Dyes and Pigments, Vol. 28, No. 2, pp. 91–99, 1995

0143-7208/95 $9.50 + 0.00

ELSEVIER

0143-7208(95)00006-2

Absorption Spectra of some *N*-Substituted-1,8-Naphthalimides

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(Received 15 November 1994; accepted 20 December 1994)

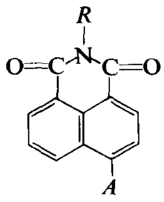
ABSTRACT

FT-IR and UV/VIS spectral data of some derivatives of N*-substituted-1,8-naphthalimides are presented, and substituent effects on their spectral properties are discussed.*

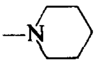
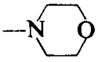
1 INTRODUCTION

Derivatives of 1,8-naphthalimides are of interest in view of their use as fluorescent dyes, laser active media, solar energy collectors, etc. We report in this paper the FT-IR and UV/VIS spectra of some *N*-substituted-1,8-naphthalimides and the influence of substituents on their absorption spectra. All compounds were synthesised by condensation of 4-bromo-1,8-naphthalic anhydride and the corresponding primary amine, followed by replacement of the bromo substituent by the appropriate amines.[1]

The dyes studied were of general formula:



I

Dye	*R*	Dye	*R*	*A*
1	$—CH_2CH_3$	**2**	$—CH(CH_3)_2$	$—NH_2$
3	$—CH_2CH_2OH$	**4**	$—CH_2CH_2Ph$	$—NH_2$
3a	$—CH_2CH_2OH$	**4a**	$—CH_2CH_2Ph$	$—NHCH_3$
3b	$—CH_2CH_2OH$	**4b**	$—CH_2CH_2Ph$	$—NHC_2H_5$
3c	$—CH_2CH_2OH$	**4c**	$—CH_2CH_2Ph$	$—NHCH_2CH_2Ph$
3d	$—CH_2CH_2OH$	**4d**	$—CH_2CH_2Ph$	
3e	$—CH_2CH_2OH$	**4e**	$—CH_2CH_2Ph$	

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2 EXPERIMENTAL

IR spectra (KBr) were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Electronic spectra (in chloroform and methanol) were measured at room temperature using a Hewlett-Packard UV/VIS 8452A spectrophotometer. The dye concentration was $4{\cdot}76 - 8{\cdot}3 \times 10^{-5}$ mol l^{-3}.

3 RESULTS AND DISCUSSION

3.1 FT-IR spectra

Stretching vibrations of the main functional groups of the dyes are listed in Table 1; because of the complexity of the spectra, deformation vibrations are not given.

All compounds containing a hydroxyl group (R = CH_2CH_2OH) showed sharp absorption bands for ν_{OH} in the range 3540–3400 cm^{-1} and for ν_{CO} in the range 1055–1047 cm^{-1}. Stretching vibrations of the primary and secondary amino groups occurred in the range 3390–3219 cm^{-1}.

The position of $\nu_{C=O}$ was of interest since it has been reported that the nature of the *N*-substituent group in the imide ring affects the position of $\nu_{C=O(str.)}$ by mesomeric and inductive effects.[2] In this present case, dyes **1**, **2** and **4** did not show any significant difference in the position of the carbonyl bands; $\nu_{C=O(str.)}$ of dye **3**, however, was shifted to a lower

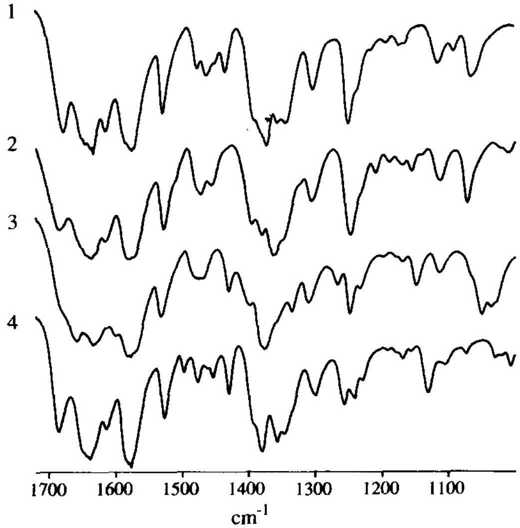


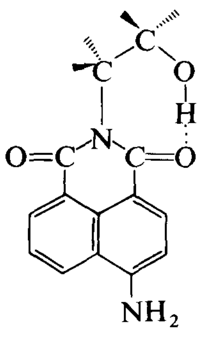
Fig. 1. FT-IR spectra of dyes **1**, **2**, **3** and **4**.

