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# Experimental and theoretical study of the intramolecular charge transfer on the derivatives 4-methoxy and 4-acetamide 1,8-naphthalimide N-substituted

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## Abstract

The photo-physical properties of the 4-methoxy and 4-acetamide 1,8-naphthalimide N-substituted with the ethyldialkylamino groups, show a photo-induced charge transfer effect (PCT). The addition of protons to the solution blocked this effect and the molecules have an intense laser emission in polar solvents such as acetonitrile and ethylene glycol. We present here the photo-physical properties of the 1,8-naphthalimide and three of these derivatives in neutral and acidified 1,4-dioxane solutions. We observed that the fluorescence quenching is minor because of the PCT effect, in this solvent of lower polarity. We also present the theoretical calculation at semi-empirical level PM3, about these neutral molecules and with a proton in the amino group $R_1$, to elucidate the experimental behaviour.
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*Keywords:* 1,8-Naphthalimides; Intramolecular charge transfer; Locally excited state; Semi-empirical calculation

## 1. Introduction

Due to their photo-physical and photo-chemical properties the 1,8-naphthalimide derivatives can be used as: fluorescence dyes for solar energy collectors [1], fluorescent markers in biological cells [2] as well as laser active media [3–5]. More recently, 1,8-naphthalimide derivatives (with unsaturated chains linked to the naphthalic ring) have been used as polymerizable material [6] and also as electroluminescent crystal in thin film [7].

The 1,8-naphthalimide derivatives N-substituted, with 4-methoxy and 4-acetamide groups in naphthalic ring (see Fig. 1; Table 1), exhibit a fluorescence emission in the green–blue zone of the spectrum. In other works we showed that when the substituent $R_1$, linked to the imide nitrogen, is an ethyl with amino terminal group, the fluorescence emission is very low in polar solvents like acetonitrile and alcohols. The addition of the acetic or sulfuric acid increases the fluorescence quantum efficiencies, and then the derivatives can show intense laser emission in these solvents, when they are excited with nitrogen pulsed laser [4,5]. We have considered the existence of a photo-induced charge transfer effect (PCT) in these molecules; therefore, the protons blocked the unbounded electron pair on the N in the amino group and because of that, inhibit this effect. The solvent has an important role in the stability of the organic polar molecules excited states. We have selected *p*-dioxane, an aprotic solvent with low dielectric constant, to analyze the solvent influence in the PCT process [8], because these molecules have very low solubility in cyclohexane. On the other hand, we have performed voltammetric cyclic measurements in acetonitrile with tetrabutyl ammonium perchlorate, to obtain the semi-reduction redox potentials. The 1,8-naphthalimide is an electronic acceptor and its fluorescence emission is quenched by intermolecular charge transfer with different amine compounds [9].

We analyze the electronic charge distribution on the 1,8-naphthalimide and the derivatives with different substituents in $R_1$ and $R_2$, and we have implemented the quantum chem-

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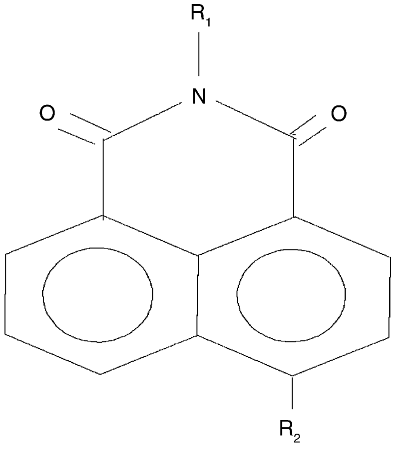

Fig. 1. Structure of the molecules.

istry calculation with the PM3 method. The energy electronic transitions, dipolar moments and atomic charge distribution are obtained. A few years ago, we made a theoretical study about some of these molecules with the CNDO/S-CI method [10], but the PM3 is better to obtain the electronic transition parameters. We have considered the *cis* and *trans* isomers in the 4-methoxy derivatives, in and out conformers in the 4-acetamide derivative, protonation forms in the 3 and 4 molecules and a tautomer 4A of the acetamide group in compound 4.

