Novel substituted 1-amino-4,5,8-naphthalenetricarboxylic acid-1,8-lactam-4,5-imides: experimental and theoretical study

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ABSTRACT: The electronic structure of the ground and the first singlet excited state of a novel class of fluorescent dyes, substituted 1-amino-4,5,8-naphthalenetricarboxylic acid-1,8-lactam-4,5-imides, was studied using both time-dependent density functional theory and semi-empirical approaches. It was found that the S_0–S_1 transition in lactamimides involves presumably HOMO–LUMO electron promotion. Strong intramolecular charge transfer from lactam nitrogen, C-2 and C-4 atoms to C-6 and C-7 atoms of the naphthalene ring occurs on S_0–S_1 transition. As a result, donor and acceptor side groups dramatically affect the long-wave absorption maximum, allowing control of its position over a range of more than 100 nm. Positions 2 and 7 are most sensitive to the electronic effects of the side groups owing to the combination of electronic and steric factors. Three novel derivatives of lactamimides bearing donor and acceptor side groups were synthesized and characterized. Their UV–visible spectra confirmed the results of calculation. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: lactamimides; TD-DFT; PM3; charge transfer; electronic structure

INTRODUCTION

Six-membered ring dicarboxyimides are commonly viewed as chemically very inert.[1] Strong hydrolyzing agents such as hot concentrated sulfuric acid or KOH–*tert*-butanol are required for their saponification to the corresponding acids. A completely different pathway is observed if, under much milder conditions, alkali metal hydroxides in methanol react with bisimides (Scheme 1). In this case the loss of a C_1 fragment from one of the carboxyimides leads to the formation of corresponding lactamimides.[1] In all cases only one of the imide rings is transformed to the lactam. Evidently, the second imide subunit is essential for the reaction to occur. The mechanism of this reaction has been described in detail by Langhals and Unhold.[2]

The naphthalenelactamimides absorb in the visible region of the spectrum with absorption bands significantly shifted to longer wavelengths compared with colorless naphthalenebisimides. Naphthalenelactamimides exhibit strong luminescence (quantum yield

>80%), large Stokes shifts and considerable photostability, typifying them as a promising new class of fluorescent dyes. We have synthesized the first lactamimide-containing polymers and found that they combined
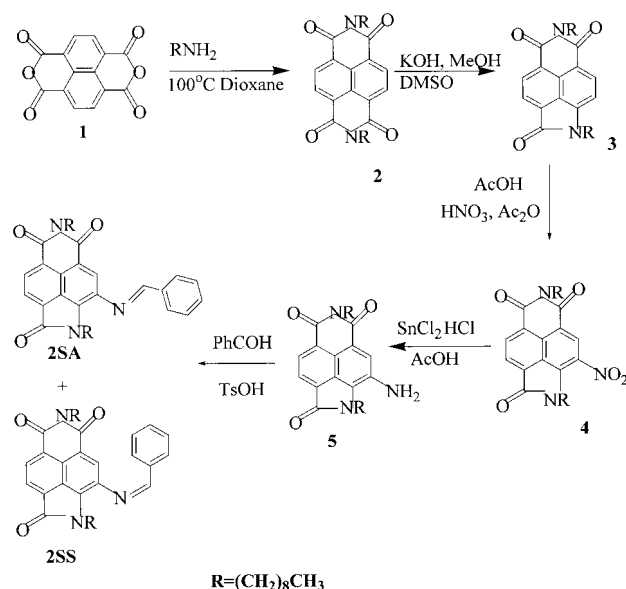
Scheme 1. Synthetic route to 2-substituted lactamimides

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good environmental stability and non-linear optical susceptibility of the third order, making them good candidates for optoelectronics.[3–5]

The red shift of long-wave absorption maximum in lactamimides is probably due to intramolecular charge transfer. In this case, the introduction of a side-group into the naphthalene ring of the lactamimide would result in modification of the absorption and emission spectra of the molecule in accordance with the electronic properties of the side group. The understanding of the correlation between the position and electronic properties of a side group on the one hand and the energy of the long-wave absorption maximum on the other is an important step toward the directional design of lactamimide dyes with predetermined absorption and emission properties. To our knowledge, only two papers have been published dealing with calculations of the electronic structure of lactamimides using a semi-empirical approach.[2,6]

