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Synthesis and absorption properties of some new bis-1,8-naphthalimides

Ivo Grabchev [a,*], Christo Petkov [b], Vladimir Bojinov [c]

[a] *Institute of Polymers, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria*
[b] *Institute of Organic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria*
[c] *University of Chemical Technology and Metallurgy, BG-1756 Sofia, Bulgaria*

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Abstract

A series of new bis-1,8-naphthalimide derivatives has been synthesized and the FT-IR and UV/vis absorption characteristics discussed. Substituents effect on the IR spectral characteristics have been investigated. A new polyimide with a 1,8-naphthalimide unit main chain has been synthesized. © 2001 Published by Elsevier Science Ltd.

Keywords: bis-1,8-Naphthalimides; bis-Fluorophores; Polyimide; FT-IR spectroscopy

1. Introduction

During recent years, 4-substituted-1,8-naphthalimide derivatives have aroused scientific interest because of their potential use as polymerizable fluorophores for synthetic polymers. A series of fluorescent polymerizable 1,8-naphthalimides [1–5] were synthesised and their ability to co-polymerize with styrene, methyl methacrylate or acrylonitrile, obtaining copolymers with intensive fluorescence [6–11] was studied. Recently, 1,8-naphthalimide dyes have been examined with regards their use in nematic liquid crystals for guest-host type electro-optical displays [12,13].

Fluorescent 1,8-naphthalimide derivatives are very interesting in view of their usage as fluorescent dyes for solar energy collectors [14], organic light-emitting diodes [15], markers in molecular biology [16], in laser active media [17,18], in medicine as antitumours [19] and as analgetics [20]. Recently, some 3-brominated compounds of 1,8-naphthalimides have been proposed for the photoinactivation of HIV [21].

The present work concerns the synthesis of new bis-fluorophores that have different substituents at the C-4 position in the 1,8-naphthalimide structure; some of their absorption properties are also investigated.

2. Results and discussion

2.1. Synthesis of bis-naphthalimides

The synthetic route to obtaining diimides **2** is presented in Scheme 1.

* Corresponding author. Fax: +359-2-70-75-23.
E-mail address: grabchev@polymer.bas.bg (I. Grabchev).

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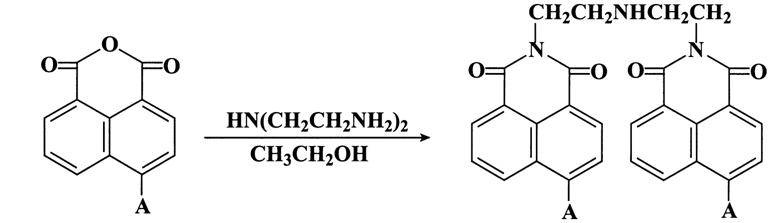


1 2

were A are: H (**a**), Cl (**b**), NO_2 (**c**).

Scheme 1.

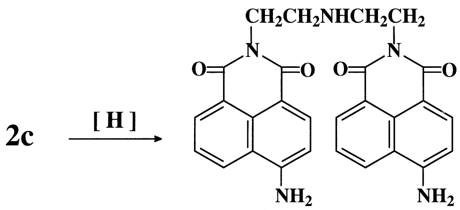
The 4-substituted-1,8-naphthalic anhydrides **1** have been used as conventional starting material for the preparation of diimides. Compounds **2a–c** were synthesized by condensation of the 1,8-naphthalic anhydrides and diethylenetriamine in boiling ethanol solution. The formation of bis-fluorophores **2a–c** followed all reactions described, as a result of the diethylenetriamine double acylation with the naphthalic anhydride derivatives **1.**

Scheme 2 shows the reduction of the nitro groups in **2c** compound with an anhydrous stannous chloride in 35% aq hydrochloric acid solution [22], yielding the dye **2d**, respectively.

Scheme 3 shows the nucleophylic substitution of the nitro group in **2c** with the amino group NR_1R_2. The reaction proceeds between dimethylamino (dye **2e**) or butylamino (dye **2f**) in *N,N*-dimethylformamide for 24 h at room temperature [13]. In this case, the electron accepting naphthalimide carbonyl group favours the nucleophilic substitution of the nitro group with the aliphatic amines HNR_1R_2.

