Excited State Processes of 2-Butylamino-6-methyl-4-nitropyridine *N*-oxide in Nonpolar Solvents. A Transient Absorption Spectroscopy Study

Joost de Klerk,[†] Ivo H. M. van Stokkum,[†] Anna Szemik-Hojniak,[‡] Irena Deperasińska,[§] Cees Gooijer,[†] Hong Zhang,^{||} Wybren-Jan Buma,^{||} and Freek Ariese^{*,†}

Laser Centre Vrije Universiteit Amsterdam, The Netherlands, Department of Chemistry, University of Wroclaw, Poland, Institute of Physics, Polish Academy of Sciences, Warsaw, Poland, and Van't Hoff Institute for Molecular Sciences, University of Amsterdam, The Netherlands

Received: October 2, 2009; Revised Manuscript Received: January 15, 2010

Earlier steady-state fluorescence studies showed that 2-butylamino-6-methyl-4-nitropyridine *N*-oxide (2B6M) can undergo fast excited-state intramolecular proton transfer (ESIPT). In a nonpolar solvent such as *n*-octane, both normal and tautomeric fluorescence was observed. Strikingly, the relative ratio of those two emission bands and the fluorescence quantum yield of the normal emission were found to depend on the excitation wavelength in violation of the Kasha–Vavilov rule. In this work, the system was investigated further by means of transient absorption spectroscopy, followed by global and target analysis. Upon excitation at 420 nm, a normal excited singlet state $S_1(N)$ is reached, which decays in about 12 ps via fluorescence and ESIPT (minor pathways) and to a long-lived "dark" state (major pathway) that is most probably the triplet $T_1(N)$. Upon 330 nm excitation, however, a more complex pattern emerges and additional decay channels are opened. A set of four excited-state species is required to model the data, including a hot state $S_1(N)$ * that decays in about 3 ps to the tautomer, to the long-lived "dark" state and to the relaxed $S_1(N)$ state. A kinetic scheme is presented that can explain the observed transient absorption results as well as the earlier fluorescence data.

Introduction

Pyridine *N*-oxides attract attention in various chemical disciplines. They find use as catalysts, reactive intermediates, drugs in the pharmaceutical chemistry, and ligands in metal complexes.^{1,2} The NO moiety of the pyridine *N*-oxide can act as electron acceptor and as electron donor. The strength can be modulated by electron donating or electron accepting groups at other positions of the pyridine ring. By inserting an *N*-alkyl group at the 2-position a molecule is created in which the amino proton might be transferred to the NO-moiety upon excitation.³ 2-Butylamino-6-methyl-4-nitropyridine *N*-oxide (2B6M) is an excellent model compound for studying such interactions; its structure is given in Figure 1. In fact, for 2B6M both excited-state intra- and intermolecular proton transfer might be possible; the latter is observed under conditions where dimers are formed.⁴

Steady-state absorption and emission spectra of 2B6M have already been reported in refs 3–6. A strong solvent dependency of the emission spectra of 2B6M was observed. Poór et al. noted a Stokes' shift as large as 8000 cm^{-1} in acetonitrile, whereas in the apolar solvent *n*-octane this Stokes' shift is much smaller.⁵ However, the room temperature absorption spectra in these solvents show only minor differences.

Poór and co-workers also studied 2B6M in polar, aprotic solvents by means of femtosecond transient absorption and picosecond time-resolved emission experiments and elucidated the electronic and structural dynamic processes occurring after excitation.⁵ They showed that the enormous solvent dependence of the emission wavelength is caused by excited-state intramo-



Figure 1. Structure of 2-butylamino-6-methyl-4-nitropyridine *N*-oxide (2B6M).

lecular proton transfer (ESIPT), which is very efficient in the polar solvent acetonitrile. After excitation of 2B6M the resulting charge transfer triggers an ultrafast (~100 fs) intramolecular proton transfer from the amino to the N–O group.⁵ Because of this efficiency, in acetonitrile only the red-shifted tautomer emission is observed and fluorescence from the normal form is fully quenched. On the contrary, de Klerk et al. reported that in *n*-octane the emission of the normal form is the most intense, whereas the tautomer emission is less red-shifted than in acetonitrile and fairly weak. Furthermore, as outlined in a previous paper considering steady-state spectra the excited state processes in nonpolar solvents are much more complex.⁶