The aim of this work was to model ground and low-lying exited states of lactamimide molecules bearing donor and acceptor substituents on the naphthalene ring using first principle methods to gain a better understanding of the electronic effects of side groups in the lactamimide moiety, especially with respect to their absorption spectra. Since no ring-substituted lactamimides have been reported to date, three novel 2-substituted lactamimides were synthesized and characterized to provide additional reference points for the calculations.

EXPERIMENTAL

All reagents were purchased from Aldrich and used as received.

N,N′-Bis(n-nonyl)-1-amino-4,5,8-naphtalenetricarboxylic acid-1,8-lactam-4,5-imide (3). This was prepared in two steps as described in the literature[3] (Scheme 1) starting from dianhydride **1**.

N,N′-Bis(n-nonyl)-1-amino-2-nitro-4,5,8-naphtalenetricarboxylic acid-1,8-lactam-4,5-imide (4). To a solution of **3** (1.108 g, 2.26 mmol) in a mixture of acetic acid (30 ml) and acetic anhydride (20 ml), 9 ml of 68% HNO_3 was added dropwise at room temperature and the reaction was stirred overnight. The reaction mixture precipitated into water. The solid formed was filtered off, rinsed with water and crystallized from ethanol. Yield, 90%; m.p. 103–105 °C. ^{1}H NMR (CDCl$_3$), δ 8.81 (s, 1H, H-3), 8.55 (d, 1H, $J = 7.2$ Hz, H-7), 8.25 (d, 1H $J = 7.2$ Hz, H-6), 4.20–4.00 (m, 4H, N-CH$_2$), 1.80–1.00 [28H, (CH$_2$)$_7$], 0.9–0.8 (m, 6H, CH$_3$). FT-IR (KBr) (cm^{-1}), 1541, 1349 (NO$_2$). Mass spectrum: molecular ion *m/z* 535.

N,N′-Bis(n-nonyl)-1,2-diamino-4,5,8-naphtalenetricarboxylic acid-1,8-lactam-4,5-imide (5). To a solution

containing SnCl$_2$ ·2H$_2$O (4.32 g, 19.1 mmol) in a mixture of concentrated HCl (10 ml) and acetic acid (20 ml), **4** (1.14 g, 2.13 mmol) was added and the reaction mixture was stirred overnight at 60 °C. The mixture was neutralized with NaHCO$_3$ to pH 7–8 and the product was extracted with hot toluene. The solvent was removed under vacuum and the crude amine was purified by column chromatography on SiO$_2$ (eluent toluene–acetone). Yield, 30%; m.p. 239 °C (decomp.) ^{1}H NMR (DMSO-d_6), δ 8.30 (d, 1H, $J = 7.2$ Hz, H-6), 8.20 (d, 1H $J = 7.2$ Hz, H-7), 8.00 (s, 1H, H-3), 3.95–4.05 (m, 4H N-CH$_2$). Mass spectrum: molecular ion *m/z* 506.

N,N′-Bis(n-nonyl)-1-amino-2-benzylideneamino-4,5,8-naphtalenetricarboxylic acid-1,8-lactam-4,5-imide (2SS, 2SA). A solution of **5** (0.40 g 0.8 mmol) and benzaldehyde (0.11 g, 1.0 mmol) was stirred overnight in the presence of 0.01 g of TsOH. The solvent was removed in vacuum and the residue was purified by column chromatography on SiO$_2$ (eluent chloroform–acetone). Yield, 8%; m.p. 143–145 °C. ^{1}H NMR (CDCl$_3$), δ 8.78, 8.73 (s, 1H, *cis*-N=CH, *trans*-N=CH), 8.50 (s, 1H, $J = 7.2$ Hz, H-6), 8.23 (s, 1H, H-7), 8, 16 (d, 1H, $J = 7.2$ Hz, H-7), 7,95, 7.94 (dd, 2H $J = 7.5$ Hz, *ortho* to C=N), 7.60–7.45 (m, 3H, *meta* and *para* to C=N), 4.25–4.05 (m, 4H, N-CH$_2$), 1.95–1.05 [m, 14H, (CH$_2$)$_7$], 1.00–0.90 (m, 6H, CH$_3$). Molecular ion, *m/z* 593.

