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Synthesis and spectral-luminescent characteristics of *N*-substituted 1,8-naphthalimides

Oleg V. Prezhdo [a], Boris V. Uspenskii [b], Victor V. Prezhdo [c,*], Wojciech Boszczyk [c], Vitalii B. Distanov [b]

[a] *Department of Chemistry, University of Washington, Seattle, WA 98915-1700, USA*
[b] *Department of Organic Chemistry, Kharkov Polytechnic Institute, 21 Frunze Street, 61002 Kharkov, Ukraine*
[c] *Institute of Chemistry, Jan Kochanowski University, 5 Chęcińska Street, 25-020 Kielce, Poland*

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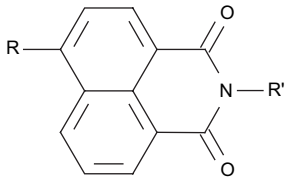
Abstract

A series of *N*-substituted 1,8-naphthalimides has been synthesized. The absorption and fluorescence spectra of the synthesized compounds show absorption in the 328–333 nm and 338–347 nm ranges and emission in the 358–391 nm range, depending on the solvent. The effect of substituents on the electronic spectra has been studied both experimentally and by electronic structure calculations. Introduction of the OH radical into the *N*-alkyl group does not increase the luminescence quantum yield, as may be expected based on the previous study with 2,5-diarylthiazoles [Tetrahedron Lett 2004;45:5291]. Only *N*-(1,1-dihydroxymethyl-2-hydroxy)ethyl 1,8-naphthalimide with three OH substituents shows an increased quantum yield, which is attributed to intramolecular H-bond.

Keywords: Organic luminophores; Luminescence; *N*-substituted 1,8-naphthalimides; Absorption spectra; Intramolecular hydrogen bond; Fluorescence quantum yield

1. Introduction

N-substituted 1,8-naphthalimides find a wide range of applications as organic dyes and luminophores [1–6]. The effects of substituents on the photophysical properties of these compounds [7] and their molecular structure are actively investigated for the qualitative and quantitative structure–spectra relationships [8–11]. Owing to the photophysical properties of these compounds new fluorescent copolymers with 1,8-naphthalimide side chains were synthesized [11–13] and used as chemosensors of metal cations and protons [14–17], as stabilizators of polymer materials [18], in liquid crystal systems [19,20]. The naphthalimides show strong absorption in the visible range [21,22].



R' = CH_3 (**1**), Ph (**2**), R = H(**a**), NMe_2 (**b**)

The singlet (S) and triplet (T) electronic transitions of imide **1a** in ethanol occur at the following wavelengths: $\lambda_{max}(S_1^{\pi\pi^*}) = 356$ nm, $\lambda_{max}(S^{n\pi^*}) = 314$ nm, $\lambda_{max}(T_1^{\pi\pi^*}) = 540$ nm, and $\lambda_{max}(T^{n\pi^*}) = 336$ nm [21]. The corresponding transitions in toluene are centered at 346, 314, 540, and 337 nm [22]. Of particular interest are the transitions involving the singlet states, since they are responsible for fluorescence. The imides under study fluoresce at room temperature. The fluorescence quantum yields show considerable solvent

* Corresponding author. Tel.: +48 81 361 4012; fax: +48 41 361 4942.
E-mail address: victor@pu.kielce.pl (V.V. Prezhdo).

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dependence. For instance, the fluorescence quantum yield of **1a** is 0.005 in hexane and 0.22 in ethanol [21]. The simulation of the electronic spectra for compound **2a** by the Pariser–Parr–Popple (PPP) configuration interaction (CI) method indicates that the $S_0 \rightarrow S_1^{\pi\pi^*}$ transition has low intensity and is associated with charge transfer from the naphthalene ring to the phenylimide fragment [23]. This result rationalizes the observed low fluorescence quantum yield, which is characterized by the same transition matrix element as the absorption intensity.

Electron-donating substituents at position 4, as in compound **1b**, are in direct conjugation with the carbonyl groups of the molecule. These substituents decrease the $S_1^{\pi\pi^*}$-state energy [24], red-shift the fluorescence spectrum and substantially increase the fluorescence yield [1]. In addition to substituents, the spectral-luminescent characteristics of molecules can be strongly influenced by the photoexcited charge transfer, changes in the excitation energy gap and formation of an intramolecular hydrogen bond (IHB) [25]. The influence of solvent polarity on the photophysical behavior of 4-amino-1,8-naphthalimides has been investigated in Ref. [26]. The present study focuses on the alkylol derivatives of 1,8-naphthalimide (compounds **I**–**V** in Table 1) due to their good solubility in many organic solvents, affinity to polymeric matrices and biological applications associated with DNA intercalation.