In fact, the photophysics and photochemistry of 2B6M in *n*-octane was shown to be exceptional, exemplified by an anomalous fluorescence behavior. The fact that fluorescence of both the normal form and the tautomeric form could be observed is not unexpected as such, but in contrast to what is normally found their intensity ratio depends on the excitation wavelength. Specifically, excitation at 420 nm $(S_0 \rightarrow S_1)$ leads to a higher

^{*} To whom correspondence should be addressed. Tel. +31 20 587524. Fax +31 20 5987543. E-mail: ariese@few.vu.nl.

[†] Laser Centre Vrije Universiteit Amsterdam.

^{*} University of Wroclaw.

[§] Polish Academy of Sciences.

[&]quot;University of Amsterdam.



Figure 2. Various processes operative in excitation and emission of 2B6M in *n*-octane as previously proposed in ref 6.

yield of "normal" fluorescence than excitation at shorter wavelengths. This is in violation of the Kasha-Vavilov rule, which states that in liquid solutions after excitation to a higher electronic state the molecule decays with 100% efficiency to the lowest vibrational level of the S₁-state, and that the fluorescence quantum yield should not depend on the excitation wavelength.⁷ Usually, a difference between the excitation and the absorption spectrum indicates the presence of more than one coexisting ground-state species. However, that possibility was rejected because we could prove that in the case of 2B6M in *n*-octane over a large range of concentrations only a single ground-state species is present, that is, the monomeric form of 2B6M.6 These unusual fluorescence results could be explained by assuming a proton transfer reaction pathway that not only starts from the lowest vibrational level of the S₁-state but also from a higher state, apparently with a rate that enables effective competition with internal conversion.

In order to facilitate the discussion and interpretation of the time-resolved absorption experiments of the current paper, we depict in Figure 2 the previously proposed scheme,⁶ showing the various processes operative in excitation and emission of 2B6M in *n*-octane. This scheme could account for the dependence of the excitation spectrum on the emission wavelength and also the dependence of the fluorescence quantum yield on the excitation wavelength. We assumed a proton transfer reaction that not only starts from the lowest S₁-state but also from a higher state. The rate of ESIPT_{S2} must be 1.1 times that of internal conversion (IC) IC_{S2} to account for the observed differences in fluorescence quantum yield of N at the two excitation wavelengths, 330 versus 420 nm.⁶

To test this model and further understand the excited state processes of 2B6M in *n*-octane, femtosecond transient absorption measurements were carried out. With that technique, we could also obtain information on the temporal evolution and relative abundancies of nonemitting species, which turned out to play a major role. A new and more complete kinetic model that includes these new results will be presented in the current paper.

Experimental Section

Materials. The synthesis of 2-butylamino-6-methyl-4-nitropyridine *N*-oxide (2B6M) has been described.⁵ The purity was checked by GC/MS using a 30 m DB5MS column (J&W Scientific, Folsom, CA, USA), scan range m/z 35–350. For the measurements, solutions were used with a 2B6M concentration of 1 mM in *n*-octane (Aldrich anhydrous grade, purity >99%). Under those conditions 2B6M exists exclusively as a monomeric species; previous room temperature absorption measurements in the same solvent at different levels between 5×10^{-7} and 1×10^{-3} M showed no sign of dimer formation or aggregation.⁶

Apparatus. The fast dynamics after femtosecond pulse excitation were studied by femtosecond transient absorption. The setup is described in detail in ref 5. An amplified Ti:Sapphire laser system (Spectra Physics Hurricane, Mountain View, CA) was used to produce a 100 fs laser pulse of $\sim 1 \text{ mJ}$ pulse energy with a repetition rate of 1 kHz. This laser pulse was split into two beams, of which one pumped an OPA to produce UV or blue pulses to excite the sample. The other beam was used to generate a white light continuum in the range of 350-900 nm to probe the photoinduced changes in absorption. The angle between the pump beam and probe beam was typically $7-10^{\circ}$. To guarantee a homogeneous optical density the pump beam irradiated a larger area of the sample than the probe beam. The instrument response function (IRF) was about 200 fs. The experiments were carried out under magic angle conditions to avoid the influence of rotational motion on the detection of the dynamics of the probe molecules. Transient absorption spectra were recorded up to 1 ns after the excitation pulse.

