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Spectroscopic properties of aromatic dicarboximides
Part 4: *N*-alkyl- and *N*-cycloalkyl-substituted 1,2-naphthalimides

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Abstract

The photophysics of a series of *N*-alkyl- and *N*-cycloalkyl-substituted 1,2-naphthalimides has been investigated. Fluorescence spectra, fluorescence quantum yields and decay times as well as triplet yields are determined in a wide temperature range. The rate coefficients for fluorescence are independent of temperature. However, the rate of non-radiative processes shows characteristic temperature dependence, consisting of a temperature independent and a temperature-dependent component: $k_{nr} = k^{\circ}_{nr} + k_{nr}^{T} = k^{\circ}_{nr} + A_{nr}\exp(-E_{nr}/RT)$, where nr designates either intersystem crossing or internal conversion. The temperature-independent component of internal conversion can be associated with a direct process in which the electronic energy is dissipated by a single mode, probably an aromatic vibrational mode. Vibrational coupling between the two lowest excited states is expected to occur for compounds with *N*-alkyl- (or *N*-cycloalkyl-) groups of high electron donating character, and is expected to increase as the solvent polarity decreases. This results in an efficient and temperature-dependent internal conversion to the ground state (pseudo-Jahn–Teller effect or proximity effect). The temperature-independent component of intersystem crossing may be identified with a barrierless transition from the lowest singlet to a lower-lying $^3(\pi\pi^*)$ triplet state, while the thermally activated isc process is probably a transition to a higher $^3(n\pi^*)$ triplet state.

Keywords: Aromatic dicarboximides; *N*-alkyl- and *N*-cycloalkyl-substituted 1,2-naphthalimides; Photophysics

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1. Introduction

The spectroscopic and photophysical properties of the 1*H*-benz[*e*]isoindole-1,3(2*H*)-dione (further designated as 1,2-naphthalimide), 1*H*-benz[*f*]isoindole-1,3(2*H*)-dione (further named as 2,3-naphthalimide) and 1*H*-benz[*de*]-isoquinoline-1,3(2*H*)-dione (further designated as 1,8-naphthalimide) isomers and of their N-substituted derivatives have been investigated in recent years [1–5]. Significant differences were found between the properties of the N–H and N–CH_3 compounds [1] on one hand and those of the *N*-aryl derivatives [2–5] on the other hand. The former compounds have been shown [1] to emit fluorescence around 390 nm and their triplet and fluorescence yields as well as the fluorescence decay times were found to depend considerably on the site where the dicarboximide moiety is fixed to the naphthalene ring. This was explained by the difference in the energy gap between the lowest $^1(\pi\pi^*)$ singlet excited state and the above lying $^3(n\pi^*)$ triplet state. On the contrary, some *N*-phenyl derivatives emit dual fluorescence (with short-wavelength and long-wavelength components around 390 nm and 495 nm, respectively) and are characterized by very efficient internal conversion which results in short fluorescence decay times and in low fluorescence and triplet yields [2–5]. It was proposed that solvent cage and geometrical relaxations induce efficient internal conversion by virtue of pseudo-Jahn–Teller coupling of the two low-lying excited states [5].

In the present work, we investigate the photophysics of a series of *N*-alkyl- and *N*-cycloalkyl-substituted 1,2-naphthalimides in a wide temperature range. The aim of the study is to reveal how the N-substituent and in particular the electron donating ability of the *N*-alkyl (*N*-cycloalkyl) substituent influences the rate of the photophysical processes, first of all, the rate of the internal conversion process.

2. Experimental details

N-Methyl-1,2-naphthalimide was prepared as described previously [1]. The other derivatives were synthesized from 1,2-naphthalic anhydride (Chemsyn Science Lab.) and the

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corresponding amine. All compounds were purified by thin layer chromatography. *n*-Hexane solvent was of HPLC grade and was used as received. Solution was degassed by several freeze–pump–thaw cycles.

