



Molecular structure and spectral properties of thionaphthalimides

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Abstract

The molecular structure and absorption spectra of monothio- and dithio-naphthalimides were compared to their naphthalimide analogues using AM1, PM3 and ZINDO/S semiempirical quantum chemical methods. The substitution of the 4R-naphthalimide oxygen atoms by sulphur atoms resulted in a red-shift of the absorption spectra by $\Delta\lambda_{\max}$ 60–65 and 100–140 nm, respectively. The thionated naphthalimide derivatives do not show observable fluorescence due to intersystem crossing to the triplet $n\pi^*$ -states localised at the C=S groups. The $n\pi^*$ -absorption bands of monothioimides are located at 525–580 nm ($\epsilon = 60$ –80) and those for dithioimides at 535–560 nm ($\epsilon = 140$ –390) and 628–686 nm ($\epsilon = 34$ –68). None of these transitions are solvent sensitive. The $n\pi^*$ -transitions of *N*-phenylthioimides have also a small contribution from $\pi\pi^*$ -states due to a partial conjugation between C=S group and π -electronic system of the *N*-phenyl ring. As a result, the $n\pi^*$ bands of aromatic substituted *N*-phenylthioimides are red-shifted as compared to those of the aliphatic *N*-methyl-thioimides.

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1. Introduction

Naphthalic acid derivatives, particularly naphthalimides of type **1** and **2** (Fig. 1), have a wide range of applications as organic dyes and luminophores [1]. The molecular structure and spectral properties of such compounds has been well investigated and described in various publications [1–8]. The absorption spectra in the visible range of the naphthalimides **1a** and **2a** show only one intensive band (Fig. 2) [2–5]. These compounds have weak fluorescence at room temperature. The quantum yield for

the methylimide derivative **1a** in hexane is 0.005 and in ethanol 0.22 [2]. Several reasons might be the cause for the weak fluorescence but all of them are somehow connected with the nature of a lowest (radiative) singlet state (S_1^*) which is either of a $\pi\pi^*$ - or an $n\pi^*$ -type [3]. Using the absorption, fluorescence, phosphorescence, and photoelectronic spectra of naphthalimides Nurmuhametov et al. [2–4], Demeter et al. [5], Bigotto et al. [6], and others concluded that the radiative state has mostly $\pi\pi^*$ -nature and their low fluorescence quantum yields can be explained by the rather narrow $S_1^{\pi\pi^*}$ – $T_1^{n\pi^*}$ energy gap. The authors also report the energies of singlet and triplet $\pi\pi^*$ - and $n\pi^*$ -states. The electronic transitions for the imide **1a** in ethanol are as follows: $\lambda_{\max}(S_1^{\pi\pi^*}) = 356\text{nm}$,

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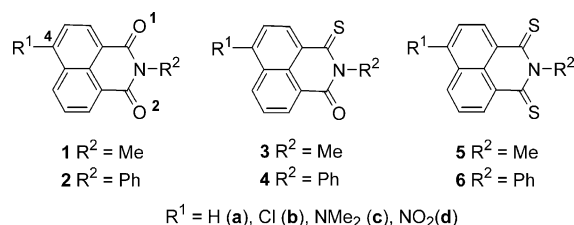


Fig. 1. The molecules studied.

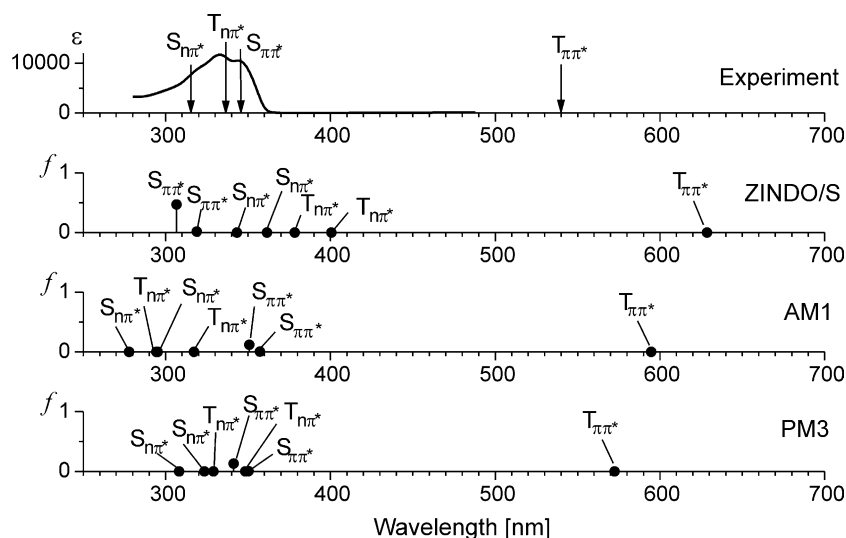
$\lambda_{\max}(S_1^{\pi\pi^*}) = 314 \text{ nm}$, $\lambda_{\max}(T_1^{\pi\pi^*}) = 540 \text{ nm}$, and $\lambda_{\max}(T_1^{n\pi^*}) = 336 \text{ nm}$ [2] (Fig. 2). Mitina et al. [7] has simulated electronic spectra for the *N*-phenylimide **2a** by the PPP CI method and drawn the conclusion that the $S_0 \rightarrow S_1^{\pi\pi^*}$ transition connected with charge-transfer from the naphthalene moiety to phenylimide fragment has low intensity. This could be considered as an additional reason for the observed low fluorescence yield.

