** from its precursor **33**. Clearly, the initial step in this reaction is the formation of the 8-acetoxyjulolidine **32** from the starting 8-hydroxyjulolidine (**14**). Subsequently, the acetoxy compound **32** is transformed into the corresponding nitroso derivative, which, as recently demonstrated,[17] undergoes condensation with its precursor **32** to give the indaminium salt **33**.

A peculiarity was observed upon condensation of the bridged aminophenol derivative **14** with the sulfamido-substituted 4-arylazonaphthalene derivative **22j**. Instead of furnishing the corresponding sulfonamido-substituted naphthoxazinium salt, only the naphthoxazinium salt **24a**, lacking an arylsulfonyl group, was produced. This compound could also be obtained by condensing 8-hydroxyjulolidine (**14**) with the 4-arylazo-1-naphthylamine **22a**. The arylsulfonyl moiety is clearly eliminated in the course of the condensation of **14** with **22j**, probably in the form of an arylsulfinic acid. This finding is in contrast to the reaction of the sulfonyl-bridged 4-arylazo-1-naphthylamine derivative **21b**



Scheme 5

with 8-hydroxyjulolidine (**14**), where condensation leads to the sulfonyl-bridged naphthoxazinium salt **30**.

A further peculiarity was observed upon condensation of the *N*-(5-carboxypentyl)-substituted 4-nitroso-1-naphthylamine **8f** obtained by nitrosation of *N*-(5-carboxypentyl)-1-naphthylamine **6f** with 8-hydroxyjulolidine (**14**), according to method B. In ethanol solution, the ethoxycarbonylpentyl-substituted naphthoxazinium perchlorate **24g** was obtained, whereas in acetic acid the carboxypentyl-substituted naphthoxazinium perchlorate **24f** was produced instead.

The structures of the naphthoxazinium salts **24**−**30** were confirmed on the basis of elemental-analysis data and by ^{1}H-NMR spectroscopy. In Table 3, ^{1}H-NMR-spectroscopic data for several of the prepared naphthoxazines are presented. The low-field shifts of the protons in the *ortho* positions of the benzo moieties at about $\delta = 8.20-8.90$ are particularly characteristic of these compounds.

As expected, the prepared naphthoxazinium perchlorates are intensely coloured and exhibit a strong fluorescence, the wavelength and intensity of which is somewhat dependent on their substitution pattern. Thus, as can be seen in Table 4, all the prepared naphthoxazinium salts exhibit long-wavelength absorptions between 605 and 670 nm. Similarly, the positions of the fluorescence maxima vary between 645 and 712 nm. The Stokes′ shift between the absorption and emission maxima is, in most cases, rather small, amounting to about 20 nm. Only for the sulfonamido-substituted naphthoxazines **27** and **30** as well as for the alkylene-bridged naphthoxazinium salt **29** does the shift exceed twice this value.

The spectral properties of phenoxazinium salts have been extensively studied by Stuzka et al.[18] and more recently by Drexhage et al.[19] The longest-wavelength absorption maxima of these compounds are found at around 630−660 nm, i.e. at shorter wavelengths than those of the compounds studied here. Evidently, annelation of the phenoxazinium chromophore by a benzo moiety leads to a bathochromic shift of about 30 nm. Remarkably, the completely bridged phenoxazinium salt **31** absorbs at almost the same wavelength as most of the naphthoxazinium salts **24**−**30**, indicating that bridging of the phenoxazine chromophore leads only to a small spectral shift.

The fluorescence intensities collected in Table 4, which are given as relative intensities compared to that of compound **28** (taken as 100%), also merit some comment. In all cases, the intensities are lower than that of the standard **28**, in accordance with the fact that all the studied compounds have an essentially rigid molecular framework, which, as known,[20] prevents non-radiative deactivation processes and thereby gives rise to low fluorescence quantum yields. The moderate quantum yield exhibited by most of the studied naphthoxazinium salts most probably stems from other types of non-radiative deactivation processes, such as the ISC process.

In order to gain a deeper insight into this behaviour, variable-temperature measurements of the fluorescence spectra of some of the naphthoxazinium salts were carried out (see Figure 1). For ease of comparison of the obtained results, the fluorescence intensity of each compound studied was set at 100% at 20°C.