Measurements. ^{1}H NMR spectra were measured using a Varian spectrometer at 300 MHz in DMSO-d_6 or CDCl$_3$ with TMS as the internal standard. UV–visible spectra were measured with a Unicam Model 300 spectrometer in CHCl$_3$. FT-IR spectra were measured using a Nicolet model 510P spectrometer in KBr pellets. The oscillator strength (*f*) was calculated from the absorption spectra according to

$$f = (4.9 \times 10^{-9})\varepsilon\Delta\nu_{1/2} \qquad (1)$$

where ε is the extinction coefficient at the peak maximum and $\Delta\nu_{1/2}$ is the half-width of the peak at its half-height in cm^{-1}.

Gaussian 98 Revision A7[7] was used for all calculations except those on excited states using single-excitation calculations with the PM3[8] method, where HyperChem (Version 5.1 was used). The ground-state geometry was optimized to a local minimum without any symmetry restrictions using polarized basis set 6–31G(d). The Becke three-parameter hybrid (B3)[9] exchange functional in combination with the Lee–Yang–Parr (LYP)[10] correlation functional (B3LYP) with split valence + polarization basis set [6–31G(d)] was used for all geometry optimizations. Vertical excitation energies and the electron density distributions for the first allowed excited state were obtained by two different methods: first the conventional configuration interaction approach consid-

Table 1. Calculated and experimental (chloroform) wavelengths (λ) and oscillator strengths (f) of lowest allowed singlet excited state

Compound	TD-B3LYP/6–31G(d)				PM3-CI				Experiment	
	f	Coefficient[a]	Excitation	λ(nm)	f	Coefficient[a]	Orbitals excited	λ(nm)	f	λ(nm)
3	0.14	0.62	HOMO–LUMO	410	0.22	0.63	HOMO–LUMO	425	0.11	440
4	0.11	0.63	HOMO–LUMO	406	0.19	0.61	HOMO–LUMO	426	0.09	438
5	0.11	0.63	HOMO–LUMO	469	0.20	0.64	HOMO–LUMO	464	0.13	480
2SS	0.10	0.62	HOMO–LUMO	463	0.24	0.60	HOMO–LUMO	447	0.08	468
2SA	0.10	0.63	HOMO–LUMO	456	0.26	0.61	HOMO–LUMO	442	0.08	468
3NO2	0.13	0.62	HOMO–LUMO	405	0.24	0.63	HOMO–LUMO	429	—	—
3NH2	0.11	0.69	HOMO–LUMO	439	0.18	0.63	HOMO–LUMO	450	—	—
3SS	0.11	0.64	HOMO–LUMO	428	0.21	0.64	HOMO–LUMO	427	—	—
3SA	0.01	0.60	HOMO–LUMO	430	0.20	0.62	HOMO–LUMO	431	—	—
6NO2	0.12	0.63	HOMO–LUMO	425	0.22	0.64	HOMO–LUMO	440	—	—
6NH2	0.13	0.61	HOMO–LUMO	418	0.11	0.51	HOMO–LUMO	438	—	—
						0.38	HOMO–1–LUMO			
6SS	0.14	0.60	HOMO–LUMO	405	0.18	0.47	HOMO–LUMO	412	—	—
						−0.45	HOMO–1–LUMO			
6SA	0.15	0.61	HOMO–1–LUMO	411	0.23	0.58	HOMO–LUMO	415	—	—
7NO2	0.08	0.64	HOMO–LUMO	450	0.16	0.65	HOMO–LUMO	459	—	—
7NH2	0.13	0.63	HOMO–LUMO	430	0.18	0.65	HOMO–LUMO	443	—	—
7SS	0.10	0.63	HOMO–LUMO	430	0.18	0.63	HOMO–LUMO	428	—	—
7SA	0.10	0.63	HOMO–LUMO	440	0.16	0.62	HOMO–LUMO	439	—	—
7NO2-2NH2	0.07	0.64	HOMO–LUMO	527	0.18	0.66	HOMO–LUMO	496	—	—