The introduction of electron-donating substituents at the 4-position, that is in conjugation with the carbonyl-function, leads to a substantial lowering of the $S_1^{\pi\pi^*}$ -state (Table 1). This reduces the intersystem crossing rates and at the same time increases the probability of the $S_0 \leftrightarrow S_1^{\pi\pi^*}$ transition. As a result, increased fluorescence and a red-shift are observed [1, p.154]. Even the chlorine atom with its weak positive mesomeric effect causes an increase of blue fluorescence in **1b** and **2b** at room temperature, while

the energy of the $S_0 \rightarrow S_1^{\pi\pi^*}$ -transition is only reduced by 440 cm^{-1} . The dimethylamino group of **1c** and **2c** causes substantially larger bathochromic ($\Delta\nu = 5160 \text{ cm}^{-1}$) and bathofluoric effects. These compounds show a dramatic increase in fluorescence quantum yield, e.g. 0.84 for **1c** in hexane [8].

Due to low-level $T_1^{n\pi^*}$ -states the introduction of a nitro-group such as in **1d** and **2d** causes a reduction of the fluorescence quantum yield. Because of their weak conjugation with the central π -electron system via the imide-bridge the nature of the R^2 substituents does not affect the absorption spectra. Thus, the absorption and emission spectral properties of imides **1** and **2** depend only on the $S_1^{\pi\pi^*} - T_1^{n\pi^*}$ energy gap that is mostly the subject of the nature of R^1 among other structural peculiarities. The lowest radiative state in the naphthalimide molecules has $\pi\pi^*$ -nature, while low fluorescence quantum yield of **1a** and **2a** is associated with intersystem crossing into the $T_1^{n\pi^*}$ -state as well as with low probability of the $S_0 \leftrightarrow S_1^{\pi\pi^*}$ transition.

This paper investigates mono- (**3**, **4**) and dithio-naphthalic acid derivatives (**5**, **6**) and compares them to their oxygen analogues **1** and **2** (Fig. 1). The substitution of oxygen by sulphur in **1** and **2** is expected to change the nature and energy of the excited states. We also wanted to see how well the existing semiempirical methods work for simulation of the molecular structure and the spectral properties of those compounds.

Fig. 2. Absorption spectrum in toluene and calculated electronic transitions in **1a**.

2. Experimental

Imides **1a–1d** and **2a–2d** [1,9,10] as well as thioimides **3a–3d**, **4a–4d**, **5a–5d** and **6a–6d** [11] were synthesised and purified according to known procedures.

All absorption spectra were measured at room temperature using a LOMO SF-26 spectrophotometer. The solutions used for the spectral measurements had concentrations (*c*) of about $1\text{--}5 \times 10^{-5}$ mol/l but higher concentrations of $c = 1\text{--}10 \times 10^{-3}$ mol/l had to be used for the measurement of the weak $n\pi^*$ -bands. The solvents for spectral measurements were purified by standard procedures. A mathematical separation of the bands by the second-order derivative method was used to verify the $n\pi^*$ -band characteristics. In this case the crude positions of the individual bands were determined by a second-order derivative and used as starting approximations. Then, the band parameters were varied and each time the resulting curve was compared with the experimental one to get the best fit. The band shape was simulated by both Lorenz and log-normal distributions, which gave about identical results. The difference in positions of $n\pi^*$ -bands obtained by these two approximations was no more than 4 nm. The obtained characteristics of spectral bands are presented in Table 1.