Homemade software in Labview was used for the collection of the transient absorption data. The complex spectra were processed by a global and target analysis,⁸ from which the rate constants of a kinetic scheme and the species-associated difference spectra (SADS) were estimated.

Results and Discussion

Excitation at 420 nm. As an illustration, Figure 3A shows a selection of the raw transient absorption spectra at different time points (1, 3, 10, and 80 ps) upon excitation at 420 nm (corresponding to the S_0-S_1 transition). The global analysis of these transient absorption data obtained at 420 nm reveals that they can be fitted with a model consisting of three species. The SADS and decay rates obtained for these analyses are given in Figure 3B. On a very short time scale close to the laser pulse presumably the Franck–Condon state is observed (not shown); it takes about 200 fs to reach the equilibrium in the S_1 (N)-state (the S_1 -state of the normal form). Its corresponding spectrum 1 subsequently transforms into both spectrum 2 and 3:

• Spectrum 1: Within 200 fs, a broad absorption spectrum from 550 to 800 nm emerges, accompanied by bleaching at 420 nm (wavelength of the pump laser) and a stimulated emission band from 450 to 550 nm. The stimulated emission band and the absorption band have the same rise time (less than 200 fs). Spectrum 1 decays in about 12 ps.

• Spectrum 2: Subsequently, a strong absorption band from 450 to 600 nm appears with a rise time of about 12 ps. This absorption band shows no decay during the experimental time window of 1 ns. In the following discussion this species will be denoted as X.

• Spectrum 3: In addition, a very weak stimulated emission around 550 nm and transient absorption is detected, also with an in-growth of about 12 ps. It has a lifetime of \sim 350 ps.

In Figure 4 representative individual transients are depicted showing their temporal behavior at a characteristic absorption wavelength. To follow the decay of the species of spectrum 1 in Figure 3B the wavelength of 780 nm corresponding to a distinct absorption maximum was selected. This transient shows two components (see Figure 4A); the positive absorption signal grows rapidly with a rise time estimated at about 200 fs and subsequently decays with a time constant of 12 ps. The transient at 530 nm (see Figure 4B), corresponding with the absorption



Figure 3. Selection of raw absorbance data (corrected for the absorbance of the ground-state sample) at various time points of 2B6M solution in *n*-octane (A) and the corresponding species associated difference spectra (SADS) (B); excitation wavelength 420 nm. Rise and decay times are indicated for each SADS spectrum.



Figure 4. Decay traces of the transient absorption signal of 2B6M in *n*-octane at 780 nm (A, normal S₁ state) and at 530 nm (B, species X); λ_{exc} = 420 nm. Note that the time scale is linear from -1 to 1 ps relative to the maximum of the IRF, and logarithmic afterward.

maximum of the species X associated with spectrum 2, is composed of only one component, a positive absorption signal that grows with a time constant of 12 ps. Up to 1 ns, no substantial decay can be observed. Instead, a small rise can be discerned, which is ascribed to the decay of the stimulated emission of the tautomer (see below).

The broad absorption band from 550 to 800 nm with a decay lifetime of 12 ps agrees well with the excited-state absorption from S_1 of the normal (N) form. According to the theoretical absorption data reported in reference⁹ the S_1-S_4 and S_1-S_3 energy differences of the normal form of 2B6M correspond to 590 and 780 nm, respectively. The assignment of spectrum 1 to the $S_1(N)$ -state is also in line with previous fluorescence lifetime measurements by means of time-correlated single photon counting (TC-SPC). The lifetime of the $S_1(N)$ emission band, ranging from 450 to 550 nm, was measured as 14 ps,⁶ very close to the decay time of spectrum 1 and Figure 4A.