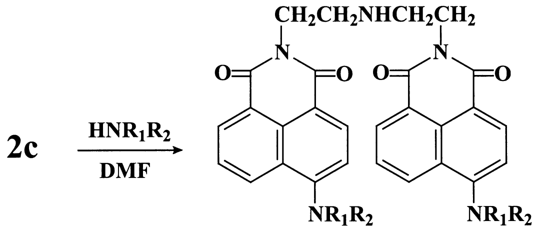
2.2. *Synthesis of polyimide* 3

Polyimide **3** was prepared by the nucleophilic substitution polymerization of **2c** with diethylenetriamine, using *N,N*-dimethylformamide as a solvent at room temperature for 24 h (Scheme 4), following a route similar to that used for compounds **2e** and **2f**.



2d

Scheme 2.



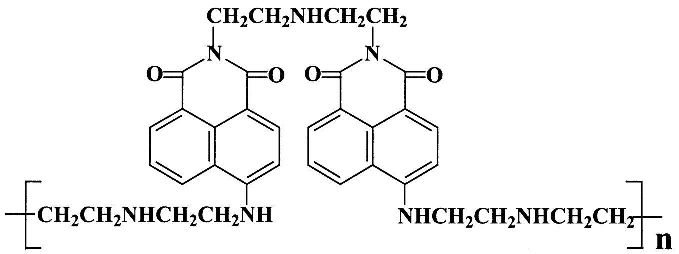
	R_1	R_2
2e	CH_3	CH_3
2f	H	$CH_2CH_2CH_2CH_3$

Scheme 3.

2.3. *IR and UV/vis absorption data*

2.3.1. *IR absorption data*

Compounds **2a–2f**, which contained an amino group (–NH), showed absorption bands in the 3378–3513 cm^{-1} region. The bands at 3065–3077 cm^{-1} can be assigned to stretching C–H vibrations and bands at 1617–1625 cm^{-1} and 1578–1590 cm^{-1}, assigned to stretching C–C vibrations. These are characteristic of the aromatic system in the naphthalene ring of the naphthalimide structure. The bands at 774–781 cm^{-1} are characteristic of aromatic ring deformation vibrations. It is well known that imides give rise to both frequency bands of the C=O absorption [23,24]. The IR spectra of compounds **2a–2f** show intensive absorption bands at 1682–1705 cm^{-1} and 1635–1664 cm^{-1}, respectively, which are characteristic of symmetrical



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Scheme 4.

and asymmetrical carbonyl group vibrations, the shift between the two bands is about 40–43 cm^{-1} depending on the compounds. The absorption bands in the 1346–1385 cm^{-1} region are characteristic for the imide C–N–C bonds for all **2a**–**2f** compounds. Compounds **2c**, containing a nitro group, possessed absorption bands at 1343 cm^{-1} for the symmetrical vibrations and at 1528 cm^{-1} for the asymmetrical vibrations of the nitro groups. The stretching vibrations of the primary amino groups in **2d** appear in the range 3240–3351 cm^{-1}. The intensive bands at 1362 and 1455 cm^{-1} in **2e** are characteristic of the CH_3 groups.

Table 1 summarizes the data obtained for infrared C=O stretching vibration for the 1,8-naphthalimides **2a**–**2f** and the Hammett σ substituent constants, corresponding to the substituents *A* [25].

The data in Table 1 show that the position of the frequencies corresponding to the C=O groups depends on the nature of the substituent *A* at a C-4 position of the naphthalene ring.