Quantum chemical simulations were carried out by the ZINDO/S [12,13], AM1 [14] and PM3 [15] semiempirical methods that are included in the GAUSSIAN 98 package [16]. The AM1 and PM3, which had been found to be the best semiempirical methods for modelling the molecular and conformational structure of naphthalic acid derivatives [17, 18], were used to calculate the energies under geometry optimisation of the thioimide molecules in the ground state. The geometry optimisation accuracy was 0.01 kcal/mol. The geometry obtained by the AM1 method was used in the ZINDO/S method for the simulations of the electronic transition. The CI included 10 occupied and 10 unoccupied MO.

3. Results and discussion

3.1. Molecular structure of imides and thioimides

Our AM1 and PM3 simulations showed that the 'naphthalimide' moiety in the monothio (**3**, **4**) and

Table 1
The $\pi\pi^*$ and $n\pi^*$ absorption bands measured in toluene

Compound	$\pi\pi^*$ bands		$n\pi^*$ bands	
	λ_{max} (nm)	$\varepsilon \times 10^{-3}$ (l mol ⁻¹ cm ⁻¹)	λ_{max} (nm)	ε (l mol ⁻¹ cm ⁻¹)
1a	335	11.8	—	—
3a	400	12.4	525	77
5a	435	15.9	535	393
			628	68
1b	340	11.8	—	—
3b	405	13.3	530	81
5b	440	11.6	542	273
			643	34
1c	405	10.1	—	—
3c	465	14.6	—	—
5c	525	14.7	—	—
1d	355	8.7	—	—
3d	415	9.9	555	60
5d	445	9.6	558	140
			654	52
2a	335	13.7	—	—
4a	400	14.0	564	70
6a	440	16.8	551	245
			677	47
2b	340	13.2	—	—
4b	408	12.9	567	67
6b	445	22.7	558	351
			686	66
2c	405	9.7	—	—
4c	460	14.3	—	—
6c	523	14.3	—	—
2d	345	8.7	—	—
4d	413	11.1	580	65
6d	445	22.4	576	301
			692	67

dithioimides (**5**, **6**) has the same planar structure as found for the imides **1** and **2** [17,18]. Interestingly these calculations also reveal that the phenyl ring in the sulphur-containing *N*-phenyl derivatives **4** and **6** seems to be more sterically hindered as in **2**. The sterical hindrance is even more significant in case of the monothio imides **4**. There is an evidence that the torsion angle (φ_{ph}) between *N*-phenyl ring and the naphthalic plane in the thioimide molecules can be as much as 90°, while a 50° value has been calculated for the oxygen analogues. The last value is found to be in good agreement with the X-ray data [19].

Table 2

Dipole moments in the ground (μ) and excited (μ^*) states and electronic charges (q) at the heteroatoms X^1 , X^2 and N according to the AM1 simulations

Compound	S_0			μ^* (D)		
	$q(X^1)$	$q(X^2)$	$q(N)$	μ (D)	$S^{\pi\pi^*}$	S_1^*
1a	−0.336	−0.336	−0.322	4.43	4.48 ^a	
3a	−0.158	−0.326	−0.255	4.54	4.71	3.78
5a	−0.135	−0.135	−0.191	4.38	0.25	6.47
1c	−0.345	−0.339	−0.321	5.63	8.12 ^a	
3c	−0.177	−0.331	−0.254	5.77	8.06	4.68
5c	−0.157	−0.147	−0.190	5.93	9.36	1.55
1d	−0.325	−0.322	−0.319	1.30	2.55 ^a	
3d	−0.125	−0.312	−0.254	1.99	3.08	7.17
5d	−0.099	−0.101	−0.190	1.63	2.38	5.76

^a In this case $S^{\pi\pi^*}$ state corresponds to S_1^* .

The dimethylamino group can exist in several conformations that are the same in the imides and thioimides. The most stable conformer with a torsion angle (φ) between the lone pair of the amino-nitrogen and naphthalimide plane is about of 45° and thus provides satisfactory conjugation of the dimethylamino group. The contribution of other conformers is too low to have a major effect. The nitro-group is twisted out of the plane of the naphthalic ring at a torsion angle of about 30° . Unfortunately, we were

unable to find experimental data on the conformation of the *N*-phenyl, dimethylamino and nitro substituents for any of the thionaphthalic acid derivatives.

The imides **1a** and **2a** are highly polarised due to the shift of electron density from the naphthalene moiety towards the imide fragment (Table 2). Electron donor substituents enlarge molecular polarity while electron withdrawing substituents reduce it. A substitution of the oxygen atoms by sulphur substantially decreases the negative charge (q) not only at this heteroatom but also at the imide nitrogen atom.

