

Influence of Structure on the Unusual Spectral Behavior of 4-Dialkylamino-1,8-naphthalimide

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Spectral behavior of 4-amino-1,8-naphthalimide derivatives differing in their amino functionality has been studied in different solvents with varying polarity. The results reveal that despite the +I effect of the methyl group, the charge-transfer absorption band maximum of *N*-ethyl-4-dimethylamino-1,8-naphthalimide (**3**) is blue-shifted with respect to that of the un-substituted and monoethyl-substituted derivatives, **1** and **2**, respectively. AM1 calculations indicate a lower ground state dipole moment of **3** compared to **1** or **2**. The single crystal structure of **3** suggests that low dipole moment and blue-shift of its CT maximum are due to twisting of the dimethylamino moiety relative to the 1,8-naphthalimide ring.

Molecules consisting of conjugating electron donor and acceptor (EDA) groups usually possess an intramolecular charge transfer (ICT) state as the lowest electronic state.¹ This ICT state dictates the spectral, photophysical, and photochemical behavior of the EDA molecules.² The energetics of the ICT state can be modulated by changing the strength of the donor and acceptor groups. An increase in the strength of the donor group is expected to result in an increased charge separation leading to an enhanced dipole moment and lowering of the energy of the ICT state of the system. Spectroscopically, this is manifested in a Stokes shift of the electronic absorption spectrum. 4-Amino-1,8-naphthalimide and its derivatives are versatile candidates for the study of ICT processes. Their spectral properties are highly sensitive to the polarity of the media and they possess large excited state dipole moments due to their ICT excited state nature.³ Herein, we report the UV-vis spectra of some 4-amino-1,8-naphthalimide derivatives where we encounter a system that shows a blue-shift of the spectral maximum despite having a stronger donor group. This unusual observation has been understood by investigating the crystal structure of the system.

The synthesis of 4-amino-1,8-naphthalimide derivatives, **1**, **2**, and **3** is straightforward and high yielding.⁴ Compound **1** has been synthesized by reacting ethylamine with 4-amino-1,8-naphthalic anhydride in refluxing ethanol for 2 h, in 85% yield. The synthesis of **2** and **3** was achieved in two steps by first reacting ethylamine with 4-chloro-1,8-naphthalic anhydride in refluxing ethanol for 6 h, to obtain the imide in 85% yield. This was followed by reaction with ethylamine or dimethylamine in *N*-methylpyrrolidinone to give **2** and **3** as orange colored material in 76% and 72% yield, respectively. All the compounds were characterized by ¹HNMR spectroscopy (see Supporting Information).

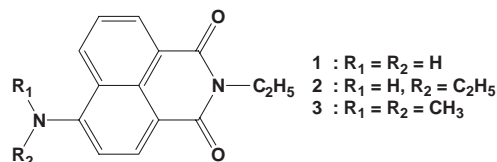


Table 1. Absorption and emission^a spectral data of **1**, **2**, and **3** in various solvents with different polarity

Solvent	$E_T(30)^c$	$\lambda_{\max}^{\text{abs}}/\text{nm}^b$			$\lambda_{\max}^{\text{flu}}/\text{nm}^b$		
		1	2	3	1	2	3
Dioxane	36.0	411	422	403	497	501	505
Tetrahydrofuran	37.4	420	427	408	505	507	513
Acetonitrile	45.6	414	430	415	516	524	531
Methanol	55.4	433	441	422	538	539	540

^a $\lambda_{\text{exc}} = 420 \text{ nm}$, ^b $\pm 2 \text{ nm}$, ^c $E_T(30)$ is a microscopic solvent polarity parameter (see Ref. 5 for details).

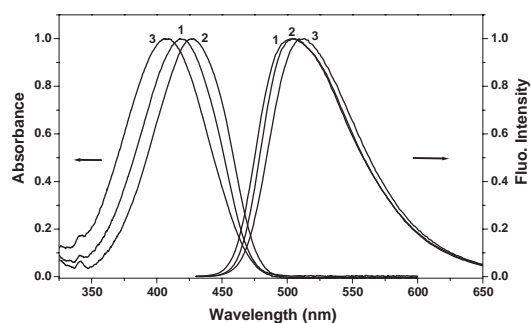


Figure 1. Absorption and emission spectra of **1**, **2**, and **3** in tetrahydrofuran. $\lambda_{\text{exc}} = 420 \text{ nm}$. All spectra were normalized at their respective peak maximum.

The electronic absorption and emission spectra of the compounds have been recorded in different solvents with varying polarity (see Supporting Information). The wavelengths corresponding to the absorption and emission peaks are listed in Table 1. The 4-amino-1,8-naphthalimide moiety in these systems gives rise to an intramolecular charge transfer (ICT) transition in the UV-vis region due to the push-pull effect of the electron-donating amino and the electron-withdrawing carbonyl groups of the fluorophore.⁶ The energy of the ICT state is determined both by the polarity of the medium and the strength of the electron donor and acceptor moieties. With an increase in the polarity of the medium, both the absorption and fluorescence maxima shift to longer wavelength. However, the shift is relatively larger for the fluorescence maximum as these compounds are more polar in the excited state.