## 2. Experimental

### 2.1. Materials

The 1,8-naphthalimide (Aldrich Chemie) was purified by recrystallization in ethanol. The other derivatives were synthesized at the Knoll-Made laboratory (Madrid), with high-purity grade, tested by NMR and recently by FTIR. The solvent used was *p*-dioxane from Merck (Uvasol grade) and acetic acid (100%) from Panreac for analysis to acidify the solutions.

Absorption spectra were registered in a double beam Cary-17 Spectrophotometer. The molar extinction coefficients were calculated by means of least-squares fit over an interval of concentrations around $10^{-4}$ M because in these concentrations neither aggregates nor reabsorption effects have been observed.

Fluorescence spectra were registered in a conventional spectrofluorometer (FS900, Edimburgh Instrument), with a resolution of 1 nm, using concentrations around $10^{-5}$ M and lower in the determination of the quantum yields. Fluorescence quantum efficiencies $\Phi_{\mathrm{flu}}$ were determined comparing the integrated fluorescence spectra of each compound with the standard Norharmane (Aldrich) in 0.1N sulfuric acid (Uvasol grade), quantum yield 0.58 [11]. Experimental error was around 5%. Fluorescence lifetimes were determined by the single photon counting technique exciting with a $H_2$ lamp (FWHM $\sim$ 1 ns). Lifetimes $\tau$ were deduced by deconvolution to the profile of the lamp and from the fit to an exponential or bi-exponential function, using least-squares fit. The goodness of the fit was checked through $\chi^2$ parameter and the residues distribution (estimated error for each measure of 0.2 ns).

Table 1
Compounds studied

| Compound | $R_1$ | $R_2$ |
|---|---|---|
| 1 | –H | –H |
| 2 | –Et | –OMe |
| 3 | $-(CH_2)_2-N(CH_2)_4$ | –OMe |
| 4 | $-(CH_2)_2-NMe_2$ | –NHCOMe |

The cyclic voltammetry measurements have been performed in acetonitrile solutions, previously deoxygenated, at room temperature (20 °C) and with tetrabutylamonium perchlorate at concentration $10^{-1}$ M as supporting electrolyte. In these conditions, the molecules have given a stable reduction voltammetric cycles. These measures were performed for sweep rates comprised in 50–200 mV/s range. Over this range $\Delta E_{\mathrm{p}}$ was constant around 70 mV and analogous to that of ferrocenium/ferrocene (Fc+/Fc) couple, which was added to the electrolytic solutions at the end of each measurement, as referred to the potential. The estimated error for the potentiostat was ±1 mV and the maximum error for each measurement ±10 mV. The concentration of all compounds was around $10^{-3}$ M [12].

The NMR measurements were registered in a Bruker DXR 500 spectrometer at variable temperature 173–308 K.

### 2.2. Computational details

We have used the PM3 semi-empirical method [13]. The calculations have been performed at optimized geometries, which reached gradients up to 0.001 kcal/mol, using the known conjugated gradient method Polak–Ribiere [14]. The excited states were obtained by means of configurations interaction (CI) with 400 monoexcited configurations singlet. This is a compromise since the test with the compound 1 reveals a good approximation. For the 4-methoxy derivatives, we have considered two orientation isomers, *cis* (*c*) and *trans* (*t*), related to molecular plane of the naphthalic ring; for the bulkier 4-acetamide we have considered two structural configurations in (i), out (o), according to orientation of the carbonyl group with the same ring. For the latter we have considered the tautomeric form (4A).

The semi-empirical calculations were carried out at two levels: full optimization of the structural parameters as distances and angles of all compounds. In the second level, we have reported all electronic properties with the molecular geometries of the first level and the atomic charge distributions in the neutral and protonated (in $R_1$ amino group) molecules. The tautomer and protonated forms are fully optimized too, to analyze the intramolecular charge transfer.