The UV–VIS spectra were obtained on a Hewlett-Packard 8452a spectrometer. Fluorescence spectra were recorded with a home-built fluorimeter equipped with a Princeton 1140 A/B detection system. Fluorescence quantum yields were determined relative to quinine sulfate in 1 N aqueous sulfuric acid solution for which the value of 0.55 was taken [6]. Fluorescence decay times were measured with time-correlated single-photon-counting technique using an Applied Photophysics SP-3 instrument [7]. All measurements could be fitted well by assuming single-exponential decay kinetics.

At 295 K, triplet yields were determined, for all compounds studied, in XeCl excimer laser flash photolysis experiments with the energy transfer method as described in a previous paper [1]. However, 9,10-dichloroanthracene was employed as triplet energy acceptor instead of 9,10-dibromoanthracene. The use of 9,10-dichloroanthracene offers definite advantages: (i) the longer triplet lifetime of the dichloro derivative facilitates more precise determination of the triplet–triplet absorbance after complete energy transfer; (ii) its lower triplet yield is another advantage because only small correction has to be made for the excited triplet formation via direct excitation. In these experiments, *N*-methyl-1,8-naphthalimide in hexane was used as reference compound for which the room temperature triplet yield is accurately known ($\Phi_T = 1.00$) [1]. The triplet yields obtained at temperatures different from 295 K were derived by using the triplet yields determined at 295 K with the energy transfer method and the relative values of the initial (maximum) triplet–triplet absorbances at 500 nm obtained for temperatures T and 295 K.

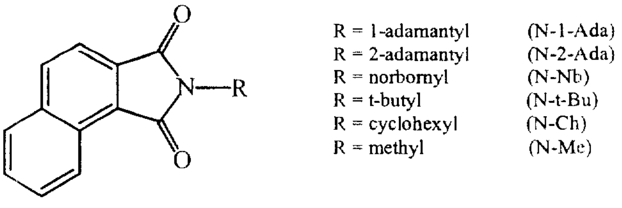
Both fluorescence yields and triplet yields were corrected for the temperature dependence of the absorption at the excitation wavelength.

The quantum yields for internal conversion were obtained by assuming $\Phi_f + \Phi_{isc} + \Phi_{ic} = 1$ on the basis that no reaction was found to occur.

3. Results and discussion

UV absorption and fluorescence spectra as well as photophysical properties (fluorescence yields, fluorescence decay times, triplet yields and internal conversion yields) were determined for the *N*-alkyl- and *N*-cycloalkyl-1,2-naphthalimide series indicated in Scheme 1.

The absorption and fluorescence spectra of *N*-methyl-1,2-naphthalimide in *n*-hexane are presented in Fig. 1. These spectra may be considered as representative for all the derivatives dealt with in this paper. The fluorescence spectra of the *N*-alkyl- and *N*-cycloalkyl derivatives of 1,2-naphthalimide have maxima in the 412–417 nm range.



Scheme 1.

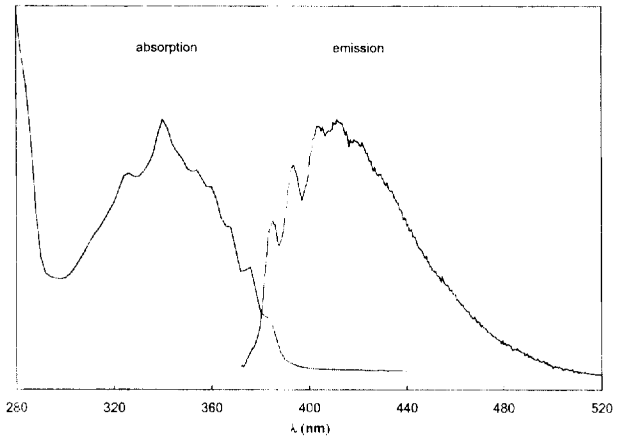


Fig. 1. Absorption and fluorescence spectra of *N*-methyl-1,2-naphthalimide in *n*-hexane at 298 K.