2. Results and discussion

With the increasing number of alkylol groups at a single carbon atom, the absorption and fluorescence spectra of the alkylol derivatives of *N*-substituted 1,8-naphthalimides in non-polar and slightly polar solvents should be strongly displaced to longer wavelengths due to the formation of IHB. The nature of the *N*-substituent should also to influence the fluorescence quantum yield. The results of the current study confirm some but not all of the expected effects as elucidated below.

The absorption spectra of the compounds under investigation exhibit two bands in the long-wavelength region, as summarized in Table 2. The solvent polarity has very low influence on the position of the two absorption maxima for all compounds. The first maximum varies between 328 and 333 nm, and the second maximum varies between 338 and 347 nm, depending on the solvent. No correlation between the position of the absorption maxima and solvent polarity can be deduced from the data.

The long-wavelength band in compounds **II**, **IV** and **V** containing OH groups has a different shape and a lower intensity in methanol, as can be justified by hydrogen bonding with the solvent. The smallest and the largest differences in the values of the molecular extinction coefficients over the range of solvents are observed for compounds **III** and **V**, respectively.

Table 1
The melting point (T_{mp}), reaction yield (%) and element analysis data (N (%)) for the synthesized compounds

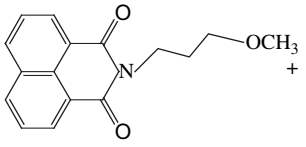
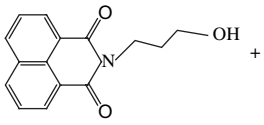
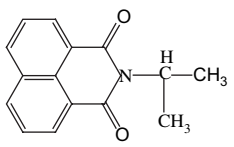
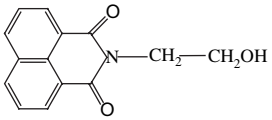
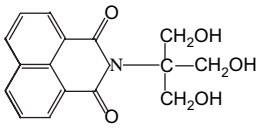
No. comp.	Compound	Yield (%)	T_{mp} (°C)	Obtained N (%)	Formula	Calculated N (%)
I		70	96–97	4.88	$C_{15}H_{21}NO_3$	5.11
II		70	93–94	5.29	$C_{15}H_{19}NO_3$	5.43
III		70	156–157	5.34	$C_{15}H_{19}NO_2$	5.74
IV		75	137–138	5.72	$C_{14}H_{17}NO_3$	5.71
V		70	223–224	4.20	$C_{16}H_{21}NO_5$	4.56

Table 2
The spectral-luminescent characteristics of the *N*-substituted 1,8-naphthalimides in solvents of different polarities

Solvent[a]	Absorption				Fluorescence		
	λ_{max1} (nm)	λ_{max2} (nm)	ε_{max1} ($dm^3\,mol\,cm^{-1}$)	ε_{max2} ($dm^3\,mol\,cm^{-1}$)	λ^F_{max} (nm)	$\Delta\nu$ (cm^{-1})	Quantum yield η
I							
Cyclohexane	330	344	4920	4760	361	1380	<0.01
Toluene	333	347	10 290	9920	378	2360	0.03
1-Chlorobutane	331	346	11 790	10 700	370	1900	0.01
Acetone	332	344	10 410	9830	377	2510	<0.01
Methanol	333	343	8990	8500	378	2690	0.11
Acetonitrile	332	346	11 450	10 380	375	2230	0.03
II							
Cyclohexane	330	343	9600	9130	361	1460	<0.01
Toluene	333	348	10 470	9580	380	2340	0.03
1-Chlorobutane	331	344	11 540	10 500	369	1970	0.01
Acetone	332	343	10 820	10 420	376	2550	<0.01
Methanol	333	343	6640	6290	378	2690	0.10
Acetonitrile	331	344	11 580	10 580	375	2420	0.04
III							
Cyclohexane	328	342	9220	8250	370	2240	<0.01
Toluene	333	346	8750	7810	378	3570	0.01
1-Chlorobutane	330	342	9270	8250	373	2430	<0.01
Acetone	332	342	8500	8500	380	2850	<0.01
Methanol	333	342	9210	8750	378	2780	0.02
Acetonitrile	330	342	9100	8250	373	2430	0.01
IV							
Cyclohexane	331	344	7780	7250	366	1720	<0.01
Toluene	333	347	7020	6420	375	2170	0.05
1-Chlorobutane	330	344	8920	8000	373	2260	0.01
Acetone	332	344	7700	7580	377	2550	<0.01
Methanol	330	344	2710	2580	378	2620	0.10
Acetonitrile	330	344	6190	5670	377	2550	0.05
V							
Cyclohexane	325	338	16 330	14 860	358	1660	0.04
Toluene	329	340	13 770	13 290	391	3830	0.09
1-Chlorobutane	327	338	15 520	15 000	367	2340	0.16
Acetone	329	338	13 770	14 980	372	2710	0.01
Methanol	327	338	6800	6000	377	3070	0.17
Acetonitrile	328	338	15 610	15 000	376	2990	0.31

[a] Dielectric constant of solvents (25 °C) [27]: cyclohexane – 2.015, toluene – 2.366, 1-chlorobutane – 7.147, acetone – 20.54, methanol – 32.70, acetonitrile – 36.87.