3.2. Absorption spectra for the thio-naphthalimides

In contrast to the naphthalimides **1** and **2** the absorption spectra of the thioimides **3–6** in toluene (Figs. 3–5) show one intensive band ($\epsilon = 8700\text{--}22700$ [$\text{l mol}^{-1} \text{cm}^{-1}$]) and, typically one or two longer-wavelength low-intensity (ϵ 30–390) bands. The location and intensities of the later bands identifies them as $n\pi^*$ -bands. In general $n\pi^*$ -bands are always hidden underneath the strong $\pi\pi^*$ -band. Mathematical separation was used to rectify the characteristics of these transitions. In case of dimethylamino derivatives we were unable to define the $n\pi^*$ -transitions because a mathematical

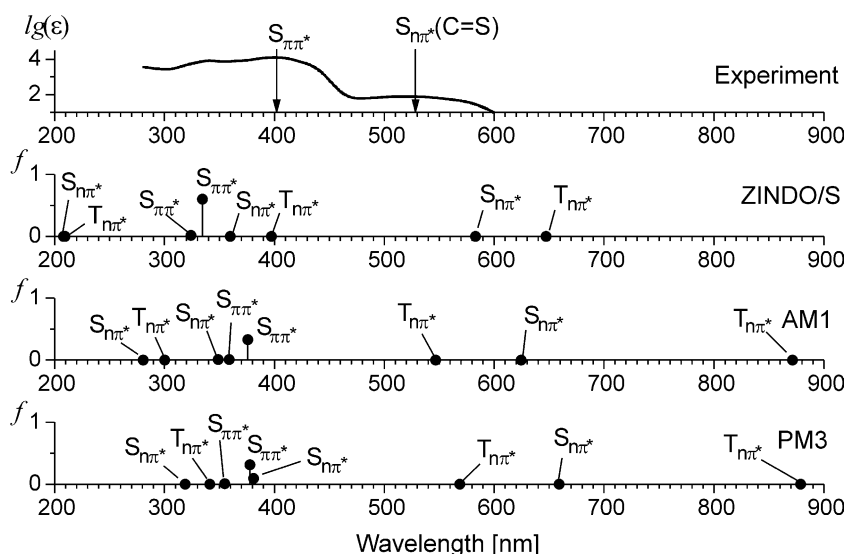


Fig. 3. Absorption spectrum in toluene and calculated electronic transitions in **3a**.

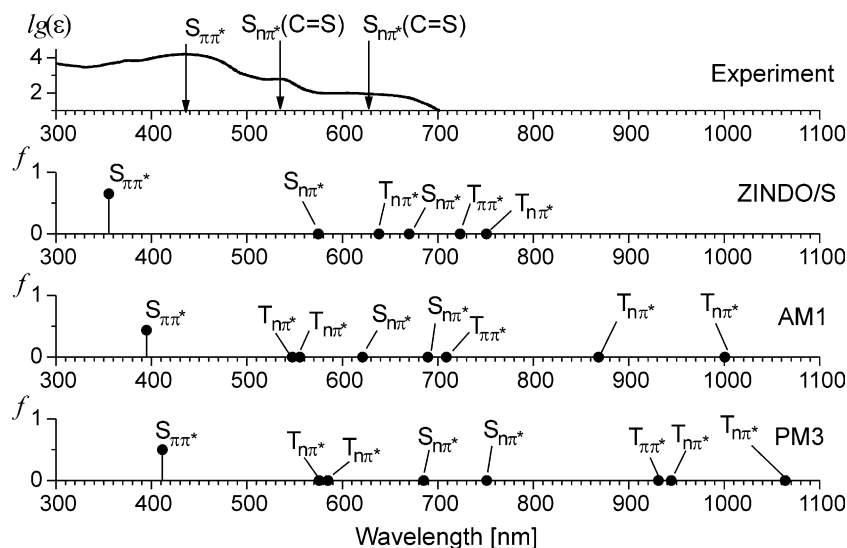


Fig. 4. Absorption spectrum in toluene and calculated electronic transitions in **5a**.

separation was not possible. The obtained data are summarised in Table 1.