In view of these fluorescence emission lifetime measurements, one should expect that the tautomeric S_1 -state, denoted as $S_1(T)$, should be created with a rise time of 12 ps and should decay with a lifetime of about 100 ps.⁶ That is why spectrum 2 cannot be assigned to $S_1(T)$; its decay is much too slow. Most probably $S_1(T)$ should be assigned to spectrum 3, which rises with a lifetime of 12 ps and decays with a lifetime of about 350 ps. Both its stimulated emission (ranging from about 520 to 650 nm) and absorption (from about 420 to 500 nm) are very weak and noisy so that the decay times cannot be determined precisely. The weak absorbances also indicate that only a minor fraction of the excited molecules decays via this pathway.

The species X corresponding to spectrum 2 in Figure 3B and the decay trace of Figure 4B is most probably created from the S_1 -state; its in-growth rate is the same as the decay rate of $S_1(N)$. However, it decays very slowly with a rate constant much smaller than $(1 \text{ ns})^{-1}$. This "dark" state was not observed in the steady-state fluorescence measurements⁶ and was therefore not included in the kinetic model of Figure 2. We tentatively identify this species as the lowest triplet state of 2B6M in the normal form $T_1(N)$, created by intersystem crossing (ISC) from $S_1(N)$. Triplet state energies were recently calculated by Makarewicz et al. for the methyl-homologue of 2B6M.¹⁰ At first sight an ISC rate as fast as 12 ps may seem exceptionally high, but a similar ISC rate was found for nitrobenzene by Takezaki et al.11,12 They concluded that a crossing of the potential curves of the S_1 and T_2 states causes a very fast decay of the S_1 -state. Of course the rate of decay of the triplet state T₁(N) to the ground state $S_0(N)$ should be expected to be much slower than 1 ns, in agreement with the observations (see Figure 4B). Note that phosphorescence, which could occur from such a triplet state, was not detected at any temperature; apparently the phosphorescence yield is negligible.

The spectra showed no indication of a tautomeric ground state, corresponding with the decay of $S_1(T)$ and with a formation rate of about 350 ps. Apparently, this state decays very rapidly to the normal ground state via back proton transfer (BPT) and therefore does not accumulate to a measurable level.

Excitation at 330 nm. Upon 330 nm excitation, 2B6M is brought into the $S_2(N)$ -state, and a more complex pattern of decays is observed (raw data shown in Figure 5A). The global analysis of the transient absorption data reveals that they can be fitted with a model containing four different decay rates and four species; the resulting estimated SADS are given in Figure 5B. It will be immediately clear that they differ from the SADS in Figure 3B. Obviously, the SADS and therefore the relative importance of the various excited state species, depend on the excitation wavelength applied, which confirms the earlier observations in fluorescence mode.⁶



Figure 5. Selection of raw absorbance data (corrected for the absorbance of the ground-state sample) at various time points of 2B6M solution in *n*-octane (A) and species associated difference spectra (SADS) (B) of 2B6M in *n*-octane; excitation wavelength 330 nm. The rise and decay times are indicated for each SADS spectrum in the legend of the graph.

• Spectrum 1: Within 200 fs, following IC and intramolecular vibrational relaxation (IVR), a broad absorption spectrum ranging from 550 to 850 nm emerges, accompanied by a stimulated emission band from 430 to 600 nm. It shows much similarity with spectrum 1 in Figure 3, but there are some significant differences as well; upon 330 nm excitation the peaks at 710 and 780 nm are distinctly more intense and the stimulated emission is broader. We assign this species to a hot S₁-state S₁(N)* (see further below).

• It is observed that spectrum 1 decays in 3 ps not only to spectrum 2 but also to spectrum 3, which both have a rise time of 3 ps. Comparing the shapes of spectrum 1 and spectrum 2 indicates that in the latter spectrum the stimulated emission is less broad but the maximum is not shifted. The same applies for the absorption, although the position of the band around 580 nm can only be estimated. In fact, spectrum 2 in Figure 5B is identical to spectrum 1 in Figure 3B; therefore it should be associated with the S₁(N)-state (trace Figure 6A).