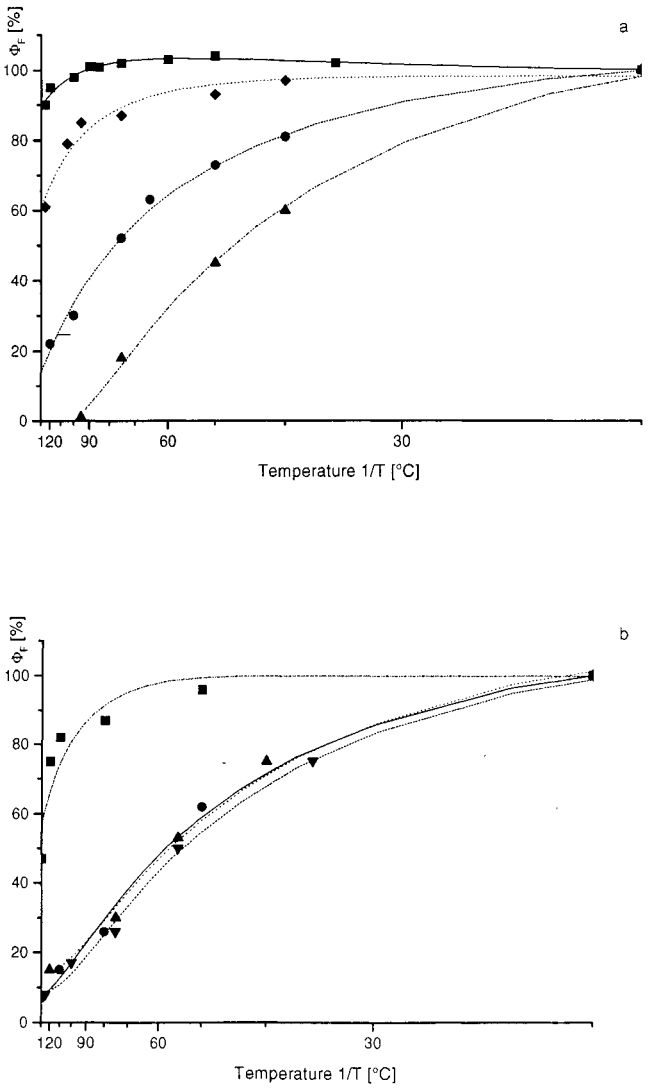
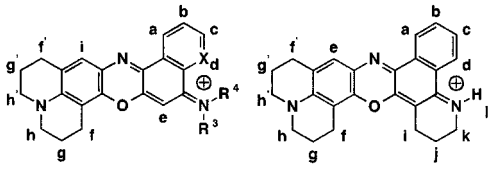


Figure 1. Dependence of the fluorescence intensities of several naphthoxazinium salts plotted against reciprocal temperatue; data measured in dichloromethane; the temperature dependence of the absorption spectra was neglected; $\lambda_{max} = \lambda_{ex}$; Figure 1a, **24d**: filled triangle, **28**: filled rhomb, **24c**: filled circle, **30**: filled square; Figure 1b, **1d**: filled triangle, tip downwards **1c**: filled triangle, tip upwards, **26**: filled circle, **28**: filled square

It can readily be seen that the studied compounds show markedly different temperature dependences of their fluorescence intensities. For the julolidine-bridged naphthoxazinium salts **24c**, **28**, and **30** with an NH group at their naphtho moieties, a rather small dependence is observed in the interval 20−120°C. On the other hand, for the non-bridged naphthoxazinium salts, e.g. for compounds **1d**, **1e**, **26**, and **27**, as well as for the dimethyl- and carboxyalkyl-substituted naphthoxazinium salts **24d**, **24f** and **24g**, much more pronounced temperature dependences are observed. Although some of these compounds have bridged alkylene groups incorporated into their chromophoric systems, their fluorescence intensities decrease significantly with increasing temperature. Clearly, the flexible alkyl groups linked at their