3.3. Simulation of the absorption spectra of naphthalimides

For the analysis of the transitions in the absorption spectra we used semiempirical methods that allow to simulate $\pi\pi^*$ - and $n\pi^*$ -transitions of different multiplicity. In order to find the best method for the approximation of experimental data we tested the ZINDO/S [12,13], the AM1 [14] and the PM3 [15] method. The calculation of the electronic transitions for some model imides, e.g. **1a–1c** and **2a–2c** show that the ZINDO/S method incorrectly simulates experimental data [2–6] with respect to the relative location of the lowest $\pi\pi^*$ - and $n\pi^*$ -levels (Fig. 2). Even for the dimethylamino derivatives **1c** and **2c** this method predicts an $n\pi^*$ -nature of the lowest singlet state (Fig. 6). This result clearly contradicts with the observed high fluorescence quantum yield of imides **1c** and **2c**. A wide-range variation of the empirical correction factors f_σ and f_π (which regulate σ and π orbital overlapping) in respect to their standard values ($f_\sigma = 1.267$ and $f_\pi = 0.585$ [13]) does not change the said shortcoming of the ZINDO/S parameterisation. As compared to ZINDO/S, the AM1 and PM3

methods allow a better simulation of the experimental data with regards to the relative location of the $\pi\pi^*$ - and $n\pi^*$ -levels as well as transition energies of the naphthalimides (Figs. 2 and 6).

According to AM1 and PM3 an $S_0 \rightarrow S_1^{\pi\pi^*}$ excitation in **1a** and **2a** does not occur with high probability. The corresponding intensity (f) of an absorption transition for the imide **1a** is only about of 5×10^{-3} (AM1). The $S_0 \rightarrow S_2^{\pi\pi^*}$ transition, which is responsible for the strongest absorption band, also has a much higher intensity ($f = 0.12$ for **1a**, AM1). The energy of the $S_0 \rightarrow S_1^{\pi\pi^*}$ transition does not change under R^1 -substitution but the $S_2^{\pi\pi^*}$ level is lowered to become the lowest $\pi\pi^*$ -type singlet state. The excitation from $S_0 \rightarrow S_1^{\pi\pi^*}$ for both dimethylamino and nitro derivatives results in a significant increase of the dipole moments. Theoretical data are found to be in a good agreement with the spectral peculiarities of naphthalimides. At the same time, all the used theoretical methods (ZINDO/S, AM1 and PM3) underestimate the conjugation effect between the R^1 substituent and the π -electron system of the imide molecules (Table 1). For instance, the calculations predict that the dimethylamino group in **1c** and **2c** ($\varphi = 45^\circ$) causes a bathochromic effect of about 1500 cm^{-1} . Even when the dimethylamino group is fully conjugated with π -electron system ($\varphi = 0^\circ$, in