The photophysical properties and rate coefficients obtained at 298 K in *n*-hexane are given in Table 1. The rate coefficients for fluorescence range between 4.3×10^6 s^{-1} and 9.8×10^6 s^{-1} for all N-substituted derivatives; there is no obvious tendency in the variation of k_f with the structure of the N-substituent. Both intersystem crossing and internal conversion are important deactivation pathways of singlet excited molecules at room temperature, however, the rate of these processes varies considerably with the N-substituent. Since non-radiative processes play the determining role in the photophysics of the investigated compounds, this causes a significant variation in the singlet lifetime and fluorescence yield. The experimental data show a tendency corresponding to an inverse correlation between the rate coefficients of the non-radiative processes and the ionization potential of the amine corresponding to the *N*-alkyl- (*N*-cycloalkyl-) group

Table 1
Photophysical properties and rate coefficients for 298 K in *n*-hexane

Compound (IP)	τ (ns)	Φ_f	Φ_{isc}	Φ_{ic}	k_f (10^7 s^{-1})	k_{isc} (10^7 s^{-1})	k_{ic} (10^7 s^{-1})
N-1-Ada (7.3)	0.58	0.0057	0.49	0.50	0.98	85	86
N-2-Ada (7.6)	0.49	0.0045	0.13	0.87	0.92	27	177
N-Nb (7.9)	20.7	0.135	0.43	0.44	0.65	2.1	2.1
N-*t* Bu (8.2)	1.46	0.011	0.87	0.12	0.74	59	8.2
N-Ch (8.2)	27.7	0.12	0.61	0.28	0.43	2.2	1.0
N-Me (8.8)	35.5	0.26	0.56	0.18	0.75	1.6	0.51

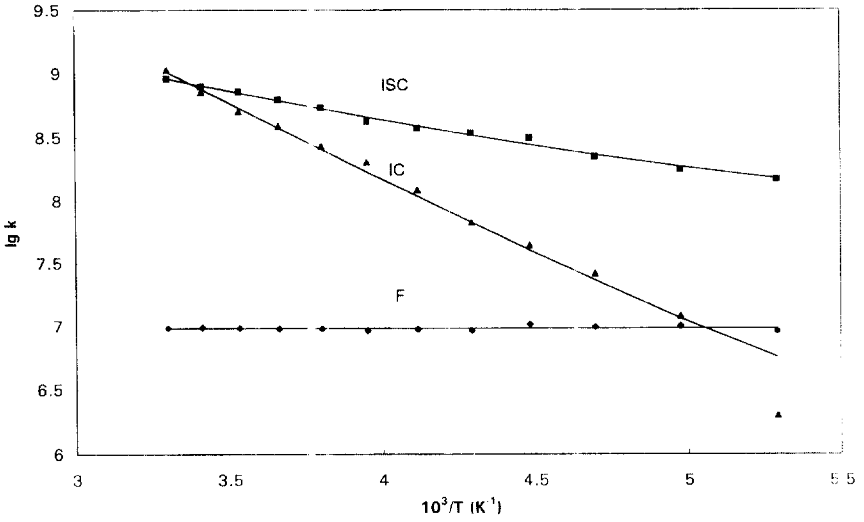


Fig. 2. Arrhenius plot of k_f, k_{isc}, and k_{ic} for *N*-1-adamantyl-1,2-naphthalimide in *n*-hexane.