Fig. 1 shows the dependence of the two C=O frequency bands of compounds **2a**–**2e** on the Hammett

Table 1
Infrared stretching vibration ν C=O and Hammett substituent constants σ for 4-substituted-1,8-naphthalimides

Compounds	A	ν^s C=O (cm^{-1})	ν^{as} C=O (cm^{-1})	σ
2a	H	1661	1698	0
2b	Cl	1660	1702	0.23
2c	NO_2	1664	1705	0.78
2d	NH_2	1645	1685	−0.66
2e	$N(CH_3)_2$	1648	1688	−0.60
2f	NHC_4H_9	1639	1682	–

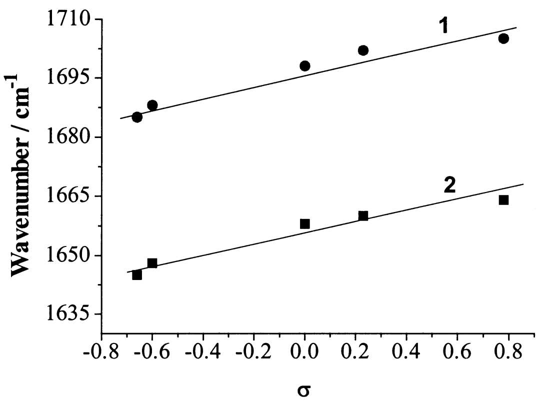

Fig. 1. Relationship between ν^s (1) and ν^{as} (2) C=O stretching vibrations and Hammett substituent constants for 1,8-naphthalimides.

constants, a linear correlation is obtained. The analytical form of the dependence upon the Hammett constants is given by Eqs. (1) and (2):

$$\nu^s(\mathrm{cm}^{-1}) = 1655 + 13.13\sigma \quad (1)$$

$$\nu^{as}(\mathrm{cm}^{-1}) = 1696 + 14.09\sigma. \quad (2)$$

which were derived using a least squares method with a correlation coefficient $R = 0.97$, S.D. = 2.22–2.46 cm^{-1} and $N = 5$ for both C=O groups.

The IR spectrum of polyimide **3** shows peaks similar to those of monomer **2c**, especially the peaks characteristic for the aromatic structure. The carbonyl group vibrations in the monomeric units **2c** are shifted with respect to the characteristic C=O vibrations for polyimide **3** with a difference $\Delta\nu = 28$ cm^{-1}. Fig. 2 shows the difference in the IR spectra for **2c** and polyimide **3** in the 1450–1750

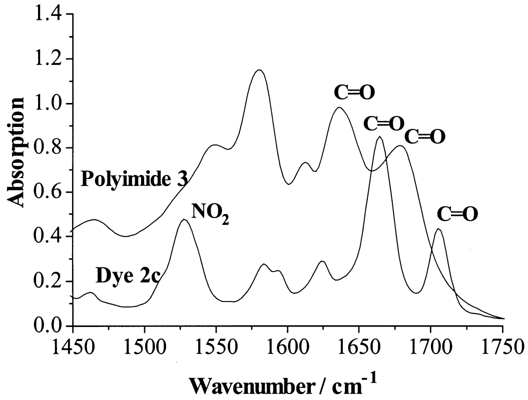

Fig. 2. FT-IR spectra of polyimide **3** and dye **2c** in KBr.

cm^{-1} region. The absorption of the carbonyl groups in **2c** exhibits a blue shift with respect to that in polyimide **3**. However, the polyimide **3** does not contain the peak at 1528 cm^{-1} that is characteristic for the nitro group. These two facts suggest the formation of a high molecular mass polyimide.

2.3.2. UV/vis absorption data

The UV/vis absorption properties of the 1,8-naphthalimide derivatives are related to the polarization of the naphthalimide molecule. Irradiation provokes an electron donor–acceptor interaction between the C-4 substituents and the carbonyl groups of the imide chromophorous system structure. This process could be also influenced by the environmental effect of the media upon this interaction.

