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Luminescent properties of substituted 4-aminophthalimides: computations vs. experiment

Aim. To perform a combined experimental and computational study on the luminescent properties of practically important class of organic dyes – 4-aminophthalimides.

Results and discussion. The absorption and fluorescence spectra of 4-aminophthalimide derivatives in polar protic and aprotic solvents were computed and matched vs. the experimental data. The changes in emission spectra are mainly related to the NH₂-group derivatization. The methyl substitution of amide hydrogen causes a bathochromic shift of about 7 nm in the absorption peak and a negligible hypsochromic shift in the fluorescence peak, while introducing alkyl substituents to the amine moiety causes bathochromic shifts in absorption and emission peaks of 30–40 nm and 10–60 nm, respectively.

Experimental part. Absorption and emission wavelengths were computed by the standard algorithm based on the ground state geometry optimization (equilibrium solvation), vertical excitation with nonequilibrium solvation, and the TD-DFT geometry optimization of the excited state structures. A reliable hybrid B3LYP functional was used in combination with DZ and TZ-quality basis sets.

Conclusions. The computed absorption wavelengths are in excellent agreement with the experimental data and are only slightly solvent-dependent. At the same time, the discrepancy with the experiment for Stokes shifts reaches about 20% at IEF-PCM-TD-B3LYP/6-31G(d). However, the general tendency for both absorption and fluorescence wavelengths is identical for all solvents within one molecule.

Key words: experimental luminescence spectra; absorption; fluorescence; Stokes shifts; 4-aminophthalimides; time-dependent density functional theory; polarizable continuum model

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Люмінесцентні властивості заміщених 4-амінофталімідів: розрахунки та експеримент

Мета. Провести комбіноване експериментально-розрахункове дослідження люмінесцентних властивостей практично важливого класу органічних барвників – 4-амінофталімідів.

Результати та їх обговорення. Розраховано і порівняно з експериментальними даними спектри поглинання і флуоресценції похідних 4-амінофталіміду в полярних протонних і апротонних розчинниках. Зміни в спектрах випромінювання в основному пов'язано з дериватизацією NH₂-групи. Введення метильного замісника до амідної групи викликає батохромний зсув близько 7 нм сигналу поглинання і незначний гіпсохромний зсув сигналу флуоресценції. Введення алкільних замісників до аміногрупи призводить до батохромних зсувів піків поглинання і випромінювання на 30–40 нм і 10–60 нм відповідно.

Експериментальна частина. Довжини хвиль поглинання і випромінювання розраховано за стандартним алгоритмом, що ґрунтується на оптимізації геометрії основного стану (рівноважна сольватація), вертикальному збудженні з нерівноважною сольватацією і оптимізації геометрії TD-DFT структур збудженого стану. Надійний гібридний функціонал B3LYP використано в поєднанні з базовими наборами DZ- і TZ-якості.

Висновки. Розраховані довжини хвиль поглинання добре узгоджуються з експериментальними даними і майже не залежать від розчинника. В той же час розбіжність з експериментом для стокових зсувів досягає приблизно 20% на рівні IEF-PCM-TD-B3LYP/6-31G(d). Однак загальна тенденція для довжин хвиль поглинання і флуоресценції однакова для всіх розчинників у межах однієї молекули.

Ключові слова: експериментальні спектри люмінесценції; поглинання; флуоресценція; стокові зсуви; 4-амінофталіміди; час-залежна теорія функціоналу густини; модель поляризованого континууму

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Люминесцентные свойства замещенных 4-аминофталимидов: расчеты и эксперимент

Цель. Провести комбинированное экспериментально-расчетное исследование люминесцентных свойств практически важного класса органических красителей – 4-аминофталимидов.

Результаты и их обсуждение. Рассчитаны и сопоставлены с экспериментальными данными спектры поглощения и флуоресценции производных 4-аминофталимида в полярных протонных и апротонных растворителях. Спектры излучения в основном связаны с дериватизацией NH₂-группы. Введение метильного заместителя в амидную группу вызывает батохромный сдвиг около 7 нм максимума поглощения и незначительный гипсохромный сдвиг максимума флуоресценции. Введение алкільных заместителей в аминную часть вызывает батохромные сдвиги пиков поглощения и излучения на 30–40 нм и 10–60 нм соответственно.

Экспериментальная часть. Длины волн поглощения и излучения рассчитаны по стандартному алгоритму, основанному на оптимизации геометрии основного состояния (равновесная сольватация), вертикальном возбуждении с неравновесной сольватацией и оптимизации геометрии TD-DFT структур возбужденного состояния. Надежный гибридный функционал B3LYP использовали в сочетании с базисными наборами DZ- и TZ-качества.