Table 2
Absorption maxima, molar extinction coefficients, fluorescence maxima, quantum efficiencies and lifetime in *p*-dioxane, and semi-reduction potentials in acetonitrile of all compounds

| Compound | $\lambda^{abs}$ (nm) | log $\varepsilon$ | $\lambda^{flu}$ (nm) | | $\Phi_{flu}$ | | $\tau_a$(ns) | | $E^{1/2}_{red}$ (V) |
|---|---|---|---|---|---|---|---|---|---|
| | | | n | a | n | a | n | a | |
| 1 | 328 | 4.200 | 371 | 375, 377 | 0.017 | 0.020, 0.023 | <0.50 | <0.5 | −1.71 |
| 2 | 355 | 4.626 | 420 | 422, 427 | 0.70 | 0.70, 0.69 | 7.39 | 7.40 | −1.84 |
| 3 | 356 | 4.383 | 422 | 428, 430 | 0.114 | 0.37, 0.45 | 6.78, 1.20 | 6.55 | −1.83 |
| 4 | 364 | 4.363 | 438 | 444, 450 | 0.112 | 0.28, 0.38 | 6.25 | 6.60 | −1.72 |

n, neutral solution; a, acidified solutions (2 and 5% AcH).

## 3. Results and discussion

### 3.1. Experimental

The spectroscopic data of the compounds, in the near-UV and visible zone, are reported in Table 2. The 1,8-naphthalimide has an absorption band with vibrational structure in the near-UV, 330–340 nm and the fluorescence band is at 371 nm; the fluorescence intensity slightly increases in presence of the protons by their interactions with the carboxylic oxygen. The low value of the fluorescence quantum efficiency is associated to an effective intersystem crossing (ISC) between the singlet excited state $S_1$ and the nearby triplet state; the ISC efficiency is reported around 0.95 and 1.0 in acetonitrile and hexane solution, respectively [15].

The compounds 2 and 3, with different $R_1$, have similar absorption spectra. Both derivatives have a broad absorption band at 355 nm. The absorption maxima do not vary with the addition of protons into the solution. The compound 4 presents the same characteristics, although its absorption maximum is red shifted at 364 nm (Fig. 2; Table 2). The absorption maxima of compounds 2–4 in *p*-dioxane are blue-shifted by 5 nm compared to acetonitrile and alcohols [4,5], because this solvent has smaller interaction with the polar groups of the molecules.

Their fluorescence spectra show a wide-band without vibrational structure, which seems to be a mirror image of the absorption band. The large Stoke's shift indicates the existence of a Franck–Condon state which relaxes to the lowest vibrational energy level in the excited state before emission; this fact is in accordance with a higher dipolar moment in the π* orbital than in the ground state. The compound 2 does not change its emission parameters with 2% (v). acetic acid in the solution, with further acid additions, the fluorescence consecutively decreased and its maximum is red shifted, Fig. 3. The compounds 3 and 4 have higher fluorescence intensity in neutral *p*-dioxane solution than in neutral acetonitrile [4]; the highest quantum efficiency values were obtained in the protonated medium with 5% (v) acetic acid; both molecules have amino groups in $R_1$. For the latter acidifications, the behaviour is similar to the compound 2, the fluorescence decreased and its maximum is red shifted. In addition, besides