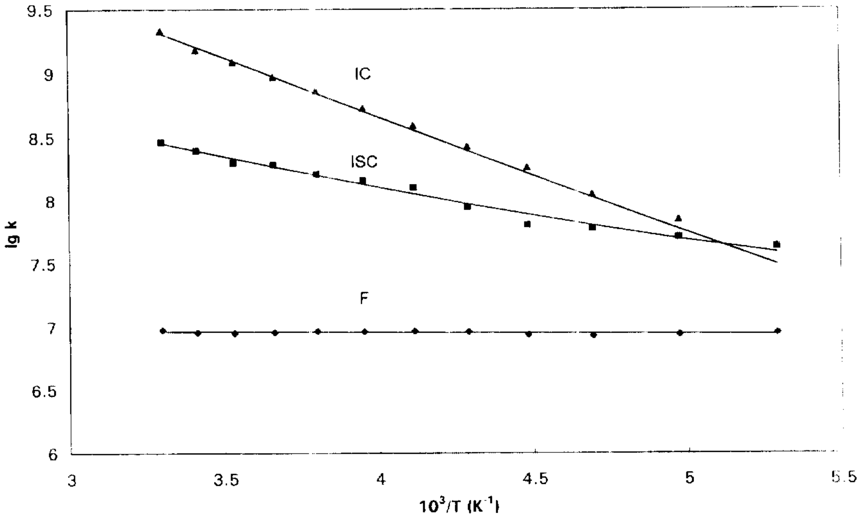


Fig. 3. Arrhenius plot of k_f, k_{isc}, and k_{ic} for *N*-2-adamantyl-1,2-naphthalimide in *n*-hexane.

(see the IP's[1] indicated in bracket in the first column of the tables). The deviation from the expected order in case of *N*-Nb and *N*-*t*-Bu as well as *N*-1-Ada and *N*-2-Ada is believed to be an apparent one which is due to the inaccuracy of the ionization potentials. (Note the large differences between reported IP's even in case of simple alkyl amines [8].) The observed tendency of the reactivity as a function of ionization potentials indicates that the non-radiative processes are enhanced by the increased electron donating ability of the *N*-alkyl- (*N*-cycloalkyl-) substituent of the naphthalimide molecule.

In order to find out more about the nature of the non-radiative processes, the temperature dependence of the photophysical properties has been studied in the temperature range of either 189–303 K or 189–333 K, and the rate coefficients have been obtained as a function of temperature (Figs. 2–7). The rate coefficients for fluorescence are temperature-independent, however, those of the non-radiative processes show characteristic temperature dependences. Both the intersystem crossing and the internal conversion rate coefficients consist of a temperature-independent and a temperature-dependent component:

$$k_{nr}=k^{\circ}_{nr}+k^{T}_{nr}=k^{\circ}_{nr}+A_{nr}\exp\left(-E_{nr}/RT\right) \qquad (1)$$

where nr designates either intersystem crossing or internal conversion.

The temperature-independent rate coefficients for intersystem crossing (k°_{isc}) and internal conversion (k°_{ic}), as well as the temperature-dependent rate parameters for isc ($k_{isc}{}^{T}$) and ic ($k_{ic}{}^{T}$) were obtained by fitting Eq. (1) type functions to the experimental data. Rate coefficients for 189 K and 303 K are given in Table 2 to represent typical low temperature and high temperature kinetic data.

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[1] The IP's are rough estimates obtained from semiempirical calculations using the Zindo-1 method which gave reasonably good agreement with the experiment [8].

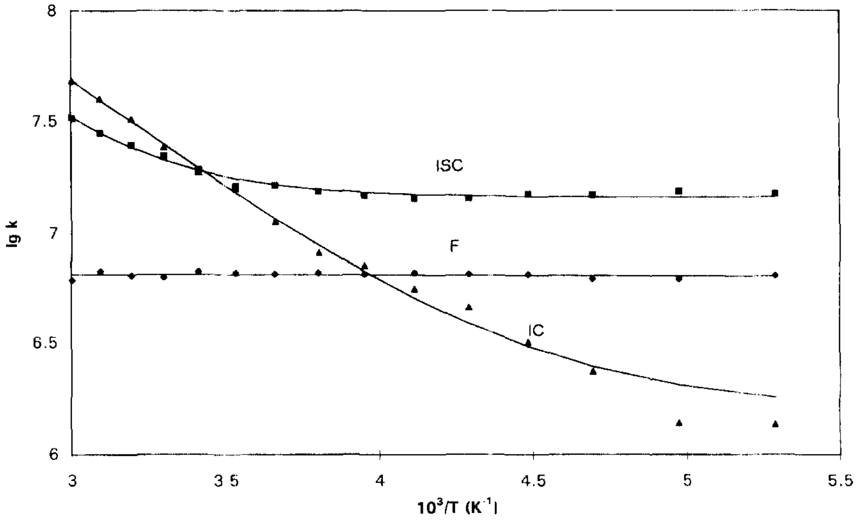

Fig. 4. Arrhenius plot of k_f, k_{isc} and k_{ic} for *N*-norbornyl-1,2-naphthalimide in *n*-hexane.