TABLE 1

IR Absorption (cm^{-1}) of Dyes **1**–**4e**

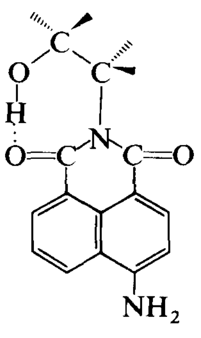
Dye	ν_{OH}	ν_{NH}	$\nu_{CH(arom.)}$	$\nu_{CH(aliph.)}$	$\nu^{s}_{C=O}$	$\nu^{as}_{C=O}$	$\nu_{CC(arom.)}$	$\nu_{CN(imide)}$	$\nu_{CO(alk.)}$
1	—	3358	3051	2976	1686[a]	1651[a]	1613	1372	—
		3250		2935	1676	1632	1574		
2	—	3359	3064	2970	1684	1652[a]	1614	1379	—
		3246		2933	1678[a]	1636	1578		
3	3538	3363	3050	2965	1665[a]	1647[a]	1600	1375	1048
		3219		2893	1657	1633	1576		
4	—	3354	3064	2957	1694[a]	1650[a]	1614	1379	—
		3244	3026	2935	1685	1638	1576		
				2863			1496		
3a	3448	3392	3068	2950	1682[a]	1652[a]	1613	1375	1053
				2877	1669	1634	1576		
							1497		
4a	—	3384	3081	2961	1698	1659	1614	1353	—
			3060	2936	1684	1636	1583		
			3021	2842			1498		
3b	3402	3337	3090	2970	1696	1664	1616	1369	1055
				2888	1684	1634	1586		
							1506		
4b	—	3376	3060	2961	1698	1659	1615	1376	—
			3025	2927	1684	1636	1587		
				2836			1498		
3c	3410	3372	3060	2965	1688[a]	1651	1614	1399	1047
				2923	1679	1639	1579		
				2893			1501		
				2807					
4c	—	3380	3060	2957	1699[a]	1660[a]	1616	1394	—
			3026	2927	1685	1638	1582		
				2855			1496		
3d	3414	—	3060	2940	1696	1650	1615	1376	1047
				2853	1687[a]	1640	1588		
				2808			1572		
4d	—	—	3056	2961	1699[a]	1660[a]	1614	1383	—
			3026	2936	1689	1651	1587		
				2846			1573		
				2825			1513		
3e	3461	—	3064	2965	1693	1652	1616	1375	1051
				2882	1686[a]	1641[a]	1588		
				2863			1514		
				2812					
4e	—	—	3056	2962	1698[a]	1658	1613	1385	—
			3026	2927	1690	1647	1588		
				2889			1514		
				2846			1493		

[a] Computed derivative.



II

or

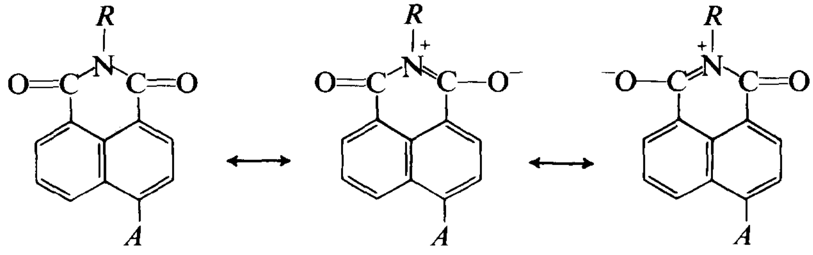


III

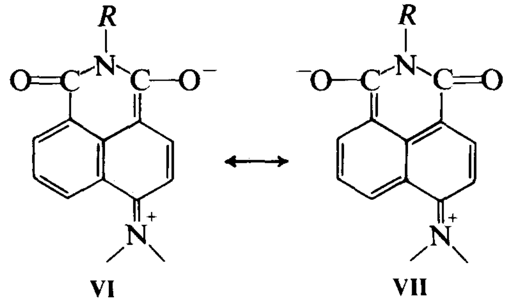
frequency (by about 30 cm^{-1}) compared with dyes **1**, **2** and **4**. FT-IR spectra of dyes **1**–**4** are given in Fig. 1. The essential difference between $\nu_{C=O(str.)}$ of dye **3** compared with the other dyes cannot be explained solely in terms of the inductive effect since the hydroxy group cannot significantly affect $\nu_{C=O(str.)}$ in view of the distance between the two groups.

It is therefore proposed that formation of an intramolecular hydrogen bond between the H atom of the OH group and the ketonic oxygen atom occurs. The CH_2CH_2OH group has unlimited conformational freedom and formation of a 7-membered ring system is not, therefore, precluded. The resultant hydrogen bond causes a reduction of the force constant of the C=O bond and hence a lower stretching frequency.[3] Structure **II** is more probable than structure **III**, because the electron donating amino group in the naphthalene ring increases to a greater extent the polarization of the C=O group attached to the same ring.