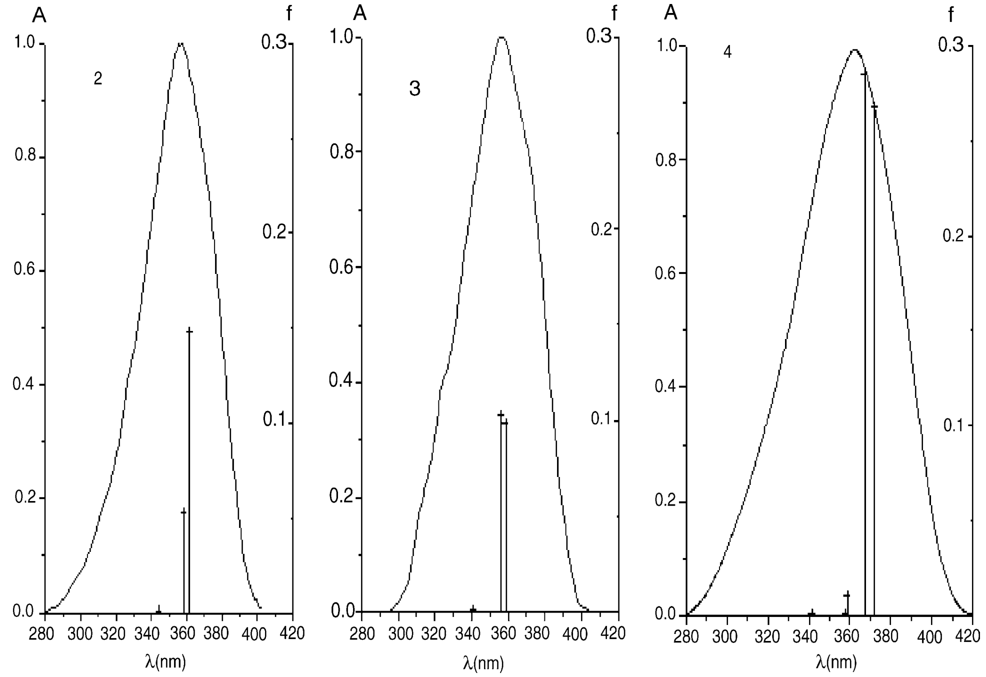

Fig. 2. A comparison between absorption spectra and theoretical data (vertical lines) for 2 and 3 *cis*-isomers and 4, 4A (−) in-configurations, respectively.

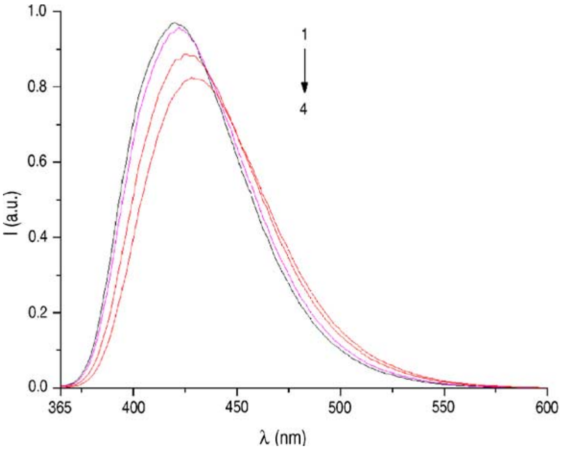

Fig. 3. Fluorescence spectrum of compound 2 in *p*-dioxane at room temperature as a function of added % AcH (v/v): (1) 0%; (2) 2%; (3) 5%; (4) 10%.

the structural differences in $R_2$ we associate this behaviour to PCT between the amino group in $R_1$ and the chromophore; when the amino group is protonated the fluorescence quantum efficiency increases, because a radiationless process is inhibited, Table 2. However, in comparison to the quantum efficiencies in polar solvent, the relative inhibition of PCT effect is lower in acidified 1,4-dioxane (the quantum efficiencies in acidified acetonitrile and ethylene glycol are 0.73, 0.45 for compound 3, and 0.68, 0.75 for compound 4, respectively [4,5]). On the other hand, the shift to the red of the fluorescence maxima is higher than in the acidified polar solvent. We considered two effects in the *p*-dioxane-acetic acid medium: a strong relative increase of the solutions polarity and an interaction by hydrogen link between the *p*-dioxane oxygens and the acetic acid; these would explain the red-shift of the fluorescence maxima and that 5% (v) of acetic acid (100%) is still necessary to obtain the fluorescence emission maximum of the 3 and 4 compounds in dilute solutions; the concentration of the acetate anion quenched the fluorescence emission of the 2–4 compounds.

The fluorescence lifetime of compounds 2–4 in neutral and acidified *p*-dioxane solutions are around 6.5–7.5 ns; the compound 3 shows a double exponential decay with a short lifetime, near 1.0 ns, and with a pre-exponential factor of 1% (however, we have not observed the short lifetime in the nanosecond range for the 4-acetamide compound; probably it is in the picosecond range). This behaviour indicates that in the neutral *p*-dioxane solutions, the 3 compound can coexist with and without PCT effect. We have obtained similar results with the 3-amino and 4-amino compounds in *p*-dioxane solutions (unpublished data). In polar molecules, with electron-donating and electron-accepting groups, as the naphthalimide derivatives, the fluorophores display specific interactions with non-polar solvent. The *p*-dioxane have zero dipolar moment, because it is a symmetrical ring; but it has two oxygens with unbonded electron pairs, which can generate interactions with the $\pi$ orbital of the naphtalene ring, and repulsive interactions with the carboxy-imido and $R_1$ amino groups. In addition the specific solvent–fluorophore interactions, can form an internal charge-transfer state (ICT) or a species without charge separation, so-called locally excited state (LE). We think that the ICT state has the shorter lifetime and its formation it is favoured in this solvent; nevertheless, the LE state has the lowest energy and higher lifetime. Addition of the acetic acid change the polarity and the acidity of the solutions and fully is inhibited in the ICT state; therefore the fluorescence maxima is red-shifted and the fluorescence lifetime in this case has a similar value to the LE state