The fluorescence band maxima λ^F_{max} and quantum yields η of the *N*-substituted 1,8-naphthalimides under investigation are presented in Table 2. The Stokes shifts increase with solvent polarity for all studied compounds. However, the Stokes shifts in methanol are higher compared to those in the more polar acetonitrile, likely due to the hydrogen bonding. Compounds **III** and **V** show anomalously large Stokes shifts in toluene relative to the other solvents. With the exception of toluene, solvents with larger dielectric constants stabilize the excited states over the ground states, thereby red-shifting the fluorescence spectra.

The position and intensity of the fluorescence bands depend appreciably on both solvent polarity and substituent at the imide nitrogen. The investigated *N*-substituted 1,8-naphthalimides are characterized by low fluorescence quantum yields ranging from 0.01 in cyclohexane to 0.11 in methanol. Compound **V** with the (1,1-dihydroxymethyl-2-hydroxy)ethyl *N*-substituent is an exception. In this case the quantum yield strongly depends on the solvent polarity and increases from cyclohexane ($\eta = 0.04$) to acetonitrile ($\eta = 0.31$).

Consider compound **V** in more detail. Simultaneous replacement of a hydrogen atom with an OH group in all three CH_3 groups of the $C(CH_3)_3$ substituent generates a complicated molecular conformation. Investigation of the resulting intramolecular potential energy surface leads to the following conclusions. The minimal energy structure has one IHB in the orthogonal position, Fig. 1a. The other OH groups do not give IHBs due to mutual repulsion and tendency to position farthest from the naphthalimide ring. All calculations performed by the molecular mechanics (MMX-M), semiempirical (AM1) and ab initio (DFT) approaches support this conclusion.

Multiple IHBs with two of the three OH groups simultaneously coordinated by the oxygen atoms of the two C=O

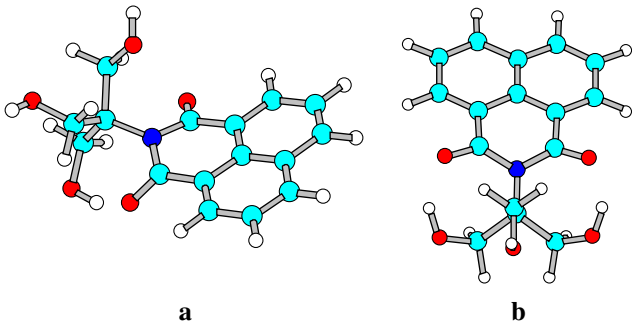


Fig. 1. Molecular structure of *N*-(1,1-dihydroxymethyl-2-hydroxy)ethyl-1,8-naphthalimide. a – Orthogonal position of intramolecular H-bond; b – double intramolecular H-bond structure.

groups are also possible in compound **V**. The computations show a multitude of such structures that are local minima with energies above the absolute single-IHB minimum. An example of double IHB structure is shown in Fig. 1b. This symmetric structure has two short O···H contacts ($R_{1,2} = 1.79$ Å) that create seven-atom cycles involving the naphthalimide ring and the substituent. The seven-member cycles exist in the closely packed conformation of homoaromatic twist. The third CH_2OH group is in the orthogonal position and does not participate in the hydrogen bonding. The energy of the structure shown in Fig. 1b is higher than that of Fig. 1a by 3 kcal/mol, according to the ab initio DFT, and by 10 kcal/mol, according to the semiempirical AM1 method.