In order to determine whether dye **3** forms intra- or intermolecular H-bonds, IR spectra in chloroform solutions of increasing dilution were recorded. Changes in the concentration of dye **3** did not lead to any change in the position and intensity of $\nu_{C=O}$ and ν_{OH}, which implies that the hydrogen bond is intramolecular. The presence of an intramolecular H-bond correlates well with UV/VIS spectral behaviour of the dyes.



IV V



It is well known that imides give rise to two C=O (str.) absorptions, namely ν_{anti} and ν_{symm} (around 1600–1700 cm^{-1}), with a separation of about 60 cm^{-1} due to imide resonance (structures IV and V). The high-frequency band in this case is the symmetric C=O (str.).[4]

On the other hand, the presence of a strong electron donating substituent in 4-amino-1,8-naphthalimides, conjugated with the carbonyl groups, gives the delocalisation structures VI and VII.[5]

In the spectra of most of the dyes studied (Fig. 2) it can be seen that ν_{anti} and ν_{symm} each appear as a doublet, giving 4 bands for the C=O groups in the range 1699–1634 cm^{-1}. This can be explained in terms of the possible resonance structures IV, V, VI and VII. First and second derivative spectra were determined in order to determine the overlapping peak in cases when some of a $\nu_{C=O(str.)}$ were masked. The $\nu_{C=O(str.)}$ indicated in Table 1 were determined by calculating mathematical deriva-

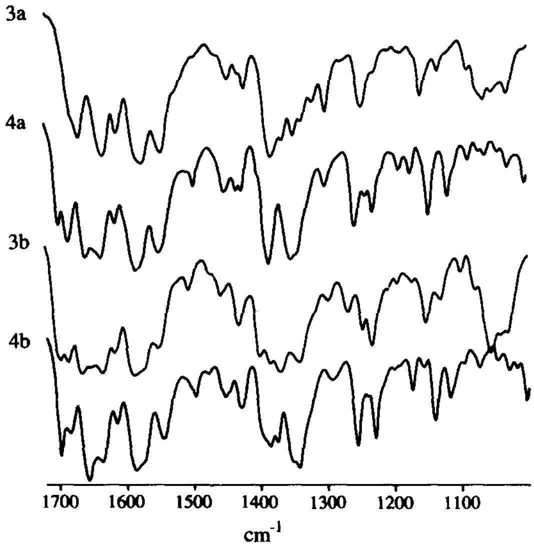


Fig. 2. FT-IR spectra of some analogous dyes from series 3 and 4.

tives. The separations between ν_{anti} and ν_{symm} were about 32–62 cm^{-1}. In all cases, when analogous dyes from series **3** and **4** were compared, $\nu_{C=O(str.)}$ for series **3** appeared at lower frequency than for series **4**. The nature of substituent A in the dyes did not influence $\nu_{C=O(str.)}$ in any definite direction.

Stretching vibrations of the naphthalene ring appeared in the range 3050–3080 cm^{-1} for ν_{CH} and 1500–1616 cm^{-1} for ν_{CC}. Additional absorption bands for ν_{CH} at ~3020 cm^{-1} were apparent for compounds containing a phenyl ring as substituent.

3.2 UV/VIS spectral data

Values of λ_{max} and log ε_{max} of the dyes in chloroform and methanol are listed in Table 2. An important characteristic of the dyes is the oscillator strength. Values of the oscillator strength (f) were calculated using the following formula:[6]

$$f = 4{\cdot}32 \times 10^{-9}\, \Delta\nu_{1/2}\varepsilon_{max}$$

where $\Delta\nu_{1/2}$ is the width of the absorption band in cm^{-1} at $\varepsilon_{max}/2$.

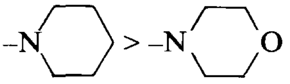
The ratio

$$B_f = \frac{\alpha_{max}}{\alpha_{vis}}$$

was used as a brightness index of the dyes (B_f) where α_{max} is the maximum optical density and α_{vis} is the area below the absorption curve.[7]

In chloroform, λ_{max} in the visible region for the dyes was in the range 396–430 nm, while in methanol it was 392–440 nm. A bathochromic shift of the $\pi \rightarrow \pi^*$ and CT absorption bands was observed between chloroform and the more polar methanol, while $p \rightarrow \pi^*$ bands were slightly hypsochromically shifted or at the same wavelength.