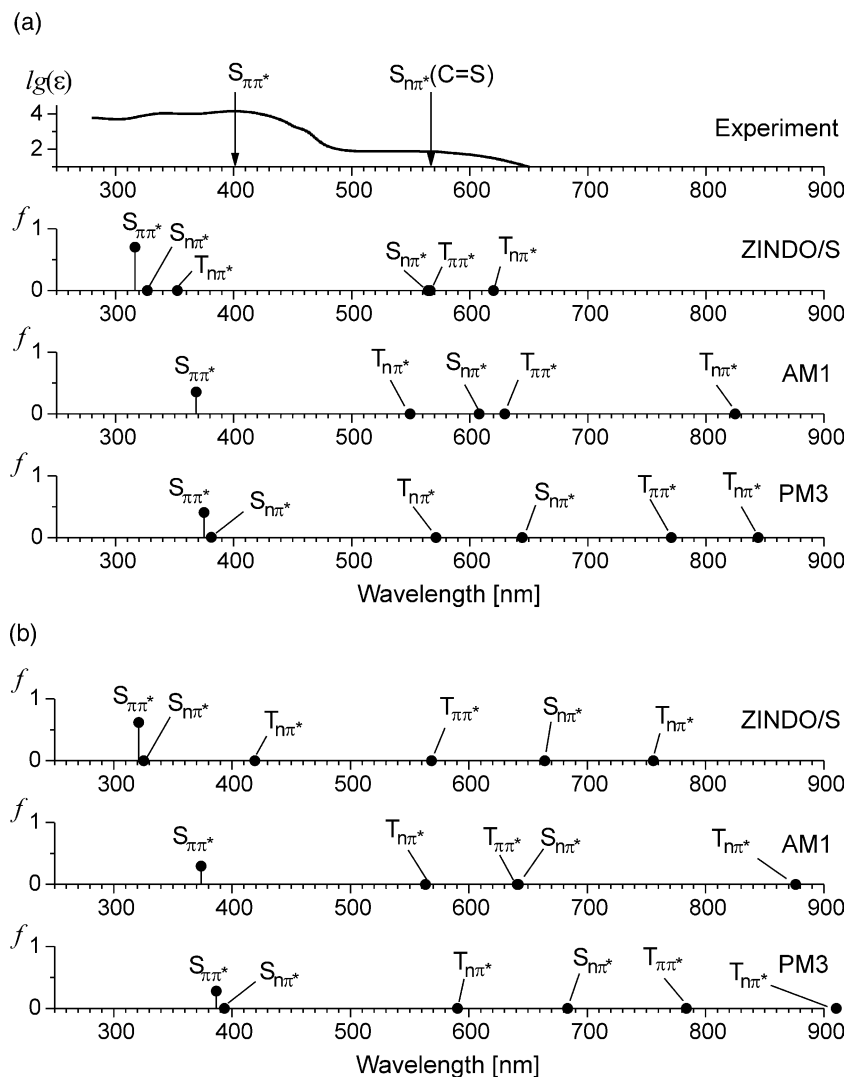


Fig. 5. Absorption spectrum in toluene and calculated electronic transitions in **4a**, where $\varphi_{\text{Ph}} = 90^\circ$ (a) and $\varphi_{\text{Ph}} = 50^\circ$ (b).

its low probability, high energy conformation), the calculated red-shift is only about 1900 cm^{-1} , while the experimental value is about 5160 cm^{-1} .

3.4. Interpretation of the absorption spectra of the thioimides

Theoretical simulations of the imide **1a** (Fig. 2), the monothioimide **3a** (Fig. 3) and the dithioimide **5a** (Fig. 4) using above methods predict that the substitution of oxygen atoms by sulphur results in an inversion of the two lowest singlet $\pi\pi^*$ -levels,

a decrease of the $S_0 \rightarrow S_1^{\pi\pi^*}$ transition energy, and an amplification of its intensity. In addition the blue-shifted carbonyl $n\pi^*$ -transitions are replaced by those of the more red-shifted thio-carbonyl groups. Independent of the used simulation method the calculated values for the electronic transitions and shifts due to thionation are in a good agreement with experimental data. It appears that AM1 and PM3 methods are slightly better than ZINDO/S with respect to predicting the location of the $\pi\pi^*$ -absorption bands.

Substitution of the oxygen atoms in the imides **1** and **2** by one and two sulphur atoms results in

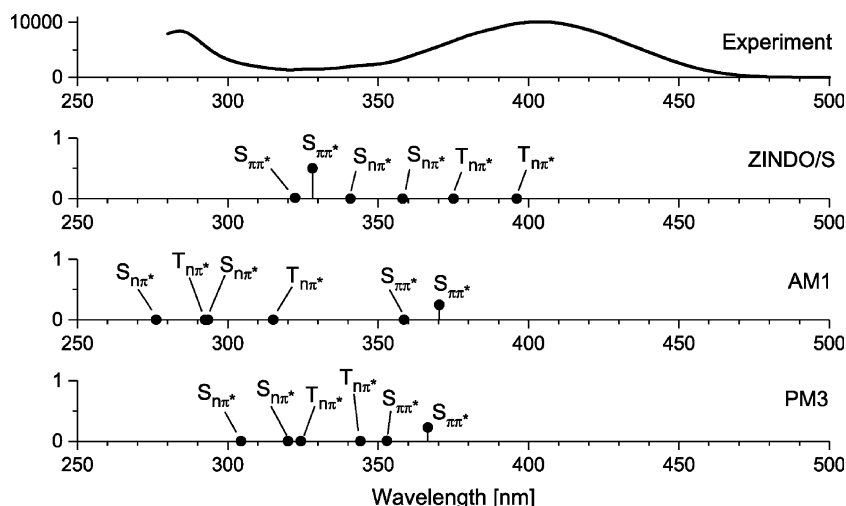


Fig. 6. Absorption spectrum in toluene and calculated electronic transitions in **1c**.