Выводы. Рассчитанные длины волн поглощения прекрасно согласуются с экспериментальными данными и лишь незначительно зависят от растворителя. В то же время расхождение с экспериментом для стоксовых сдвигов достигает примерно 20% на уровне IEF-PCM-TD-B3LYP/6-31G(d). Однако общая тенденция для длин волн поглощения и флуоресценции одинакова для всех растворителей в пределах одной молекулы.

Ключевые слова: экспериментальные спектры люминесценции; поглощение; флуоресценция; стоксовы сдвиги; 4-аминофталимиды; временно-зависимая теория функционала плотности; модель поляризуемого континуума

4-Aminophthalimide **1** combines electron-donating amino group conjugated with the phthalimide moiety; this determines its distinct fluorescent properties (Stokes shifts > 100 nm) [1]. The derivatives of **1** continuously attract great attention because of biological applications [2], particularly as fluorescent markers [3] and environment-sensitive probes [4]. The fluorescence spectra of **1** not only strongly depend on the substituents [2, 5], but are remarkably solvent-sensitive due to the intramolecular charge transfer nature of the emitting state. It has been found that bathochromic shifts of the emission spectra of **1** in protic solvents are much greater than those observed in aprotic ones: the emission maximum shifts from 430 nm in toluene to 550 nm in water [6–7]. Additionally, the excited state of **1** has a relatively long lifetime of ca. 15 ns [8], but drops substantially in protic solvents, such as alcohols and especially in water [8, 9]. Due to its long excited state lifetime and high solvatochromism **1** is an ideal probe for monitoring the relaxation of various media, especially where H-bonds are involved [7]. It was extensively used to monitor microenvironments and solvation of a variety of substrates, including micelles, cyclodextrins, hydrogels, and ionic liquids [6, 10]. Most recent studies include the synthesis of 4-aminophthalimide C-nucleosides as isosteric fluorescent DNA base substitutes [11] probing the aggregation behavior of substituted **1** [12]. The modeling of hydrogen-bonding dynamics of **1** in aqueous solution [13] and modulation of **1** spectral properties by hydrogen bonds in water [14] were successfully performed using the time-dependent density functional theory (TD-DFT) approach. All above raises

the importance of computational prediction of luminescent properties of the derivatives of **1**, and it is the subject of current study.

Results and discussion

Herein, we studied the luminescent properties of 4-aminophthalimide **1** derivatives, namely 4-amino-*N*-methylphthalimide **2**, 4-amino-*N*-ethylphthalimide **3**, 4-amino-*N*-(*n*-propyl)phthalimide **4**, 4-amino-*N*-(*iso*-propyl)phthalimide **5**, 4-amino-*N*-cyclohexylphthalimide **6**, 4-amino-*N*-(1-adamantyl)phthalimide **7**, 4-(*N*-ethyl)amino-*N*-methylphthalimide **8**, and 4-(*N,N*-diethyl)amino-*N*-methylphthalimide **9** (Fig. 1) prepared as described earlier [2, 5].

Since the experimental fluorescence spectra of 4-aminophthalimide derivatives are determined by the allowed transitions between the S_0/S_1 electronic states [15], the frontier orbitals of **1** and its methyl derivative **2** were first analyzed through the optimization of their S_1 -state geometries (Fig. 2).

As the amine nitrogen contributes substantially both to HOMO and LUMO, the introduction of substituents to the amino group should lead to shifts in both the absorption and emission bands. In contrast, the phthalimide nitrogen mostly contributes to the HOMO (Fig. 2). The above set of model molecules **1–9** allows us to vary the substitution pattern in both directions.

First, the ability of the TD-DFT approach to reproduce the experimental absorption spectra of compounds **1–9** was tested (Table 1). The computations of the vertical excitation step of substituted **1** with even relatively small basis sets provided absorption wavelengths in good agreement with the experiment.