The absorption spectra of compounds **2a**–**2f** were recorded in methanolic solution. A comparison of the absorption spectra reveals the strong influence of polarization on spectral properties. The absorption maxima for compounds **2a**–**2c** are in the UV region at $\lambda_A = 322-344$ nm due to the electron-accepting nature of the substituents *A*. Exchange of the electron-accepting nitro group by the electron-donating amino groups leads to a large bathochromic shift of the absorption maxima in the visible region. As a consequence of molecular polarization that results in donor–acceptor interaction between the carbonyl and amino groups, an additional broad absorption band, bathochromically shifted from compound **2c**, appeared. The absorption maxima are at $\lambda_A = 432$ nm for dye **2d**, $\lambda_A = 422$ nm for dye **2e** and $\lambda_A = 440$ nm for dye **2f**, respectively. This is attributable to intermolecular electron charge transfer from the unbound electron pair of the nitrogen atom at C-4 position towards the electron accepting carbonyl groups.

The basic photo-physical characteristics of compounds **2a**–**2f** and polyimide **3** in different solvents will be discussed in another paper.

3. Experimental

3.1. Materials

Commercial 1,8-naphthalic anhydride (Aldrich) and 4-cloro-1,8-naphthalic anhydride (Aldrich) were used. 4-Nitro-1,8-naphthalic anhydride was obtained according to the described method [16].

*3.1.1. Synthesis of bis(N-ethyl-1,8-naphthalimide)amine **2a***

A 0.01 M diethylenetriamine sample was added to 0.02 M 1,8-naphthalic anhydride in 50 cm^3 of absolute ethanol and heated at reflux for 2 h. After cooling to room temperature, the precipitate was filtered and washed with ether, dried and crystallized with ethanol. Yield: 98%, m.p. 238–240°C. FT-IR (KBr) cm^{-1}: 3513, 2961, 2902, 2840, 1698, 1658, 1590, 1385, 1237, 778. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 2.94$ (t, 4H, $2\times CH_2\underline{CH_2}NH$); 3,88 (t, 4H, $2\times NCH_2\underline{CH_2}NH$); 6.48 (br. s, 1H, NH); 7.64–8.66 (m, 6H, ArH). Anal. Calcd. for $C_{28}H_{21}N_3O_4$ (463.1) N 9.07%, Found N 9.18%.

*3.1.2. Synthesis of bis(4-chloro-N-ethyl-1,8-naphthalimide)amine **2b***

A 0.01 M diethylenetriamine sample was added to 0.02 M 4-chloro-1,8-naphthalic anhydride in 50 cm^3 of absolute ethanol and heated at reflux for 30 min. After cooling to room temperature, the precipitate was filtered and washed with ether, dried and crystallized with ethanol. Yield: 96%, m.p. 217–220°C. FT-IR (KBr) cm^{-1}: 3445, 2961, 2921, 2828, 1702, 1660, 1589, 1346, 1235, 781. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 2.96$ (t, 4H, $2\times CH_2\underline{CH_2}$ NH); 3.90 (t, 4H, $2\times N\underline{CH_2}CH_2NH$); 6.72 (br. s, 1H, NH); 7.88–8.62 (m, 5H, ArH). Anal. Calcd. for $C_{28}H_{20}N_3O_4Cl$ (497.6) N 8.44%, Found N 8.51%.

3.1.3. Synthesis of bis(4-nitro-N-ethyl-1,8-naphthalimide)amine **2c**

A 0.01 M diethylenetriamine sample was added to 0.02 M 4-nitro-1,8-naphthalic anhydride in 50 cm^3 of absolute ethanol and refluxed for 1 h. After cooling to room temperature, the precipitate was filtered and washed with ether, dried and crystallized with ethanol. Yield: 96%, m.p. 186–189°C. FT-IR (KBr) cm^{-1}: 3442, 2961, 2924, 2841, 1705, 1664, 1583, 1343, 1232, 786. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 2.98$ (t, 4H, 2×$CH_2\underline{CH_2}NH$); 3.92 (t, 4H, 2×$N\underline{CH_2}CH_2NH$); 6.84 (br. s, 1H, NH); 7.92–8.84 (m, 5H, ArH). Anal. Calcd. for $C_{28}H_{20}N_5O_8$ (554.1) N 12.63%, Found N 12.79%.