With respect to the substituent A, the dyes were bathochromically shifted in the order:

$-NHC_2H_5 \geq -NHCH_2CH_2Ph \geq -NHCH_3 > -NH_2 >$ 

A bathochromic shift with an increase in the electron donor properties of A was observed with the acyclic amines; the strong hypsochromic effect of the piperidine and morpholine ring has been explained by Peters and Bide in terms of steric inhibition of resonance.[5]

Comparing the absorption maxima of analogous dyes from series **3** (R=CH_2CH_2OH) and series **4** (R=CH_2CH_2Ph), it can be seen that dyes

TABLE 2
UV/VIS Spectroscopic Data for Dyes **1**–**4e**

Dye	*CHCl$_3$*					*CH$_3$OH*				
	λ_{max} (*nm*)	*log* ε	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)	*f*	B_f	λ_{max} (*nm*)	*log* ε	$\Delta\nu_{1/2}$ (*cm*$^{-1}$)	*f*	B_f
1	262	4·385				262	4·082			
						276	4·046			
	416	4·123	4275	0·245	4·51	434	3·930	4142	0·152	4·66
2	260	4·159				258	4·394			
	288	4·077								
	402	4·292	4922	0·417	3·70	430	4·117	4674	0·264	3·90
3	258	4·510				258	4·108			
	412	4·237	4359	0·325	4·15	432	3·853	4050	0·125	4·46
4	262	4·630				260	4·209			
	408	4·301	4521	0·390	3·24	430	4·107	4319	0·239	2·39
3a	262	4·357				260	4·231			
	278	4·308				280	4·198			
	430	4·155	3912	0·241	4·39	436	4·125	3758	0·216	4·56
4a	264	4·276				260	4·324			
	288	4·171				284	4·347			
	344	4·226				340	4·026			
	424	4·356	4235	0·415	3·30	440	4·248	3734	0·286	3·60
3b	282	4·086				258	4·247			
	346	4·152				282	4·223			
	362	4·091				340	4·047			
	430	4·043	3655	0·175	4·45	432	4·025	3696	0·169	4·14
4b	344	4·702				284	4·387			
	358	4·635				342	4·367			
	428	4·518	3902	0·556	3·45	440	4·248	3718	0·284	3·62
3c	260	4·449				258	4·236			
	282	4·389				282	4·226			
	430	4·380	4089	0·423	3·14	440	4·149	3628	0·221	3·54
4c	262	4·373				262	4·477			
	288	4·330				284	4·504			
	344	4·386				340	4·134			
	426	4·618	3771	0·676	1·72	440	4·374	3868	0·395	2·85
3d	262	4·217				342	3·999			
	288	4·084				356	3·983			
	416	4·269	4472	0·359	3·19	408	4·137	4555	0·269	3·14
4d	260	4·544				324	4·819			
	344	4·388				342	4·391			
	410	4·403	4346	0·474	2·77	410	4·274	4903	0·398	2·45
3e	262	4·173				252	4·283			
	288	4·016								
	344	4·163								
	396	4·355	6438	0·629	2·21	392	4·089	4913	0·261	2·88
4e	240	4·874				256	4·432			
	256	4·770				340	4·010			
	398	4·607	4785	0·837	2·51	402	4·294	5457	0·464	2·20

3 are the more bathochromic in chloroform, but that in methanol dyes from series **4** are the more bathochromic. This can be explained by the fact that in chloroform, dyes containing the CH_2CH_2OH group may form an intramolecular hydrogen bond only, while in methanol an intermolecular H-bond with the solvent is possible. The longest wavelength absorption band is due to the intramolecular charge transfer from the electron donating substituent *A* towards the carbonyl groups from the imide ring. The presence of an intramolecular H-bond causes additional polarization of the carbonyl group, which is the reason for the bathochromic and hypochromic effect of dyes **3–3e** in chloroform. The cyclisation also causes a bathochromic shift, with attendant decrease in intensity.

The value of the oscillator strength varies from 0·175 to 0·837 in chloroform and from 0·169 to 0·464 in methanol. For all dyes the calculated value in methanol is lower than in chloroform. This is due to the hypochromic effect of methanol. The data in Table 2 show that dyes **3–3e** have lower values for the oscillator strength than the analogous dyes **4–4e**, probably due to the intramolecular H-bond. The lower dye strength of dyes **3** is compensated for by their higher brightness. The higher lightness of colour of dyes containing the CH_2CH_2OH group has also been established from their CIELAB coordinates L^*, measured on dyed polyamide fabrics.[1]

The value of the brightness index varies from 2·20 to 4·50, which indicates that the dyes studied have pure and bright colours; in spite of their broad absorption bands ($\Delta\nu_{1/2} = 3700-4500\ \mathrm{cm^{-1}}$), the dyes are bright because of their fluorescence.

3 CONCLUSIONS

Absorption spectral data show that in 1,8-naphthalimides, in which the N-imide atom is substituted with an CH_2CH_2OH group, an intramolecular hydrogen bond with the ketonic oxygen is formed. This H-bond significantly affects the spectral properties of these compounds.

N-substituted-1,8-naphthalimides containing primary, secondary or tertiary N atoms at the 4-position in the naphthalene ring show four $\nu_{C=O(str.)}$ absorption bands due to the four possible resonance structures.

ACKNOWLEDGEMENT

The authors thank Professor Dr B. Aleksiev for helpful comments.

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