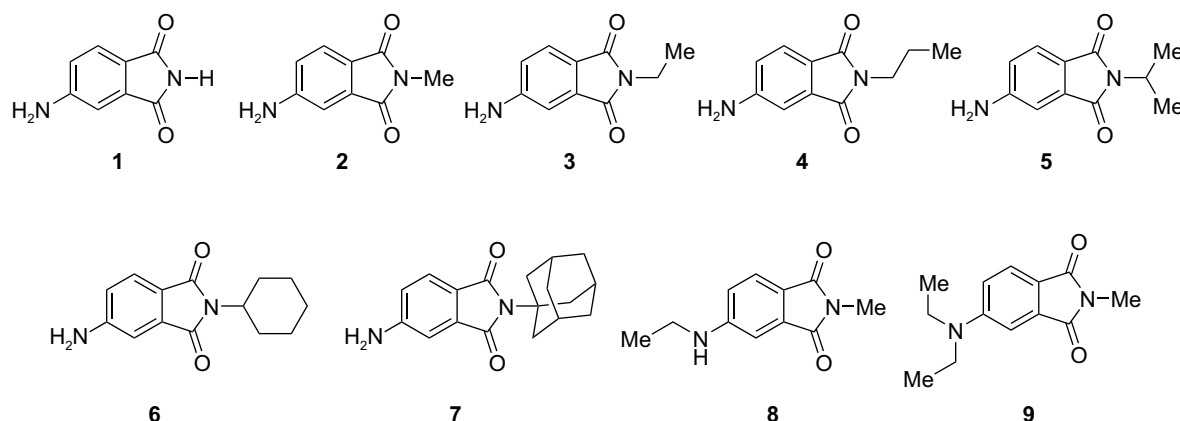


Fig. 1. The structures of 4-aminophthalimide derivatives studied

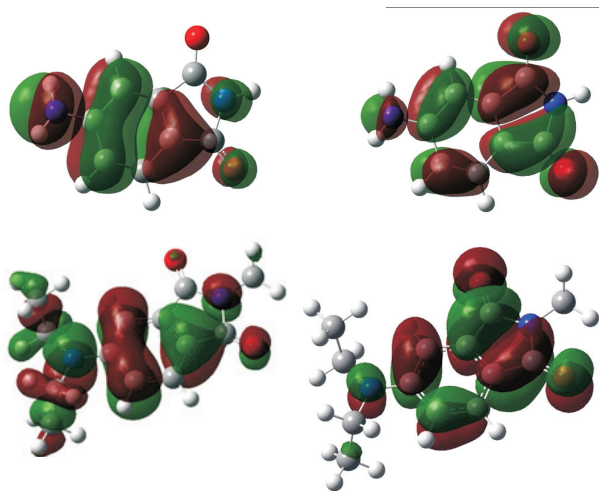


Fig. 2. The structure of HOMO (left) and LUMO (right) corresponding to $S_0 \rightarrow S_1$ transition in 4-aminophthalimide (**1**, top) and 4-(*N,N*-diethylamino)-*N*-methylphthalimide (**9**, bottom) computed at B3LYP/cc-pVTZ

It should be mentioned that the previous TD-DFT computations of the S_1 absorption peak were calculated to be at 344 nm for **1** [13].

The 6-31+G(d,p) basis set tends to overestimate wavelengths by 5 to 24 nm, while cc-pVDZ underestimates them by 3 to 9 nm. Generally, the 6-311++G(2d,2p) basis set provides the best correlation between theory and experiment (less than ± 8 nm deviation). The larger basis set causes an insignificant improvement of the quality, but the deviation on emission spectra (see below) is even larger than for the cc-pVDZ basis set. From the whole set of molecules only 4-(*N*-ethyl)-amino- **8** and 4-(*N,N*-diethylamino)-*N*-methylphthalimides are excited by visible light. The correlation-consistent cc-pVDZ basis set provides the best results for *N*-ethyl- and *N,N*-diethylamino-substituted derivatives **8** and **9** (the exact coincidence and -3 nm deviation compared to $+24$ and $+22$ nm for 6-31+G(d,p) and $+16$ and $+15$ nm for 6-311++G(2d,2p)); it gives a hint of computing the similar structures without including diffuse functions in order to lower computational costs and using even smaller basis sets for estimating excitation energies. For a more adequate evaluation of solvent effects a basis set containing the diffuse functions should be used.

Most excellent agreements were found with the cc-pVDZ basis set for doubly *N,N*-alkylated derivatives **8** and **9**. According to the results of Table 1, the cc-pVDZ basis set failed to reproduce the experimental measurements for *N*-(1-adamantyl)phthalimide **7**. Despite successfully computing excitation energies for **7**, the cc-pVDZ basis set failed to converge on the excited state geometry optimization step. Thus, the 6-31+G(d,p) is sufficient for estimating excitation energies of **7**, and a larger basis set is compulsory for computing fluorescence spectra.

Further, we made an attempt to reproduce the fluorescent properties of **1** and its methyl derivative **2**

with the TD-B3LYP/cc-pVDZ approach (Table 2). The absorption wavelengths obtained from the vertical excitation of **1** with the linear response solvation are in good agreement with the experiment, while the computed emission wavelengths exhibit considerably larger deviation and result in ca 40 nm deviations in the theoretical Stokes shifts from those observed experimentally for **1**. As calculated, the methyl substitution causes an insignificant bathochromic effect in **2** increasing the absorption wavelength by 6–7 nm compared to unsubstituted **1**; it is consistent with the nature of frontier orbitals (see above).