3.1.4. Synthesis of bis(4-amino-N-ethyl-1,8-naphthalimide)amine **2d**

Anhydrous stannous chloride (0.03 M) was slowly added at 60°C over 1 h to a suspension of bis(4-nitro-*N*-ethyl-1,8-naphthalimide)amine (**2c**) (0.01 M) in 30 ml 35% aq. hydrochloric acid solution. The precipitated stannic salt of the **2d** was filtered, washed and dried. Yield: 49%, m.p. >300°C. FT-IR (KBr) cm^{-1}: 3351, 2962, 2854, 1685, 1645, 1578, 1371, 1246, 774. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 2.58$ (s, 6H, CH_3); 2.90 (t, 4H, 2× $NCH_2\underline{CH_2}NH$); 3.84 (t, 4H, 2×$N\underline{CH_2}CH_2NH$); 6.76 (br. s, 1H, NH); 6.94–8.22 (m, 5H, ArH). Anal. Calcd. for $C_{30}H_{26}N_5O_4$ (520.1) N 13.46%, Found N 13.58%.

3.1.5. Synthesis of bis(4-dimethylamino-N-ethyl-1,8-naphthalimide)amine **2e**

A 0.03 M dimethylamine was added to 0.01 M bis(4-nitro-*N*-ethyl-1,8-naphthalimide)amine (**2c**) dissolved in 60 cm^3 *N,N*-dimethylformamide at room temperature. After 24 h, 600 cm^3 of water were added and the precipitate was filtered off and washed with water and then dried in a vacuum at 40°C. Yield: 84%, m.p. 188–191°C. FT-IR (KBr) cm^{-1}: 3365, 2952, 2842, 1688, 1646, 1582, 1362, 1244, 781. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 0.94$ (t, 3H, CH_3); 1.40–1.62 (m, 4H, $\underline{CH_2CH_2}CH_3$); 2.96 (t, 4H, 2×$NCH_2\underline{CH_2}NH$); 3.22 (t, 4H, ArNH CH_2); 3.92 (t, 4H, 2×$N\underline{CH_2}CH_2NH$); 5.60 (br. s, 1H, ArNH); 6.52 (br. s, 1H, NH); 6.98–8.60 (m, 5H, ArH). Anal. Calcd. for $C_{32}H_{40}N_5O_4$ (558.2) N 12.54%, Found N 12.67%.

3.1.6. Synthesis of bis(4-butylamino-N-ethyl-1,8-naphthalimide)amine **2f**

Dye **2f** was synthesized following the procedure described for dyes **2e**, using butylamine. Yield: 86%, m.p.121–124°C. FT-IR (KBr) cm^{-1}: 3378, 2956, 2930, 2868, 1682, 1639, 1580, 1361, 1246, 774. ^{1}H-NMR (DMSO-d_6, 100 mHz) $\delta = 2.92$ (t, 4H, 2×$NCH_2\underline{CH_2}NH$); 3.88 (t, 4H, 2×$N\underline{CH_2}$ CH_2NH); 5.26 (br. s, 2H, $ArNH_2$); 6.30 (br. s, 1H, NH); 7.12–8.28 (m, 5H, ArH). Anal. Calcd. for $C_{28}H_{24}N_5O_4$ (494.1) N 14.17%, Found N 14.12%.

3.1.7. Synthesis of polyimide **3**

0.01 M of **2c** and 0.01 M of diethylenetriamine were placed in 50 cm^3 of *N,N*-dimethylformamide. The mixture was stirred at room temperature for 24 h. After that the solution was precipitated with 200 cm^3 of water and the precipitate filtered. Yield: 83%, m.p. <300°C. FT-IR (KBr) cm^{-1}: 3305, 2952, 2853, 1678, 1636, 1580, 1363, 1246, 773.

3.2. Characterization

IR spectra were measured on a Bruker IFS-113v spectrometer at 2 cm^{-1} resolution using KBr pellets. ^{1}H-NMR spectra were recorded on a JEOL JNM-PS spectrometer, operating at 100 MHz in d_6-DMSO and using TMS as an internal standard (chemical shifts δ in ppm). The electronic spectra of the dyes in methanol were recorded on a Hewlett Packard 8452A spectrophotometer with 2 nm resolution at room temperature.

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