[a] The largest coefficient; all other excitation coefficients are <0.2.

ering single substitutions out of the Hartree–Fock ground state using a PM3 semiempirical hamiltonian (PM3-CI) and second the time-dependent functional theory (TD-DFT) which is a first principles theory usually providing an accuracy for excitation energies exceeding that of the CI singles method and often comparable in accuracy to the most advanced other *ab initio* approaches.[11] Time-dependent density functional theory provides a formally rigorous extension of Hohenberg–Kohn–Sham density functional theory, which is independent of time, to the situation where a system, initially in its ground stationary state, is subjected to a time-dependent perturbation.[12] A stationary action principle may be derived, analogous to the minimum energy principle of the Hohenberg–Kohn theory, and this can be used to derive the time-dependent Kohn–Sham equation.[13–17] The B3LYP hybrid functional in combination with the 6–31G(d) basis set was used for this study with the frozen core approximation. In the case of the PM3-CI method, all orbitals were used for correlation. The modeled molecules had hydrogens at nitrogen atoms instead of *n*-nonyl groups in the case of synthesized model compounds which were introduced to facilitate their purification.

RESULTS AND DISCUSSION

Three different groups were chosen as substituents for lactamimide: nitro, amino and benzylidenamino groups, to include the most important electronic effects manifested by substituents. The first group is a strong

acceptor, the second is a strong donor and the third is a moderate donor having an extended conjugation system. The nitration of lactamimide **3** under mild conditions [room temperature in the presence of $Ac_2O–CH_3COOH–HNO_3$ produces the 2-nitro-substituted compound **4** in almost quantitative yield (Scheme 1)]. The signal of H-2 (doublet at 7.05 ppm) is completely absent from the ^{1}H NMR spectrum of **4** and H-3 is shifted downfield from 8.40 to 8.80 ppm owing to the electron-withdrawing NO_2 group appearing as a singlet instead of doublet in lactamimide **3**. On the other hand, the signals of H-6 and H-7 almost maintained their positions, shifting 0.05–0.07 ppm downfield compared with lactamimide **3**. Another confirmation of the fact that the nitration occurs at position 2 of the lactamimide ring comes from analyzing the HOMO of lactamimide. As can be seen from Fig. 2, C-2 contributes most to the HOMO of four carbons (C-2, C-3, C-6 and C-7). This means that the attack of electrophile should occur at C-2.

The reduction of nitro compound **4** by $SnCl_2 \cdot 2H_2O$ leads to the 2-amino intermediate **5** whereas the reaction of amine **5** with benzaldehyde in the presence of TsOH results in a lactamimide containing Schiff base. Even though only one spot appeared on the TLC plate for the Schiff base, the ^{1}H NMR spectrum show that the compound is a mixture of almost equal quantities of *cis* (**2SS**) and *trans* (**SA**) isomers. Two signals of almost identical intensity corresponding to N=CH protons of different isomers at 8.78 and 8.74 ppm and two very close doublets corresponding to protons *ortho* to the CH=N group with $J = 7.5$ Hz separated by just 0.005 ppm
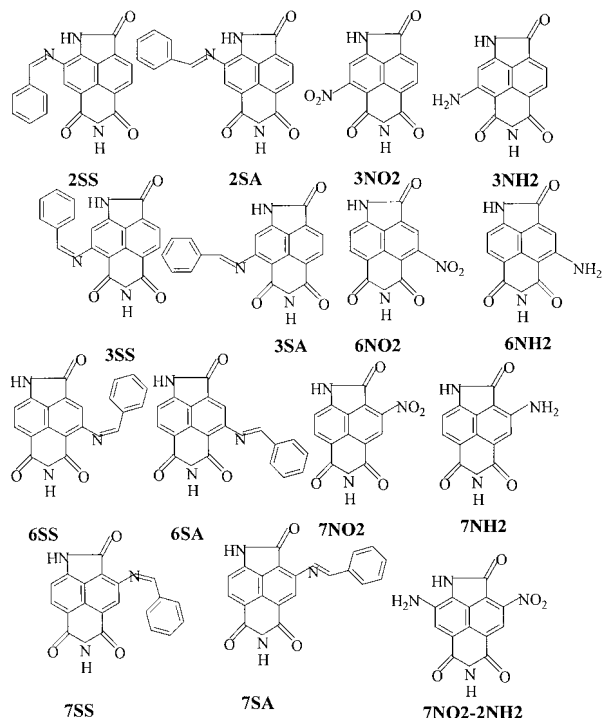
Figure 1. Structures of the substituted lactamimides studied