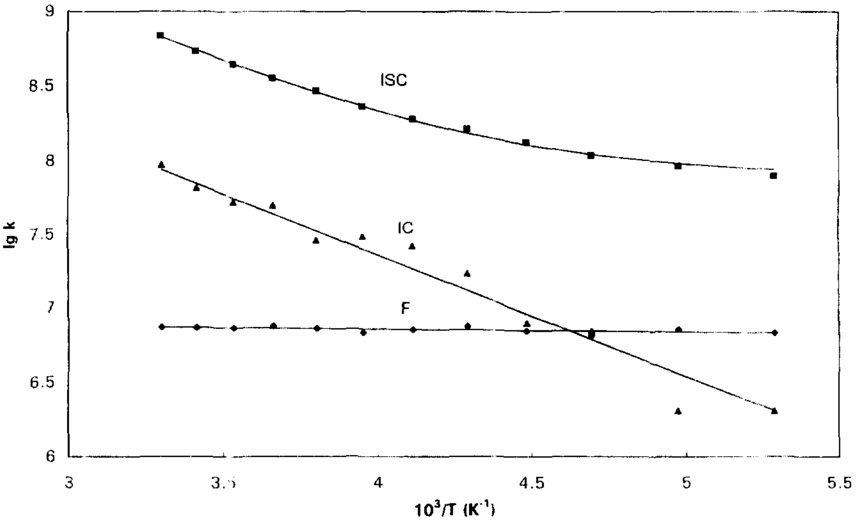

Fig. 5. Arrhenius plot of k_f, k_{isc} and k_{ic} for *N*-*t*-butyl-1,2-naphthalimide in *n*-hexane.

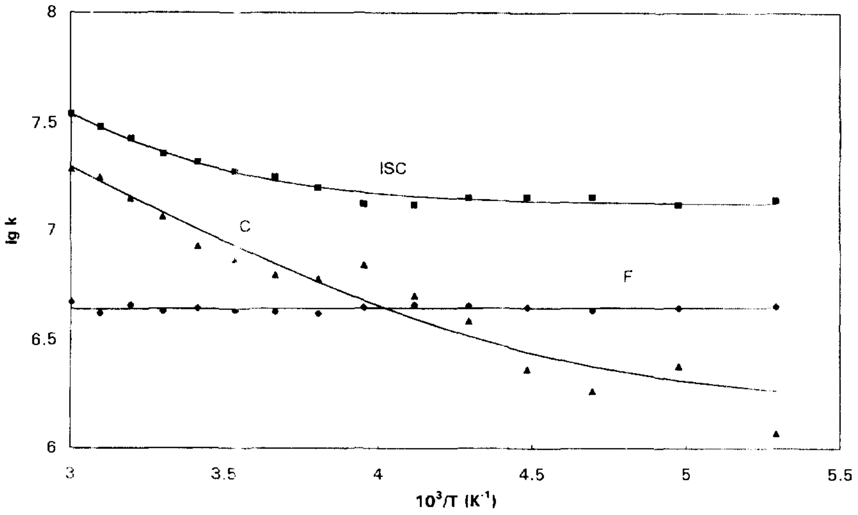

Fig. 6. Arrhenius plot of k_f, k_{isc} and k_{ic} for *N*-cyclohexyl-1,2-naphthalimide in *n*-hexane.