The reduction potential informs about the electronic density of the chromophore in the ground state. When the value $E_{\mathrm{red}}^{1/2}$ increases, the molecules has a higher tendency to accept the electrons given by the exterior medium [9]. The data obtained for these molecules show (Table 2) that the 4-methoxy derivatives 2 and 3 have a similar value, −1.84 and −1.83 V, inside the experimental error. A comparison with the absorption spectra data of both compounds shows, that the $R_1$ groups have a weak influence on the electronic density of the chromophore in the ground state. There is correlation between electrochemical and spectroscopic properties [12]. The 4-methoxy group has an electron-donating character explaining that the reduction potentials of 2 and 3 compounds are more negative than the 1,8-naphthalimide; there is conjugation between the $\pi$ orbital of the chromophore and this group.

The reduction potential value of compound 4 is very similar to the one of compound 1; this indicates that the acetamide group has a weak electron-donating character. NMR measures of the compound 4 in dichloromethane at variable temperature (173–308 K) were obtained, and they do not give a coalescence point between the amide–imidol forms; the precision of this technique is a ratio 1/1000 between both forms. We have considered the existence of the tautomeric equilibrium between amide–imidol $-\mathrm{NH{-}C{=}O{-}CH_3} \leftrightarrow -\mathrm{N{=}C{-}OH{-}CH_3}$ in the theoretical calculations. The results seem to confirm the experimental data in the ground state; the in-acetamide has a dipole moment, which is very similar to the one in compound 1 and their enthalpy of formation is more negative than the in-imidol form.

### 3.2. *Theoretical calculation*

The optimized geometry presents planar conformation for compound 1, which is in agreement with X-ray data and other experimental studies [16,17]; the H substitution of the *N*-imide by an aliphatic chain modified the planarity and the angle between this atom and the carboxyl group is up to 4°. The dihedral angles between the $R_1$ group and the molecular plane are: 86° for ethyl and 72° for the ethyl with amino terminal group. When there is a proton in the 3 and 4 molecules, the dihedral angle of $R_1$ is 84°, as can be seen in Fig. 4; the proton is orientated to the carboxyl oxygen, and a hydrogen bond can be formed. The substitutions in position 4 have a longer torsion angle about 50°, for the acetamide group, be-

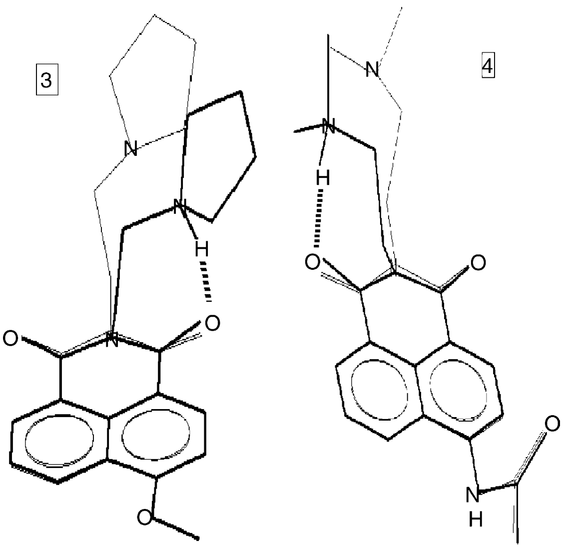

Fig. 4. Theoretical geometry orientation for 3 (*cis*-isomer) and 4 (in-configuration) molecules in neutral (–) and protonated (—) forms.

cause the bulky substituent provokes a steric hindrance with the naphthalene ring. The 2 and 3 compounds have a planar conformation on the *cis*-isomer, and a torsion angle about 70° to the *trans*-isomer. For the compounds 2–4, we were unable to find experimental data.