a significant red-shift of the absorption maxima of the mono- (**3**, **4**) and the dithio-imides (**5**, **6**). Neither R^1 substituents of different electronic nature nor R^2 substituents in the imide moiety have an effect on these shifts (Table 1). A bathochromic effect has been also observed earlier in some other classes of thiocarbonyl compounds [3, p.180]. Worth mentioning are also the magnitude of the measured spectral shifts, that are in the range of 3000–4900 cm^{-1} (for monothio) and 5600–7100 cm^{-1} (for dithio) compounds. These values are significantly larger than the calculated ones (1900–2700 and 3200–5100 cm^{-1} , respectively). Based on the obtained experimental and theoretical data we drew the conclusion that the observed decrease in energy of the lowest $S_0 \rightarrow S^{\pi\pi^*}$ transition under thionation is rather due to the higher polarity of the sulphur atom as compared to oxygen atom than a change in the electron withdrawing power of the $C=X$ group ($X=O, S$). Similar effects were observed earlier not only in series of thiocarbonyl compounds but as well for heterocyclic sulphur containing molecules, e.g. the strong long-wavelength shift observed upon replacement of a furan ring by a thiophene moiety in a series of 2,5-diarylazoles has also lead to an increase in polarity [20]. The high polarisability is connected with unoccupied $3d$ -orbitals which are neglected by the used semiempirical methods. This results in the said difference

between the calculated and experimentally obtained energies for an electronic transition.

3.5. Influence of the R^1 substituent

The introduction of an R^1 substituent in the thioimide structure leads to a red-shift of $\pi\pi^*$ -band regardless of the nature (donor or acceptor) of the substituent (Table 1). As in the keto-imide series **1** and **2** the magnitude of the red-shift is underestimated by the ZINDO/S, AM1 and PM3 methods (Figs. 4 and 7). The largest shift caused by a dimethylamino group.

We found evidence that the excitation in the lowest $S^{\pi\pi^*}$ -state of thioimides is accompanied by an increase in dipole moment similarly to that in the imide molecules (Table 2). The increase is small in case of the monothioimide **3a** ($\Delta\mu = 0.2$ D according to AM1) but becomes bigger in the dithioimide molecules and/or under the influence of R^1 substitution. Thus, the highest increase ($\Delta\mu = 2$ D) is observed in the dimethylamino derivative **5c**. The difference in dipole moments results in different solvatochromic properties of the compounds. Thus, no noticeable solvatochromic effects are observed for the thioimide **3a**, while **3c** and **5c** show bathochromic shift of about 1300 and 1800 cm^{-1} , respectively, on changing from toluene to DMF.

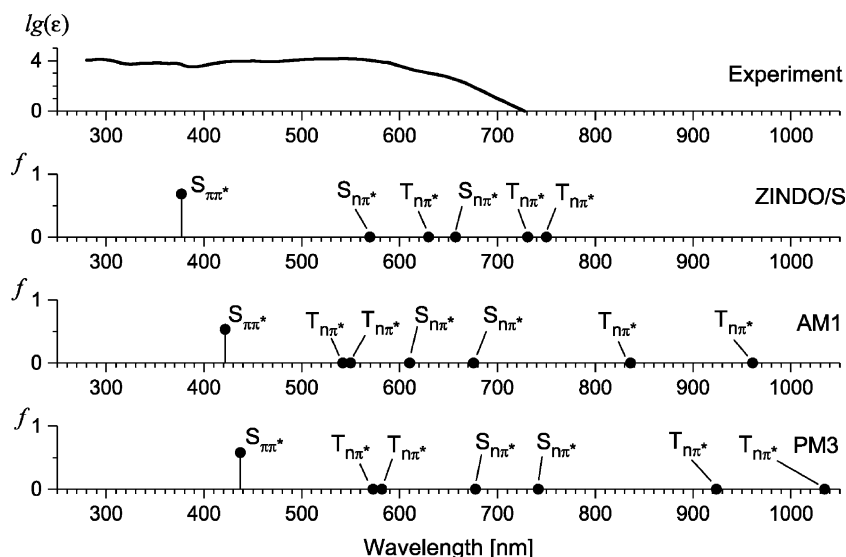


Fig. 7. Absorption spectrum in toluene and calculated electronic transitions in **5c**.

3.6. Thioimide $n\pi^*$ -bands

The $n\pi^*$ -absorption bands for the monothioimides **3** and **4** can be found in the range of 525–580 nm ($\epsilon = 60$ –80), which is the reported spectral region for aromatic thioketones [21, p.114]. The $n\pi^*$ -bands for thiobenzophenone can be found at 588 nm ($\lg \epsilon = 2.0$), for xanthione at 560 nm ($\lg \epsilon = 1.4$) and that for *N*-methylthioacridone at 580 nm ($\lg \epsilon = 1.2$) [3, p.180]. In the dithioimide series **5** and **6** the $n\pi^*$ -absorption exhibits a significantly higher extinction coefficient (up to $\epsilon = 140$ –390) in addition to a spectral shift. While *N*-methylthioimides **5** show bathochromic shifts as compared to **3**, *N*-phenylthioimides **6** undergo hypsochromic shifts as compared to **4** (Table 1). In addition a new $n\pi^*$ -band at 628–686 nm ($\epsilon = 34$ –68) appears in the spectra of dithioimides. The introduction of the R^1 chlorine substituent in **3a**, **4a**, **5a**, and **6a** leads to a moderate red-shift of the $n\pi^*$ -bands. A slightly larger shift is observed on introduction of a nitro group in this position.