appeared in the spectrum of the Schiff base. On the other hand, the mass spectrum showed only one molecular ion. It was impossible to separate the *cis* and *trans* isomers either by column chromatophraphy or by repeated recrystallization, and therefore the mixture of isomers was used for measurements.

Table 1 gives lowest singlet excited state modeling data and Fig. 1 shows the structures of the lactamimides. As can be seen from Table 1, there is good agreement between the calculated and measured wavelengths and oscillator strengths of the model molecules. It is noteworthy that the PM3-CI method produced energies just as good as the much more sophisticated TD-DFT theory, while the ZINDO-1[18] parametrized for modeling of electronic spectra and CIS/6–31G(d)[19] methods gave poor results (370 and 285 nm, respectively, for lactamimide **3**). The coefficients of wavefunctions and oscillator strengths obtained from the PM3-CI model are similar to these from the TD-DFT method.

Several important observations can be made inspecting Table 1. An acceptor NO_2 group at positions 2 and 3 has little effect on the long-wave absorption maximum, causing a slight blue shift, whereas a donor amino group at all positions and especially at position 2 causes a red shift of the long-wave absorption maximum. An acceptor NO_2 group causes an appreciable red shift of the long-wave absorption maximum in the **7NO2** molecule. Benzylideneamino groups behave similarly to amino groups, but the red shift of the long-wave absorption maximum is smaller in most cases. Neither donor nor

acceptor substituents at C-6 affect the absorption spectra significantly.

Fortunately, as can be seen from Table 1, the long-wave absorption maximum of substituted lactamimides is to a great extent due to electron promotion from HOMO to LUMO, and therefore by analyzing the HOMO and LUMO distributions across the molecule one can understand the nature of the effect of donor and acceptor substituents on the long-wave absorption maximum in lactamimides. The positions most sensitive to the substitution are C-2 and C-7. On inspecting the HOMO and LUMO of lactamimide **3** it can be seen that whereas C-2 contributes significantly to the HOMO, C-7 contributes far less. On the other hand, C-2 contributes almost nothing to the LUMO whereas C-7 contributes significantly to this orbital. The acceptor substituents decrease the energies of molecular orbitals whereas donor groups destabilize them owing to an increase in the electron repulsion term. Therefore, the introduction of a donor group in position 2 will destabilize the HOMO to a greater extent than the LUMO, leading to the red shift of the long-wave absorption maximum in lactamimides having a donor side group in position 2. Similarly, the introduction of an acceptor side group in position 7 will stabilize the LUMO to a greater extent than the HOMO resulting again in a red shift of the absorption maximum. This conclusion is totally confirmed by comparison of the HOMO and LUMO energies of lactamimide **3** with these of 2-amino- and 7-nitrolactamimides (Table 2). From this point of view it is easy to understand why an NO_2 group in position 2 causes a blue shift in the absorption spectra: in this case the HOMO stabilize better than the LOMO, causing a larger separation between orbitals.