In Table 3, we report the energies of transition from singlet states with the highest oscillator strength and the enthalpies of formation. We observed a good correlation between the theoretical and experimental values of the fundamental (Fig. 2; Tables 2 and 3); weak differences between the position of the isomers are observed. The enthalpies of formation show a barrier smaller than 2 kcal/mol between the *cis–trans* isomers and in–out conformers; both forms can consequently contribute to the transition at room temperature. If we analyze the dipolar moments in the ground state (Table 4) and we compare them with the semi-reduction redox potential (Table 2), we deduce that the favoured form is the *cis*-isomer for methoxy derivatives and in-conformer for the compound 4. The tautomeric forms 4A (imidol) have values of the energy transition and oscillator strength in good accordance with the experimental data but their lower enthalpy of formation indicates that it is not the main form in the ground state and their dipolar moment increase in the excited state are lower than the in- or out-amide conformers.

Table 3
Theoretical data of the energy transitions, oscillator strengths and enthalpies of formation of all compounds

| Compound | λ (nm) | $f^*$ | $\Delta H_f$ (kcal/mol) |
|---|---|---|---|
| 1 | 334.8 | 0.15 | −36.38 |
| 2 | *c* 361.8 | 0.15 | −76.54 |
| | *t* 355.9 | 0.15 | −74.91 |
| 3 | *c* 356.1 | 0.10 | −77.45 |
| | *t* 352.7 | 0.16 | −75.85 |
| $3 + H^+$ | *c* 369.9 | 0.30 | 64.80 |
| | *t* 363.2 | 0.25 | 67.77 |
| 4 | i 372.1 | 0.27 | −78.99 |
| | o 374.9 | 0.32 | −80.32 |
| $4 + H^+$ | i 399.7 | 0.37 | 66.89 |
| | o 403.9 | 0.46 | 66.78 |
| 4A | i 367.2 | 0.28 | −71.32 |
| | o 372.8 | 0.36 | −73.88 |
| $4A + H^+$ | i 388.3 | 0.41 | 74.64 |
| | o 392.7 | 0.49 | 71.14 |

[*] Only transition of the greatest *f*.

The compound 1 has an electronic transition with π–π* character, which energy corresponds to the second singlet state of the other molecules. The first singlet state of 2–4 compounds has a mixture of n–π* character with a *f*-value which is lower than 0.01. Whereas this n–π* transition does not change with electron-donating groups in $R_2$, the other one has a bathochromic effect and the second singlet is the first; this is in accordance with another theoretical calculation about similar molecules [18]. The PM3 method is a good semi-empirical program to predict the π–π* fundamental transition energy for all compounds (Fig. 2); the experimental dipolar moment 4.73 D for compound 1 [20], is very similar to the 4.80 D value calculated by us (Table 4). For other derivatives, the parametrization system underestimates the conjugation effect of $R_2$ in the naphthalimide moiety, and the dipolar moments are lower than the ones in other publication of similar 1,8-naphthalimide derivatives [15].

The dipolar moments differences between the ground and excited states of the *cis*-methoxy, 2 and 3 compounds, are 0.70–0.44 and of the in- and out-acetamide groups 1.38–1.77, respectively; these values show the change of the electronic redistribution by the $S_0$–$S_1$ transition. The PCT effect is higher for acetamide derivatives, which is in accordance with the highest fluorescence quantum yields that we have measured in more polar solvent like ethylene glycol ($\mu = 2.28$ D) and dichloromethane($\mu = 1.60$ D) for this molecule [5,19].

Table 4 shows the atomic charge distribution: the oxygens and nitrogen of the imide group have negative charge since the naphthalic ring stays with a positive charge for all molecules. For the compound 1 the oxygens' charges are identical, nevertheless, for the others the charge is more negative in one oxygen than in the other one. The values of the nitrogen charge are low in comparison to the AM1 calculation method [21], but the qualitative behaviour is well represented.