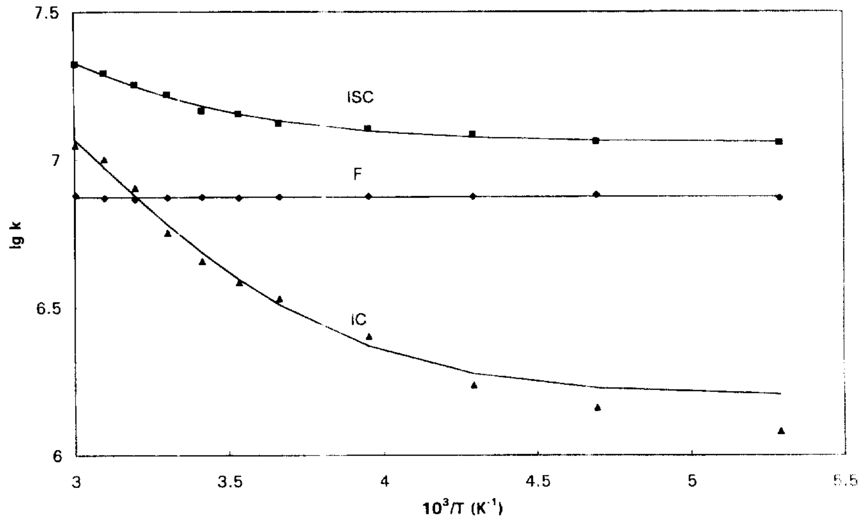

Fig. 7. Arrhenius plot of k_f, k_{isc}, and k_{ic} for *N*-methyl-1,2-naphthalimide in *n*-hexane.

Table 2
Temperature-independent (k°) and temperature-dependent (k^{T}) rate coefficients for non-radiative processes in *n*-hexane

Compound (IP)	Intersystem crossing			Internal conversion		
	k°_{isc} (10^7 s^{-1})	k_{isc}^{189} (10^7 s^{-1})	k_{isc}^{303} (10^7 s^{-1})	k°_{ic} (10^6 s^{-1})	k_{ic}^{189} (10^6 s^{-1})	k_{ic}^{303} (10^6 s^{-1})
N-1-Ada (7.3)	7.2	7.9	84	1.6[a]	4.12	1030
N-2-Ada (7.6)	1.6	2.2	27	1.6[a]	29.3	2050
N-Nb (7.9)	1.5	< 0.1	0.68	1.6	0.22	24
N-*t*-Bu (8.2)	7.8	0.9	60	1.6[a]	1.88	88
N-Ch (8.2)	1.3	< 0.1	1.0	1.9	0.26	10
N-Me (8.8)	1.1	< 0.1	0.50	1.3	< 0.1	4.5

[a] Assumed value (see text).

Rate coefficients for fluorescence are not included in the table since they are invariant in the investigated temperature range (and are independent of the *N*-alkyl substituent, see above). The k°_{isc} and k°_{ic} temperature-independent components of the rate parameters of the non-radiative processes do not change significantly from one compound to the other. This was verified experimentally for k°_{isc} in case of most of the compounds studied, which gave an average of $k^{\circ}_{isc} = (1.4 \pm 0.3) \times 10^7$ s^{-1}. However, significantly higher values were obtained for two compounds (*N*-1-Ada and *N*-*t*-Bu) where the alkyl group is connected to the N-atom through a tertiary C-atom. (This deserves further investigations.) Regarding the internal conversion rate coefficients, accurate k°_{ic} values could be determined in the available temperature range only for *N*-Me, *N*-Ch and *N*-Nb, which gave an average of $k^{\circ}_{ic} = (1.6 \pm 0.3) \times 10^6$ s^{-1}. For the rest of the compounds, measurements at temperatures below 189 K would have been required to obtain reliable rate coefficients, however, the freezing of the solvent limited the usable temperature range. The temperature-independent internal conversion could be well represented by a single value of $k^{\circ}_{ic} = 1.6 \times 10^6$ s^{-1} for all of the compounds studied. Therefore, curve fitting and extraction of k_{ic}^{T} from the experimental data was carried out for *N*-1-Ada, *N*-2-Ada and *N*-*t*-Bu with a fixed k°_{ic} value of 1.6×10^6 s^{-1}.