On inspecting the HOMO and LUMO of lactamimide **3** one would expect a significant red shift of the long-wave absorption maximum for 3- and 6-nitro-substituted lactamimides; however, this is not the case and the absorption spectra of **3** are little affected by NO_2 at positions 3 and 6. This apparent contradiction can be understood by analyzing the optimized geometries of nitro derivatives. Whereas the deviation of the NO_2 group from the lactamimide plane for **7NO2** is only 26.7°, for of 3- and 6-nitro-substituted lactamimides this deviation is 72.3 and 68.3°, respectively (Fig. 2). Such a twisting is due to the steric hindrance between the oxygen atoms of the nitro and carbonyl groups which is stronger for the carbonyl of the imide ring. As a consequence, there is little overlap between the P_z orbitals of the nitro groups and those of the lactamimide moiety in **3NO2** and **6NO2** molecules resulting in a weaker electronic interaction between the side group an lactamimide fragment. As can be seen from Fig. 2, the NO_2 group contributes little to the LUMO in the case of **3NO2** and **6NO2** whereas in **7NO2** the P_z orbitals of the nitro group contributes significantly to LUMO.

Unlike nitro groups, amino groups are in-plane with the lactamimide fragment in any position owing to the

Table 2. Shift of orbital energies (hartree) caused by substitutuents relative to lactamimide **3**: Mulliken charges at heavy atoms of lactamimide **3** in the ground and first exited singlet states at the TD-B3LYP/6–31G(d), PM3-CI and CIS/6–31G(d) levels of theory

| Molecule | Energy[a] | | Atom | Mulliken charge (e) | | | | | |
| | HOMO | LUMO | | TD-B3LYP/6–31G(d) | | PM3-CI | | CIS/6–31G(d) | |
				Ground state	First exited singlet state	Ground state	First exited singlet state	Ground state	First exited singlet state
3	0	0	C-1	0.42	0.47	−0.01	−0.14	0.49	0.50
4	−0.02235	−0.02200	C-2	−0.18	−0.10	−0.15	−0.06	−0.26	−0.20
5	0.02043	0.00575	C-3	−0.20	−0.22	0.04	−0.06	−0.15	−0.19
2SS			C-4	0.03	0.20	−0.19	−0.07	−0.17	−0.02
2SA			C-5	0.02	−0.09	−0.13	−0.14	−0.15	−0.20
3NO2	0.01537	0.00280	C-6	−0.19	−0.25	−0.02	−0.06	−0.17	−0.23
3NH2	−0.01786	−0.01668	C-7	−0.21	−0.27	−0.02	0.00	−0.21	−0.23
3SS	0.02068	0.01439	C-8	0.09	−0.04	−0.11	−0.18	−0.06	−0.14
3SA	0.01603	0.01248	C-9	−0.18	−0.25	−0.12	−0.06	−0.18	−0.12
6NO2	0.01150	0.00809	C-10	0.11	0.09	0.05	0.01	0.08	0.07
6NH2	−0.01514	−0.01773	C-11	0.57	0.59	0.33	0.29	0.88	0.86
6SS	0.01557	0.01182	O-12	−0.48	−0.47	−0.35	−0.35	−0.60	−0.58
6SA			N-13	−0.72	−0.71	−0.03	−0.01	−0.97	−0.97
7NO2	0.00826	0.0787	C-14	0.60	0.55	0.31	0.30	0.89	0.86
7NH2	−0.01538	−0.02227	O-15	−0.48	−0.53	−0.35	−0.35	−0.59	−0.60
7SS	0.02052	0.01139	C-16	0.58	0.53	0.29	0.22	0.85	0.79
7SA	0.01271	0.00443	O-17	−0.46	−0.48	−0.32	−0.30	−0.56	−0.57
N-Me	0.00713	0.00428	N-18	−0.79	−0.60	0.08	0.27	−0.97	−0.88