The optimized geometry shows that the $R_1$ chain is folded to the molecular plane (with an dihedral angle of 72°); when the amino group of $R_1$ is protonated and the proton is directed to one oxygen as it can be seen in Fig. 4. A resonant hydrogen bond is possible and stabilization, by additional folding, can explain the higher fluorescence quantum efficiency of compound 3 than 2 in polar and protic solvent and the different lifetimes [4,5]. There are recent confirmations of a similar intramolecular hydrogen bond by IR-measurements to the 4-amino *N*-2-ethylalcohol 1,8-naphthalimide, with $-CH_2-CH_2-OH$ group linked to the imidic nitrogen [22].

Table 4
Atomic charge distribution and dipolar moments of ground and excited state for neutral and protonated forms

| Compound | $q(O^{Left})$ | $q(O^{Right})$ | $q(N)$ | $q(X^{R2})$ | $q(C_4)$ | $\mu$ (D) | $\mu^*$ (D) |
|---|---|---|---|---|---|---|---|
| 1 | −0.359 | −0.359 | −0.032 | 0.108 | −0.044 | 4.81 | 5.21 |
| 2 | *c* −0.362 | −0.365 | −0.053 | −0.186 | 0.157 | 4.84 | 5.55 |
| | *t* −0.358 | −0.358 | −0.053 | −0.208 | 0.114 | 4.06 | 4.42 |
| 3 | *c* −0.371 | −0.366 | −0.031 | −0.186 | 0.154 | 3.70 | 4.14 |
| | *t* −0.368 | −0.360 | −0.031 | −0.208 | 0.111 | 2.62 | 2.98 |
| $3 + H^+$ | *c* −0.334 | −0.461 | −0.099 | −0.174 | 0.210 | – | – |
| | *t* −0.330 | −0.454 | −0.098 | −0.203 | 0.168 | – | – |
| 4 | i −0.359 | −0.366 | −0.031 | 0.024 | −0.016 | 4.70 | 6.08 |
| | o −0.357 | −0.368 | −0.030 | 0.025 | −0.011 | 1.30 | 3.07 |
| $4 + H^+$ | i −0.455 | −0.333 | −0.100 | 0.022 | 0.039 | – | – |
| | o −0.455 | −0.338 | −0.099 | 0.021 | 0.066 | – | – |
| 4A | i −0.359 | −0.369 | −0.034 | −0.179 | 0.042 | 3.52 | 4.04 |
| | o −0.361 | −0.372 | −0.034 | −0.222 | 0.071 | 3.76 | 4.00 |
| $4A + H^+$ | i −0.455 | −0.335 | −0.101 | −0.205 | 0.097 | – | – |
| | o −0.457 | −0.338 | −0.101 | −0.260 | 0.127 | – | – |

* For excited singlet state of highest strength oscillator.

## 4. Conclusions

The photo-physical parameters of the 4-methoxy *N*-ethyl 1,8-naphthalimide have similar values in *p*-dioxane as in acetonitrile solution. When introducing an aliphatic chain with electron-donating amino-groups in the imidic nitrogen, radiationless processes were generated which have a lower effect in *p*-dioxane than in the other polar solvents. The addition of protons inhibits the ICT state in *p*-dioxane and then the amino-group protonated can be oriented to one oxygen, forming a seven-member ring by the hydrogen bridge bond. We considered that *p*-dioxane decreases the acetic acid dissociation constant and favours the hydrogen link itself (similar behaviour was referred in the bibliography between *p*-dioxane and hydrochloric acid [23]). This solvent has affinity with the protons and with the water molecules and it is not recommended to be used as solvent with the 4-methoxy and 4-acetamide 1,8-naphthalimide derivatives as laser active media.

The theoretical calculations show that the most effective CT is from the naphthalic ring, with donor groups in the 4 position, to the imide moiety in the ground state. The enthalpies of formation indicate that the *cis–trans* isomer for the 4-methoxy derivatives and the in–out conformers for 4-acetamide can contribute to the π–π* electronic transition.

Moreover, the amide–imidol tautomeric equilibrium could be deplaced to the imidol form in the excited state, because the highest dipolar moment increase correspond to out-amide conformer (which has the more negative enthalpy of formation and lower dipolar moment) in the ground state and the out- or in-imidol forms in the excited state. However, they are taken account that the gas phase results are not always sufficient to explain the real interactions of the molecules in solution.

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