The temperature-dependent components of both the isc and the ic processes vary in the series; the k_{nr}^{T} values increase with increasing electron donating ability of the *N*-alkyl- (*N*-cycloalkyl-) group, for which the decrease of the IP's of the appropriate *N*-alkyl- (*N*-cycloalkyl-) amines is considered an appropriate measure. Therefore, we conclude that the correlation between the overall rate parameters of the non-radiative processes and the amine ionization potentials actually reflects an inverse correlation between the temperature dependent component of the rate coefficient of isc (k^{T}_{isc}) and ic (k^{T}_{ic}) on one hand and the amine ionization potentials on the other hand.

Considering the kinetic data presented in Table 2, the temperature-independent non-radiative processes (i.e., those characterized by the rate coefficients k°_{isc} and k°_{ic}) are expected to be dominant at very low temperatures. Even at 189 K (the lowest temperature of our measurements), the temperature-independent processes are rate determining for the naphthalimides with *N*-alkyl- (*N*-cycloalkyl-) substituents of small electron donating ability (i.e., *N*-Me, *N*-Ch, *N*-Nb and *N*-*t*-Bu), while the rates of the temperature-independent and temperature-dependent non-radiative processes are roughly comparable for the two adamantyl derivatives. Since $k^{\circ}_{isc} \geq k^{\circ}_{ic}$, the dominant photophysical processes at low temperatures is the temperature-independent intersystem crossing from the excited singlet to the triplet state.

At higher temperatures (i.e., around 303 K and above), the greater contribution to the rate of non-radiative processes comes from the temperature-dependent reactions. This is especially so for the adamantyl derivatives characterized by *N*-cycloalkyl substituents of high electron donating ability (see Table 2).

Because derivation of the Arrhenius parameters for the temperature-dependent isc and ic processes required fitting of a three-parameter equation (see Eq. (1)), only rough estimates were obtained for the *A*-factors and activation energies. The most important conclusion which emerges from these estimations is that *the variation of the rate of the temperature-dependent internal conversion* (k_{ic}^T) *is determined by the variation of the A-factor rather than that of the activation energy.*

The activation energies of the ic processes range between 15 and 23 kJ mol^{-1} and show no systematic variation while the A_{ic}-factors increase by more than two orders of magnitudes from the *N*-methyl (approx. 10^{10} s^{-1}) to the *N*-adamantyl derivatives with increasing electron donating ability of the substituent ($A_{ic}/10^{10}$ s^{-1} = 2.0 (*N*-Me), 0.6 (*N*-Ch), 4.0 (*N*-*t*-Bu), 6.3 (*N*-Nb), 160 (*N*-2-Ada), 630 (*N*-1-Ada)). Moreover, the variation of the temperature-dependent intersystem crossing rate (k_{isc}^T) largely depends on the activation energies. Thus, the relatively low activation energies of the *N*-adamantyl derivatives (approx. 10 kJ mol^{-1}) and of *N*-*t*-Bu (approx. 16 kJ mol^{-1}) explain the high isc rate coefficient of these compounds.

The two components of ic and isc in the rate coefficient expression (1) indicate that both internal conversion and intersystem crossing are achieved along two pathways, one is a temperature-independent reaction and the other one is a thermally activated process.

The temperature-independent component of internal conversion can be associated with a direct process in which the electronic energy is dissipated by a single vibrational mode. Since the k°_{ic} is found to be practically independent of the *N*-alkyl structure, the dominant vibrational mode is expected to be one of the vibrational modes of the 1,2-naphthalimide moiety, probably an aromatic vibrational mode [9,10].