Substitution of the amino hydrogen atoms of the parent system, **1**, by alkyl groups is expected to enhance the charge separation in the molecule because of the inductive (+I) effect of the alkyl groups. The absorption band maxima of a monoalkyl-substituted derivative, **2**, are, as expected, red-shifted due to the +I effect of the ethyl group. Interestingly, despite the +I effect of methyl groups, the absorption band maxima of a dialkyl-substituted derivative, **3**, are blue-shifted with respect to those of **1** (Figure 1) though the emission band maxima of these systems are in order.

Table 2. AM1 calculated ground-state dipole moment (μ_g) and C4–N1 bond length (r_{CN}) for **1**, **2**, and **3**

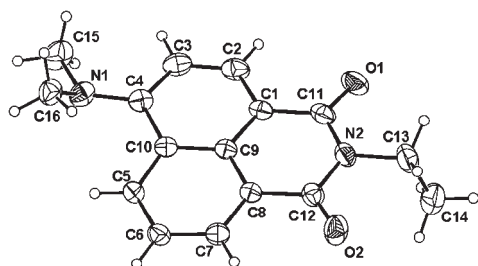
Compounds	μ_g (D)	r_{CN} (Å)
1	6.29	1.3829
2	6.85	1.3803
3	4.80	1.4377

AM1 calculations have been carried out to find out the dipole moments of the systems.⁷ The C4–N1 bond length and the ground-state dipole moment of the systems are presented in Table 2. The theoretical parameters confirm that a better electron donating dimethylamino moiety contributes less charge to the naphthalimide moiety. The C4–N1 bond length, which is a measure of the charge separation, is in the order $2 < l < 3$. The AM1 calculated ground-state dipole moment is found to be lowest for **3** even though the molecule contains relatively stronger donor than **1**. Thus, the experimentally observed results are in agreement with the theoretically calculated parameters.

In fact, we observed this kind of behavior previously with similar systems and to account for the observation we had to assume a twisting of the dialkylamino moiety relative to the 1,8-naphthalimide ring.⁸ In this letter, by determining the single crystal structure of the **3**, we are able to prove that our conjecture is indeed correct.

The ground-state structure should, in principle, explain the observed absorption phenomena and with a view to provide evidence to the proposed account, we investigated the structure of **3** by means of X-ray crystallography. Single crystals suitable for X-ray diffraction were grown by the slow evaporation of $CDCl_3$ solution in the NMR tube. Compound **3** crystallizes in an orthorhombic space group $Pna2_1$.⁹ The molecular view is shown in Figure 2 and the selected geometric parameters are listed in Table 3. The C4–N1 distance is shorter than the normal C–N single bond indicating that the lone pair of electrons on the nitrogen atom are delocalized on the naphthalimide ring with the carbonyl group acting as an electron-withdrawing group. It is interesting to note that the dimethylamino moiety is twisted with respect to the plane of 1,8-naphthalimide ring with a $\angle C10-C4-N1-C16$ torsion angle of $52.4 (3)^\circ$. This twist angle in the ground state structure of the molecule is responsible for the higher absorption energy and lower ground state dipole moment observed in **3** as compared to the corresponding un-substituted and mono-substituted derivatives, **1** and **2**, respectively.

In summary, we have shown that the anomalous spectral behavior of 4-dialkylamino-1,8-naphthalimide is due to the twist-

**Figure 2.** ORTEP diagram of **3** with labeling of all non-H atoms represented by thermal ellipsoid at the 30% probability level.**Table 3.** Selected geometric parameters of **3** as obtained from X-ray crystallography

Twist angle ($^\circ$) ^a	$\angle C10-C4-N1-C16$	52.4 (3)
Angles around N ($^\circ$) ^b	$\angle C4-N1-C15$	117.7 (3)
	$\angle C4-N1-C16$	119.7 (2)
	$\angle C15-N1-C16$	111.6 (3)
C–N bond length (Å)	C4–N1	1.386 (4)

^aTorsion angle. ^bThree angles around the amine nitrogen atom.

ing of the dialkylamino moiety relative to the naphthalimide ring. That the fluorescence spectral behaviors of the systems follow the expected trend implies that the molecules become planar on electronic excitation.

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- X-ray data for **3**: $C_{16}H_{16}N_2O_2$; $M = 268.31$; Orthorhombic, $Pna2_1$; $a = 10.511 (2) \text{ \AA}$, $b = 13.005 (3) \text{ \AA}$, $c = 9.772 (2) \text{ \AA}$, $V = 1335.8 (5) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calc}} = 1.334 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha \text{ radiation}) = 0.089 \text{ mm}^{-1}$, $\lambda = 0.71073 \text{ \AA}$, $T = 293 \text{ K}$. Reflections collected: 2049 (Enraf-Nonius Mach3 four circle CAD-4 diffractometer), 2049 unique, 184 parameters refined using 1404 reflections with $I > 2\sigma I$ to final R indices: $R1 = 0.0473$, $wR2 = 0.1111$, $GOF = 1.039$. Hydrogen atoms were introduced geometrically and refined using a riding model with a displacement parameter equal to 1.2 (CH, CH_2) or 1.5 (CH_3) times that of the parent atom. All non-hydrogen atoms were refined anisotropically. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-253130. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html. (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).