In order to compute the fluorescence wavelengths for all molecules studied a small basis set 6-31G(d) was chosen as it allowed us to optimize the most time-consuming stage of the frequencies calculation of excited states for the whole set of compounds. However, we excluded adamantane derivative as its excited state optimization represented particular challenge. The absorption and fluorescence wavelengths obtained, as well as Stokes shifts, are shown in Table 3.

As noted above, the absorption wavelengths are well reproducible for the whole set of substituted 4-aminophthalimides even when a small basis set is used. Concerning the fluorescence wavelengths, deviations from the experimental spectral data are no more than 25 nm for molecules with only substituted imide moiety (errors in computed Stokes shifts are less than 20%). At the same time, for **8**, which has the ethyl substituent on the amine moiety, the theoretical emission wavelength is 42 nm larger than the experimental emission wavelength. General tendencies in fluorescence wavelengths (a negligible hypsochromic shift for imide-substituted 4-aminophthalimides and remarkable bathochromic shifts for amine-substituted derivatives) were reproduced appropriately by our computations with even rather narrow basis set – 6-31G(d). Calculations using ethanol as a model solvent showed the similar tendencies as observed in other solvents.

As seen from Fig. 3, values of absorption and emission wavelengths for all molecules studied in different solvents are in direct relations with their dielectric constants. Thus, general tendencies in both absorption and fluorescence wavelengths are consistent for all solvents within one molecule.

Experimental part

Experimental spectra were obtained on a Jasco FP-8300 spectrometer. All calculations were performed with the Gaussian09 suite of programs [16]. The B3LYP [17] hybrid functional was selected for the TD-DFT [18–19] computations. The bulk solvent effects were assessed by means of the polarizable continuum model (PCM) [20] in its linear response (LR) formalism for geometry optimizations and frequency calculations, whereas both the LR and state-

Table 1

Maximal absorption wavelengths ($\lambda_{\max}^{\text{abso}}$, nm) determined for substituted 4-aminophthalimides using the TD-B3LYP functional with various basis sets (all data refer to methanol solutions)

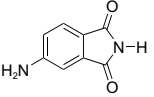
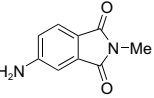
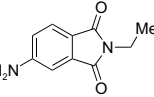
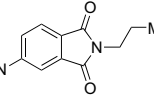
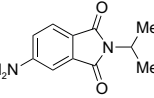
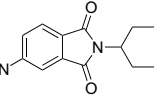
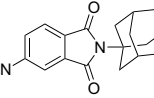
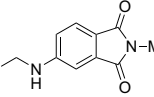
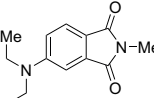
No.	Structure	B3LYP/6-31+G(d,p)	B3LYP/6-311++G(2d,2p)	B3LYP/cc-pVDZ	Exp.
1		380	372	362	371
2		385	378	368	–
3		385	377	368	–
4		385	377	369	376
5		384	376	369	378
6		385	377	370	378
7		381	375	766	374
8		415	407	391	391
9		426	419	401	404

Table 2

Maximal absorption and fluorescence wavelengths computed for 4-aminophthalimide **1** and 4-amino-*N*-methylphthalimide **2** with TD-B3LYP/cc-pVDZ with bulk solvation effects modeled for different solvents

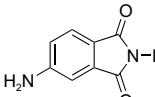
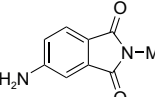
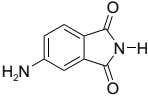
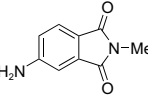
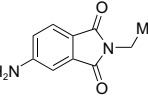
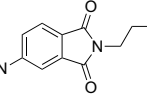
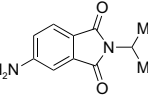
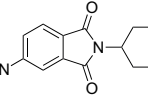
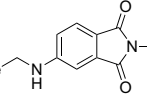
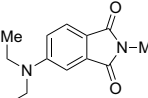
No.	Molecule	Solvent	Theoretical		Experimental	
			$\lambda_{\max}^{\text{abso}}$, nm	$\lambda_{\max}^{\text{fluo}}$, nm	$\lambda_{\max}^{\text{abso}}$, nm	$\lambda_{\max}^{\text{fluo}}$, nm
1		methanol	362	589	371	530
		acetonitrile	362	590	–	–
2		methanol	368	585	–	545
		acetonitrile	369	586	366	475