The presence of low-level triplet $C=S-n\pi^*$ -states results in strong quenching of the S_1 state in all thionaphthalic derivatives. This suggests that thioimides can be suitable dyes for the development of biomedical markers based on fluorescence quenching

techniques [22–24] as well as for the DNA intercalation and photocleavage processes [25].

Experimentally, the $n\pi^*$ -bands for *N*-phenyl-substituted thioimides shifted towards longer wavelengths compared to those of aliphatic *N*-methylthioimides. However, the quantum chemical simulations of the *N*-phenyl derivatives, using a torsion angle of 90° between phenyl ring and the naphthalic moiety, show the opposite. (Fig. 5(a)). Nevertheless, an adjustment of the torsion angle to 50 – 60° is in agreement with the experimental data (Fig. 5(b)). This suggests that the observed bathochromic shift of the $n\pi^*$ -bands, when *N*-methyl is being substituted by *N*-phenyl, is due to the increase of conjugation of the thio-carbonyl group with *N*-phenyl ring. The calculations also show that the extension of the conjugation results in a slight delocalisation of the $n\pi^*$ transitions towards *N*-phenyl ring. Thus the $n\pi^*$ -transitions in the *N*-phenylthioimides can be considered as not ‘clean’ $n\pi^*$ transitions because they include a small contribution of $\pi\pi^*$ -states. Mixing of $n\pi^*$ -states with $\pi\pi^*$ -states that are localised on the naphthalene moiety can be found in all thioimides. Perhaps this perturbation is responsible for a lack of solvatochromism of the $C=S$ $n\pi^*$ -band. All the $n\pi^*$ -transitions in thioimides (**3**–**6**) in various solvents (toluene, ethanol, DMF, and acetic acid) are

located at the same wavelength, while typically $n\pi^*$ -bands undergo a blue-shift and $\pi\pi^*$ -bands show a red-shift under an increase in the solvent-polarity [3,21, 26]. The same non-solvatochromic behaviour can be found for the $n\pi^*$ -bands of thiobenzophenone, where the C=S bond is in conjugation with the benzene rings. Remarkably, in our investigation of $n\pi^*$ -transitions of compounds **3–6** solvatochromism was not found, despite a noticeable change of dipole moments in some of these molecules (Table 2). The excitation to $n\pi^*$ -states results in an increase of the dipole moment in thioimides **3a**, **5a**, **3c**, and **5c**, but a decrease is obtained for nitro derivatives **3d** and **5d**. Nevertheless, the above data demonstrates that the $n\pi^*$ -bands in all these compounds exhibit a low degree of solvent sensitivity.

4. Conclusions

The subsequent substitution of the 4R-naphthalimide oxygen atoms by sulphur atoms results in a red-shift of absorption spectra of 60–65 nm (mono-substitution) and 100–140 nm (di-substitution), respectively. Thio-naphthalimido-derivatives have no observable fluorescence due to the intersystem crossing in the C=S-triplet- $n\pi^*$ -states. The $n\pi^*$ -absorption bands appear at 525–580 nm ($\epsilon = 60$ –80) for monothioimides and at 535–560 nm ($\epsilon = 140$ –390), and at 628–686 nm ($\epsilon = 34$ –68) for dithioimides. They do not appear to be solvent sensitive. There seems to be evidence that the $n\pi^*$ -transitions in *N*-phenyl-thioimides contain a small fractional contributions of $\pi\pi^*$ -states due to partial conjugation between the lone-pair in the thio-carbonyl groups and the π -electron system of the *N*-phenyl ring. As a result, they appear red-shifted as compared to those of the aliphatic *N*-methyl analogues. The ZINDO/S, AM1 and PM3 parameterisations underestimate the conjugation effect of substituents in the naphthalimides and thionaphthalimides as well as the estimation of the polarisability of the sulphur atoms in the thioimides. The AM1 and PM3 methods are better than the ZINDO/S in simulating the energy of the $S^{\pi\pi^*}$ - and $T^{\pi\pi^*}$ -states in the naphthalic imides and thioimides.

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