X = CH: 24, X = N: 25 28·$HClO_4$

Table 3. ^{1}H-NMR-spectral data of selected naphthoxazinium perchlorates

Compd.	[a]	[b]	[c]	[a]	[b]	[c]	R^3	[b]	[c]	R^4	[b]	[c]
24b	a	8.27	(d)	e	7.13	(s)	CH_3	3.44	(s)	CH_3	3.44	(s)
	b	7.87	(t)	f	2.91	(m)						
	c	7.73	(t)	g	1.99	(m)						
	d	8.77	(d)	h	3.63	(m)						
				i	7.55	(s)						
24e	a	8.42	(d)	e	7.14	(s)	CH_2	3.92	(t)	H	9.31	(s)
	b	7.90	(t)	f	2.88	(m)	CH_2	3.01	(t)			
	c	7.80	(t)	g	1.98	(m)	CN					
	d	8.73	(d)	h	3.61	(m)						
				i	7.51	(s)						
24f	a	8.41	(d)	e	6.88	(s)	CH_2	3.57	(t)	H	9.37	(s)
	b	7.87	(t)	f	2.83	(m)	$[CH_2]_3$	1.51	(m)			
	c	7.75	(t)	g	1.96	(m)	CH_2	2.26	(t)			
	d	8.63	(d)	h	3.57	(m)	COOH	12.02	(s)			
				i	7.37	(s)						
24g	a	8.43	(d)	e	6.93	(s)	CH_2	3.58	(m)	H	9.38	(s)
	b	7.86	(t)	f	2.87	(m)	$[CH_2]_3$	1.62	(m)			
	c	7.84	(t)	g	1.99	(m)	CH_2	2.33	(t)			
	d	8.68	(d)	h	3.58	(m)	$COOCH_2$	4.04	(q)			
				i	7.42	(s)	CH_3	1.15	(l)			
25	a	8.92	(dd)	e	8.86	(s)	H	8.54	(s)	H	8.54	(s)
	b	7.92	(t)	f	2.82	(m)						
	c	8.99	(dd)	g	1.96	(m)						
	d	7.35	(s)	h	3.60	(m)						
				i	7.35	(s)						
28	a	8.27	(d)	g	1.98	(m)						
	b	7.85	(t)	h	3.52	(m)						
	c	7.75	(t)	i	2.74	(t)						
	d	8.61	(d)	j	1.98	(m)						
	e	7.36	(s)	k	3.66	(t)						
	f	2.83	(m)	l	10.05	(d)						

[a] Assignments in accordance with the given formulae. – [b] Chemical shift in ppm. – [c] Multiplicity.

Table 4. Absorption and emission data of bridged phenoxazinium perchlorates **1** and **24–31** measured in dichloromethane solution

Compd.	R^1	R^2	R^3	R^4	λ_{max} (log ε)	λ_F (Φ_F%)[a]
1a	C_2H_5	C_2H_5	H	H	645 (4.49)	663 (47)
1b	C_2H_5	C_2H_5	CH_3	H	643 (4.98)	665 (42)
1c	C_2H_5	C_2H_5	C_2H_5	H	645 (5.08)	666 (40)
1d	C_2H_5	C_2H_5	CH_3	CH_3	669 (5.09)	687 (35)
24a	–	–	H	H	664 (4.19)	687 (5)
24b	–	–	CH_3	H	667 (5.13)	679 (64)
24c	–	–	C_2H_5	H	668 (5.01)	683 (68)
24d	–	–	CH_3	CH_3	687 (5.21)	701 (65)
24e	–	–	$[CH_2]_2CN$	H	669 (5.03)	688 (52)
24f	–	–	$[CH_2]_5COOH$	H	669 (5.03)	684 (48)
24g	–	–	$[CH_2]_5COOC_2H_5$	H	668 (5.06)	681 (27)
25	–	–	H	H	654 (4.81)	673 (32)
26	C_2H_5	C_2H_5	–	–	605 (4.81)	645 (60)
27	C_2H_5	C_2H_5	–	–	642 (4.92)	668 (51)
28	–	–	–	–	671 (5.25)	688 (100)
29	–	–	–	–	675 (4.84)	712 (35)
30	–	–	–	–	634 (5.35)	677 (42)
31	–	–	–	–	668 (5.35)	677 (42)

[a] Relative quantum yield, referenced to the quantum yield of compound **28** (100%).

chromophoric systems facilitate effective non-radiative processes, thereby diminishing the proportion of radiative processes in the total deactivation cascade. Consequently, the presence or otherwise of non-rigid groups on the naphthalene or benzene moieties of the naphthoxazinium salts is largely irrelevant.