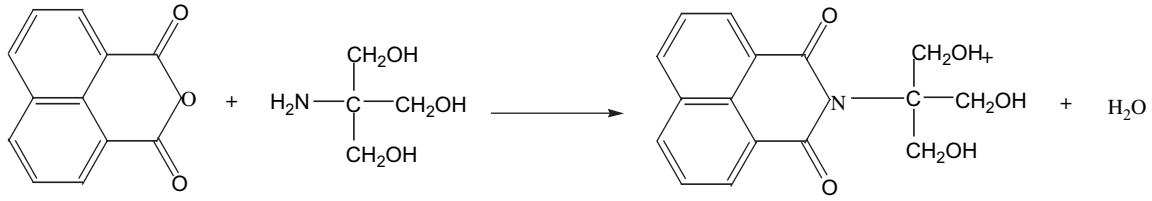
A great number of molecular structures of compound **V** with two IHBs are asymmetric. These structures are based on the metastable conformation of *N*-butyl-1,8-naphthalimide with one CH_3 group in the screened position. The first IHB is formed from the gosh position and shows a relatively long O···H contact ($R_{O\cdots H} \sim 2.1$ Å). The second IHB is formed from the screened position and shows a shorter O···H contact ($R_{O\cdots H} \sim 1.9$ Å). The conformation of the seven-member cycles involving the asymmetric IHBs is intermediate between the armchair, bath and twist. The energy of the asymmetric structures with double IHB coordination lies between the energies of the minimal structure (Fig. 1a) and the symmetric double IHB structure (Fig. 1b), and is closer to the energy of the latter.

Three IHBs can be formed simultaneously. In this case the strongest IHB with $R_1 = 1.92$ Å occurs from the screened position. The other two IHBs are weaker ($R_2 \sim 2.1$ and $R_3 \sim 2.35$ Å) and are formed from the two gosh positions to the same C=O group. The threefold IHB structure has approximately the same energy as the doubly coordinated structures.

The quantum-chemical analysis shows that the ability of *N*-alkylol-1,8-naphthalimide to create IHBs depends on the number of CH_2OH groups simultaneously present in the molecule. Strong IHBs can be formed with the CH_2OH groups in both screened and gosh positions relative to the naphthalimide ring. The presence of bulky alkyl or alkylol substituents at the carbon atom directly connected with the imide nitrogen atom encourages IHB formation from the orthogonal position. In molecules with multiple CH_2OH groups, a single IHB from the orthogonal position is most favorable, since the rather bulky OH groups repel each other and the naphthalimide ring.

3. Experimental

Imides **I**–**V** (Table 1) were synthesized by refluxing 1,8-naphthalic anhydride (1.98 g, 0.01 mol) and the corresponding amine (0.01 mol) in concentrated acetic acid (50 ml):



The reaction mixtures were refluxed for 8 h, poured into cold water, and the resulting solids were filtered off. The solid products were boiled with an aqueous solution of sodium bicarbonate (10%, 50 ml) for 20 min and insoluble solid residues were then dried in vacuo. Column chromatography on aluminium oxide with the C_6H_6 eluent gave light-brown solutions, which were evaporated to obtain crystalline products. The element analysis for nitrogen content was carried out by the Dumas–Pregdtl techniques [28]. The product melting points, yields and element analysis data are given in Table 1. The related synthesis procedures can be found in Refs. [29,30].

The absorption and fluorescence spectra of compounds **I**–**V** were measured with the "Specord M-500" spectrophotometer and Kontron SFM-25 spectrofluorimeter, respectively, in a 1-cm cuvette in 5×10^{-5} mol/l solutions at room temperature. The fluorescence quantum yields were measured relative to the 2-aminopyridine standard ($\eta = 0.74$). The spectral-luminescent characteristics were investigated in solvents of different polarity with the dielectric constants ranging from 2.015 to 36.87. The results are summarized in Table 2.

The geometric and spatial structures of the *N*-alkylol-1,8-naphthalimides were computed by both the semiempirical AM1 quantum-chemical method [31], molecular mechanics augmented for the π-conjugation effects within the framework of the π-electronic VESCF approach using the MMX-M force field and the ab initio density functional theory with the B3LYP functional and the 6-31 g* basis as implemented in Gaussian 98 [32]. The solvent effects were investigated with

the polarizable continuum model (PCModel) [33]. The electronic spectra were simulated by the INDO/S method with the Ridley–Zerner parameterization [34].

4. Conclusions

The structure and photophysical properties of the synthesized series of *N*-substituted 1,8-naphthalimides were investigated both experimentally and by electronic structure calculations. The ability of *N*-alkylol-1,8-naphthalimide to form IHBs depends on the number of CH_2OH groups simultaneously present in the molecule. Strong IHBs can be formed with the CH_2OH groups in both screened and gosh positions relative to the naphthalimide ring. Substituents to the *N*-alkyl do not increase the luminescence quantum yield if they contain a single OH group. Only *N*-(1,1-dihydroxymethyl-2-hydroxy)ethyl 1,8-naphthalimide with multiple OH groups shows an increased quantum yield that is attributable to the strong IHB in this compound. A much more significant increase in the luminescence quantum yield has been observed in the cases where the IHB forms a quasi-aromatic cycle [25].

Acknowledgments

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