[a] B3LYP/6–31G(d) level of theory.
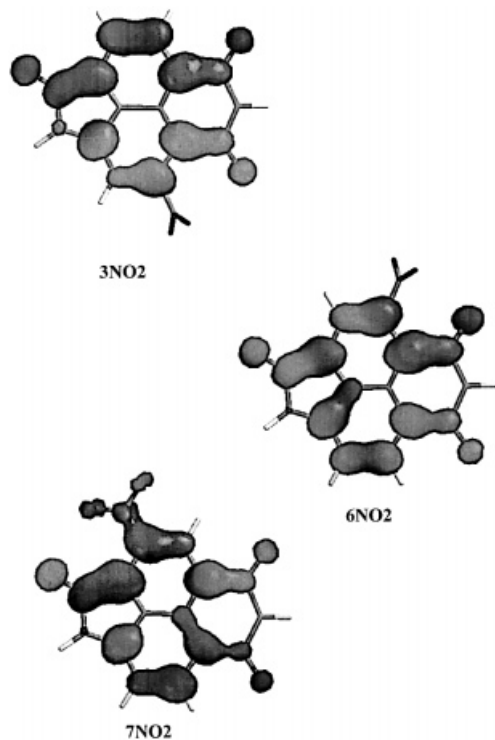
Figure 2. B3LYP/6–31G(d) optimized geometries and LUMO of **3NO2**, **6NO2** and **7NO2** molecules

Figure 3. HOMO, LUMO and HOMO-4 of lactamimide **3**

smaller size. Although the strongest red shift of the long-wave absorption maximum is observed for **5** (about 40 nm), the introduction of amino groups in other positions also causes some bathochromic shift. In the case of the **3NH2** molecule, even though C-3 barely contributes to the HOMO, adjacent C-2 and C-4 contribute significantly (Table 3). The $+M$ effect of the NH_2 group is strong enough to increase the electron density at C-2 and C-4,

Table 3. Eigenvector coefficients larger than 0.02 of LUMO, HOMO and HOMO-4 of molecule **3** at the B3LYP/6–31G(d) level of theory

Atom	Atomic orbitals	LUMO	HOMO	HOMO-4
C-1	$2P_z$	−0.22	−0.22	0.02
	$3P_z$	−0.15	−0.15	0.02
C-2	$2P_z$	0.1	−0.20	0.06
	$3P_z$	0.09	−0.16	0.04
C-3	$2P_z$	0.19	0.14	0.03
	$3P_z$	0.19	0.1	0.02
C-4	$2P_z$	−0.14	0.29	−0.03
	$3P_z$	−0.15	0.22	—
C-5	$2P_z$	0.22	−0.15	−0.22
	$3P_z$	0.23	−0.11	−0.14
C-6	$2P_z$	−0.16	−0.05	−0.15
	$3P_z$	−0.17	−0.04	−0.12
C-7	$2P_z$	−0.17	0.13	0.06
	$3P_z$	−0.17	0.09	0.05
C-8	$2P_z$	0.22	0.12	0.21
	$3P_z$	0.23	0.1	0.14

destabilizing the HOMO. Thus, Mulliken charges at C-2, C-4 atoms in molecules **3** and **3NH2** are −0.18, 0.03 and −0.24, −0.04, respectively, explaining the moderate (19 nm) red shift in the **3NH2** molecule. Inspecting the HOMO and LUMO of molecule **3** one would expect that donor amino groups at positions 6 and 7 would lead to a slight blue shift of the long-wave absorption maximum because C-6 and C-7 contribute more to the LUMO than to the HOMO (Fig. 3). However, according to the calculations, the **6NH2** and **7NH2** molecules show a slight red shift of the long-wave absorption maximum. The explanation of this phenomenon is not apparent and may be a combination of two trends. In molecule **3**, apart from main the HOMO–LUMO configuration having a coefficient of 0.62 there is a contribution from the HOMO-4 → LUMO configuration with a coefficient of −0.14 to the first singlet excited state. As can be seen from Fig. 3, among all the carbons of the naphthalene ring C-5, C-6 and C-8 contribute significantly to HOMO-4. This means that destabilization of HOMO-4 when a donor side group is introduced in position 6 or 7 will lead to a red shift of the long-wave absorption. Another important circumstance is that the lone electron pair on nitrogen in all amino derivatives contributes very significantly to the HOMO, destabilizing it with compared with that of unsubstituted lactamimide **3**. The eigenvector coefficients of the P_z orbital of the amino nitrogen in HOMO are 0.26, 0.27, 0.29 and 0.25 for **5, 3NH2, 6NH2** and **7NH2**, respectively. These two factors cause a moderate red shift in **6NH2** and **7NH2**.