Table 3

Theoretical and experimental absorption and fluorescence wavelengths, as well as Stokes shifts, computed for a set of 4-aminophthalimide derivatives using IEF-PCM-TD-B3LYP/6-31G(d) approach with bulk solvation effects modeled in methanol

No.	Structure	Theoretical			Experimental		
		$\lambda_{\max}^{\text{abso}}, \text{nm}$	$\lambda_{\max}^{\text{fluo}}, \text{nm}$	Stokes shift, nm	$\lambda_{\max}^{\text{abso}}, \text{nm}$	$\lambda_{\max}^{\text{fluo}}, \text{nm}$	Stokes shift, nm
1		363	553	190	371	530	159
2		369	552	182	–	545	–
3		369	550	180	–	544	–
4		369	549	180	378	543	165
5		369	550	181	378	544	166
6		371	–	–	378	543	165
8		393	597	204	391	555	164
9		404	618	214	404	–	–

specific formalisms were applied to compute transition energies. The Gaussian09 defaults for the PCM cavity definitions were retained in all calculations.

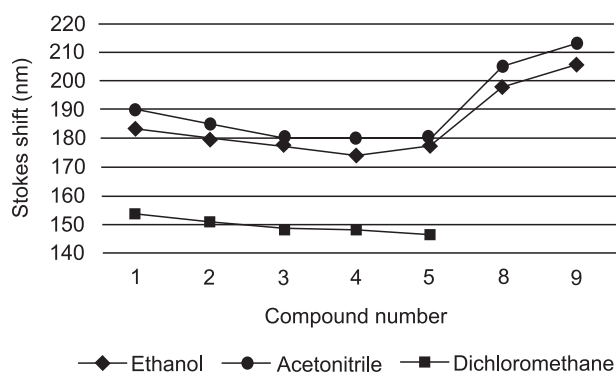


Fig. 3. Stokes shifts computed for a set of 4-aminophthalimide derivatives 1–9 using the IEFPCM-TD-B3LYP/6-31G(d) approach with the bulk solvation model in ethanol, acetonitrile, and dichloromethane

The absorption maxima computed in the presence of the solvent reaction field were determined by using a non-equilibrium model, whereas the excited-state minimizations and the fluorescence calculations in solution were performed within the equilibrium approximation. Absorption and emission wavelengths were computed by the standard algorithm based on the ground state geometry optimization and frequencies (equilibrium solvation), vertical excitation with nonequilibrium solvation, TD-DFT geometry optimization of the excited state structure, computation of vibrational frequencies of the excited state structure, the state-specific equilibrium solvation of the excited state, and computation of the ground state energy with nonequilibrium solvation at the excited state geometry. Absorption wavelengths were obtained from the vertical absorption step; the emission wavelength was calculated by subtracting energies of the equilib-

rium solvated excited state and the nonequilibrium solvated ground state and converting it to the wavelength scale. The Stokes shifts were computed by subtracting vertical absorption and emission energies and converting to the wavelength scale.

Conclusions

Using the TD-B3LYP/6-31G(d) method we computed the absorption and fluorescence wavelengths of 4-aminophthalimide derivatives in methanol, ethanol, acetonitrile, and dichloromethane. They were in good agreement with the experimental measurements. Substitution on the amino group had the most significant impact on the emission spectra. Theoretical errors in the computations of Stokes shifts did not exceed 20% at IEF-PCM-TD-B3LYP/6-31G(d). Absorp-

tion wavelengths computed with vertical approximation even with small basis sets reproduced well the experimental results for all molecules studied, excluding 4-amino-*N*-(1-adamantyl)phthalimide, which was the most challenging task. Using IEF-PCM-TD-B3LYP/6-31G(d) model computations we assessed solvent effects on absorption and emission wavelength in polar protic and aprotic solvents. It turned out that this combination of the solvation model and the basis set gave only approximate evaluation of the solvent effects. Thus, more advanced functionals, different solvation models (including explicit solvation), and larger basis sets are needed to improve the computational prediction.

Conflict of interests: authors have no conflict of interests to declare.

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Received: 24. 12. 2019

Revised: 31. 01. 2020

Accepted: 27. 02. 2020

Acknowledgements

We are grateful to Dr. H. P. Reisenauer (University Giessen) for the help with spectral measurements and the Institute of Organic Chemistry of University Giessen (Prof. Dr. P. R. Schreiner) for computational resources.

The research was carried out according to the budget theme of the Ministry of Education and Science of Ukraine

"Highly effective modification of the metal surface with environmentally friendly compounds to impart new functional properties" (the state registration No. 0117U003854; the research period 2017–2020).