A further interesting observation is the dependence of the absorption and emission properties of the bridged phenoxazinium salts **24**−**31** on the polarity and the pH of the solvent used, especially if there is a free proton on one of their terminal amino groups. Thus, by the addition of bases to solutions of such salts, strong hypsochromic effects, accompanied by partial or complete loss of their fluorescence ability, may be observed. For example, the absorption maximum of the bridged naphthoxazine derivative **28**, which is found at about 670 nm in aqueous ethanol at pH = 4, is shifted to about 500 nm by increasing the pH value to above 9. Hence, the phenoxazinium perchlorates **24**−**31** can also be used as acid-base indicators. Details concerning this feature will be published elsewhere in due course.

Experimental Section

General: Melting points were determined by means of a Boetius heating-table microscope and are uncorrected. − IR spectra were recorded in KBr pellets with a Philips PU 9624 FT-IR spectrometer, while visible and near-infrared spectra were recorded with a Shimadzu UV 3101 spectrophotometer. − NMR spectra were recorded with Varian Gemini 300 or JEOL JNM FX 200 spectrometers, operating at 300 and 200 MHz, respectively (^{1}H). − Fluorescence spectra were measured with a Perkin−Elmer LS 50 B spectrofluorimeter and are corrected. − Elemental analysis data were obtained with a LECO CHNS 932 analyser.

4-Arylazo-1-naphthylamines 18−23. − General Procedure: At 0°C, a solution of the appropriate *p*-chloro- or *p*-nitrophenyldiazonium salt (0.1 mol) in aqueous sulfuric acid was added to a methanolic solution (100 mL) of the appropriate 1-naphthylamine (0.1 mol) under stirring. After 0.5 h, the cooled reaction mixture was neutralized with aqueous ammonia, and the precipitated product was filtered off and recrystallized from *n*-butanol.

Bridged Phenoxazinium Dyes 24−31 and Indaminium Dye 33. − General Procedures; Routes A−C: An ethanolic solution (50 mL) of the appropriate aromatic amine (0.01 mol) and the appropriate 4-nitroso-1-naphthylamine, containing perchloric acid (1.5 mL, 70%), was refluxed for 5 min. After leaving the mixture to stand overnight at room temperature, the product formed was filtered off and recrystallized from nitromethane.

Routes E and F: A mixture of 8-hydroxyjulolidine (**14**) (0.01 mol, 1.9 g) and the appropriate 4-arylazo-1-naphthylamine (0.01 mol), dissolved in DMF (50 mL) containing perchloric acid (1.5 mL, 70%), was refluxed for 5 min. After cooling to room temperature, the reaction mixture was concentrated in vacuo, the product was filtered off, and recrystallized from nitromethane. In some cases it was found necessary to purify the product by column chromatography on silica gel, using acetonitrile as the eluent.

Route G: To a mixture of 8-hydroxyjulolidine (**14**) (0.02 mol, 3.8 g), magnesium perchlorate (0.05 mol, 11.2 g), and acetic anhydride (50 mL), fine-grained sodium nitrite (0.01 mol, 0.70 g) was added under stirring at 20°C. After stirring for a short time, the indaminium perchlorate **33** was precipitated, which, if desired, could be isolated in 54% yield; m.p. 163−165°C. − UV (CH_2Cl_2): λ_{max} (log ε) = 723 nm (4.62). − ^{1}H NMR ([D$_6$]DMSO): δ = 1.89 (m, CH_2, 8 H), 1.90 (s, 6 H, CH_3CO), 2.62 (t, 8 H, CH_2), 3.60 (t, 8 H, NCH_2), 7.10 (s, 2 H, CH). − $C_{28}H_{32}ClN_3O_8$ (574.03): calcd. C 58.59, H 5.62, N 7.32; found C 59.06, H 5.83, N 6.68. − By refluxing the aforementioned reaction mixture for 30 min and then cooling it, crystalline benzoxazinium perchlorate **31** was deposited. It was filtered off and recrystallized from nitromethane; yield 80%, m.p. > 360°C. − ^{1}H NMR ([D$_6$]DMSO): δ = 1.95 (m, 8 H, CH_2), 2.82 (m, 8 H, CH_2), 3.57 (m, 8 H, NCH_2), 7.35 (s, 2 H, CH). − $C_{24}H_{26}ClN_3O_5$ (471.94): calcd. C 61.08, H 5.55, N 8.90; found C 60.86, H 5.92, N 8.86.

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