By comparing the electron densities in the ground and excited states one can appreciate the entire picture of electron transitions in the molecules. Table 2 gives the Mulliken charges of the lactactamimide **3** molecule in the

S_0 and S_1 states calculated at three different levels of theory; TD-B3LYP/6–31G(d), PM3-CI and CIS/6–31G(d). All methods show that there is a significant charge transfer in the $S_0 \rightarrow S_1$ transition in the lactamimide. TD-DFT theory apparently provides the best agreement between the locations of the long-wave absorption maxima of substituted lactamimides and the electron density distribution in the ground and excited states. Thus, according to the TD-DFT model, the electron density transfers from N-18, C-1, C-2 and C-4 to C-16, C-9, C-8, C-7, C-6, C-5, C-14 and O-15. In other words, acceptor side groups at C-6 and C-7 should stabilize the excited state, resulting in a red shift of the long-wave absorption maximum, which agrees with the calculated excitation energies for the **6NO2** and **7NO2** molecules. On the other hand, CIS/6–31G(d) and especially PM3-CI underestimate the charge transfer to C-6 and C-7 atoms. According to the semi-empirical PM3-CI model, the Mulliken charge at C-7 changed from -0.02 in the S_0 to 0.00 in the S_1 state, implying destabilization of the excited state in **7NO2** compared with the unsubstituted lactamimide **3**, giving rise to a blue shift of the long-wave absorption maximum for **7NO2**. This result shows inconsistency between the excitation energies and charge density distributions for this semi-empirical model.

The benzylideneamino group behaves similarly to the amino group in most cases. Owing to the weaker donor nature, the red shift of the long-wave absorption maximum is less than that in the corresponding amino-substituted lactamimides (Table 1). There is no significant difference between the absorption maxima of *cis* and *trans* isomers, but, *cis* isomers absorb at a slightly shorter wavelength owing to steric hindrance disrupting the conjugation. The 3- and 6-benzylideneamino-substituted lactamimides absorb at shorter wavelengths than the 2- and 7-substituted compounds owing to steric hindrances. Thus, the dihedral angles between the benzene ring of the *trans*-benzylideneamino group and the lactamimide fragment are 26.5, 64.4, 65.4 and 33.9° for molecules **2SA, 3SA, 6SA** and **7SA**, respectively.

CONCLUSIONS

The long-wave absorption maximum in 1-amino-4,5,8-naphthalenetricarboxylic acid-1,8-lactam-4,5-imides is due to an S_0–S_1 transition with intramolecular charge transfer which can be satisfactorily described in terms of promotion of an electron from the HOMO to the LUMO, as followed from TD-DFT and PM3-CI modeling of the S_1 state. The intramolecular charge transfer occurs presumably from the lactam nitrogen and C-2 and C-4 carbons to C-6, C-7 and C-9 on excitation. As a result, donor substituents at position 2 and acceptor side groups at position 7 cause a red shift of the long-wave absorption maximum in lactamimides. Therefore, the simultaneous introduction of a strong donor and a strong acceptor at positions 2 and 7, respectively, would cause a very strong red shift of the long-wave absorption maximum. Thus, according to TD-B3LYP/6–31G(d) calculations (Table 1), the 1,2-diamino-7-nitro-4,5,8-naphthalenetricarboxylic acid-1,8-lactam-4,5-imide (**7NO2-2NH2**) molecule has an S_0–S_1 transition at 527 nm showing a 117 nm red shift compared with the unsubstituted lactam **3**. Carbonyl oxygen atoms of the imide ring cause considerable steric hindrance for substituents at positions 3 and 6, thus decreasing the electronic interactions between the P_z orbitals of the lactamimide ring and those of the side group. As a result, NO_2 groups have little effect on the absorption spectra of **3NO2** and **6NO2**. In conclusion, the position of the long-wave absorption maxima in lactamimides can easily be modified over a wide range by the introduction of suitable side groups in positions 2 and 7 of the lactamimide ring.

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