The efficient internal conversion observed in the photophysics of *N*-phenyl-naphthalimides has been explained by solvent cage and geometrical (twisting) relaxation induced pseudo-Jahn–Teller coupling of the low-lying singlet excited states (proximity effect) [5]. However, in case of *N*-alkyl-1,2-naphthalimides, the two lowest unrelaxed singlet states may be well separated, therefore, the possibility of relaxation induced vibronic interaction between these states requires careful consideration.

In the explanation of the effect of the *N*-alkyl- (*N*-cycloalkyl-) substituent on the photophysics we assume—in accordance with the model suggested for the *N*-phenyl-naphthalimides [5]—that the electron transfer in the $S_0 \rightarrow S_1$ transition occurs from the naphthalene moiety to the π^* orbitals of the carbonyl groups giving a S_1 singlet state (of $^1A_2$ symmetry), while electron transfer in the $S_0 \rightarrow S_2$ transition occurs from the amine moiety to the π^* orbitals of the carbonyl groups resulting in a S_2 singlet state (of $^1B_1$ symmetry). Therefore, a change of the *N*-alkyl substituent is expected to change the energy of the S_2 state.

The position of the excited state energy levels of *N*-Me in polar solvents were estimated [1] and the energy gap between $S_1(\pi\pi^*)$ and $S_2(n\pi^*)$ was found to be around 63 kJ mol^{-1}. The change of the solvent from a polar to a nonpolar one is expected to increase the energy of the $\pi\pi^*$ state and decrease considerably that of the $n\pi^*$ state (see for instance the case of fluorenone where this effect causes a reversal in the order of the two lowest singlet excited states [11]). Therefore, the gap between the $S_1(\pi\pi^*)$ and $S_2(n\pi^*)$ singlet excited states of *N*-Me in *n*-hexane (the solvent used in the present work) is expected to be significantly smaller than in a polar solvent. Nevertheless, the separation of S_1 and S_2 remains probably big enough to exclude considerable interaction between the two lowest singlet excited states of *N*-Me. However, replacement of the *N*-Me group by other groups of higher electron donating ability results in a decrease of the S_2 state energy and consequently in a vibronic coupling of the two lowest singlet excited states in *n*-hexane. This coupling is expected to be weaker in case of compounds *N*-Ch, *N*-*t*-Bu, and *N*-Nb, while it is stronger for the two adamantyl derivatives characterized by N-substituent groups of high electron donating ability.

As a consequence of the vibronic coupling of the two low-lying excited states, efficient internal conversion is expected to occur (pseudo-Jahn–Teller effect [12,13] or proximity effect [14]). Internal conversion efficiency depends on the extent of coupling and hereby on the electron donating ability of the N-substituent.

Two consequences, which are in accordance with the experimental observations, immediately derive from this model: (i) vibrational coupling between the two lowest excited states is expected to be stronger and radiationless decay to be more efficient for compounds with *N*-alkyl groups of higher electron donating character; (ii) if vibrational coupling results in a very low frequency of the vibronically active mode in the lower state, this causes a strong temperature dependence of internal conversion, because the excited levels of the active mode are thermally populated to a great extent [15–17]. This explains the temperature-dependent component of internal conversion.

The fact that intersystem crossing just like internal conversion consists of a temperature-independent and a temperature-dependent component may suggests that isc and ic have something common in their mechanisms.

The information available on the triplet state energies of the *N*-alkyl-1,2-naphthalimides is very meagre which renders interpretation of the experimental results difficult. An estimation of the singlet and triplet energy levels of *N*-methyl-1,2-naphthalimide in acetonitrile [1] shows the lowest triplet state (a $\pi\pi^*$ state) to be below and the second triplet state (a $n\pi^*$ state) to be above the lowest $\pi\pi^*$ singlet state. The temperature-independent component of intersystem crossing may be identified with a barrierless transition from the lowest singlet to a lower-lying triplet state. The S_1–T_1 energy gap is probably similar for all investigated compounds which explains the constant k°_{isc} rate coefficients in the series. The thermally activated intersystem crossing process is probably achieved by singlet state coupling with a higher triplet level, however, further research is required to reveal the nature of this process.

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