• The shape of spectrum 1 and in particular the widths of the stimulated emission spectra point to a hot state $S_1(N)^*$, presumably a state that still has to undergo vibrational cooling.¹³ It should be emphasized that this state does not only decay to $S_1(N)$ but also directly to X. This direct route could not be



Figure 6. Decay traces of the transient absorption signal of 2B6M in *n*-octane at 780 nm (A, hot S₁ state), at 510 nm (B, species X) and at 591 nm (C, rise and fall of normal S₁ state) ($\lambda_{exc} = 330$ nm). Note that the time scale is linear from -1 to 1 ps relative to the maximum of the IRF, and logarithmic afterward.

ignored in the global analysis procedure. Unfortunately, it cannot be established whether $S_1(N)^*$ also decays directly to the tautomeric state $S_1(T)$, a point to be discussed below.

• Similar to what is found upon 420 nm excitation, spectrum 2 in Figure 5B is converted into spectrum 3 with a decay time of 12 ps. Following the interpretation of Figure 3B, the conversion of spectrum 2 into spectrum 3 accounts for the complete conversion from $S_1(N)$ to X (trace Figure 6B) on the one hand and to the tautomer $S_1(T)$ on the other. Unfortunately, detailed information about the latter state can hardly be inferred from Figure 5B; this is obvious in view of the minor differences between spectrum 3 and spectrum 4.

• Eventually, spectrum 4 is obtained. It represents exclusively species X since the excited tautomer $S_1(T)$ has a decay of 100–400 ps as concluded from Figure 3B and our previous lifetime measurements.⁶ Similar to Figure 3B, species X has a very long lifetime; its decay takes much longer than 1 ns (see Figure 6B).

Unfortunately, the direct formation of the tautomer $S_1(T)$ starting from the hot state $S_1(N)^*$, which decays with a lifetime of 3 ps, cannot be unambiguously established from the available transient absorption information. The fraction of X strongly dominates spectrum 3, which agrees with the associated formation efficiencies; X is formed very rapidly, but does not show any decay on the time scale of the measurement. Nonetheless it is not improbable that $S_1(N)^*$ is also directly converted into $S_1(T)$, since an ESIPT* process at the ps time scale would not be extraordinarily fast (in acetonitrile the ESIPT takes place on a time scale around 100 fs).⁵ More importantly, the steady-state results can only be understood if ESIPT* competes with the rate of ISC*. On the basis of the fluorescence data reported earlier and the current transient absorption data, a new and more elaborate kinetic scheme was derived as shown in Figure 7. The corresponding rate constants are listed in Table 1.



Figure 7. Scheme of the excited-state processes of 2-butylamino-6methyl-4-nitropyridine *N*-oxide in nonpolar solutions.

TABLE 1: Excited State Processes and Corresponding RateConstants in ns⁻¹ of the Various Decay Routes afterExcitation at 420 or 330 nm, Based on the TransientAbsorption Measurements (This Work) and on the SteadyState Fluorescence Data⁶

from	to	process	rate constant (ns^{-1}) $\lambda_{exc} =$ 420 nm	rate constant (ns^{-1}) $\lambda_{exc} =$ 330 nm
$S_2(N)$	hot S ₁ (N)*	IC + IVR		>5000
hot S1(N)*	$S_1(N)$	VR		150
hot S1(N)*	$T_1(N) = X$	ISC*		ca. 160
hot S1(N)*	$S_1(T)$	ESIPT*		ca. 20 ^a
$S_1(N)$	$T_1(N) = X$	ISC	ca. 30	
$S_1(N)$	$S_1(T)$	ESIPT	ca. 10 ^a	
$S_1(N)$	$S_0(N)$	IC(N)	ca. 40	
$S_1(N)$	$S_0(N)$	Flu(N)	0.05	
$S_1(T)$	$S_0(T)$	Flu(T)	0.02	
$S_1(T)$	$S_0(T)$	IC(T)	10	
$T_1(N) = X$	$S_0(N)$	(no phosph)	~	1

^{*a*} Estimated values; ratio ESIPT*/ESIPT = 2.2 (see text).

The rate constants were calculated or estimated based on the following observations:

• The lifetime of the hot state $S_1(N)^*$ (excitation at 330 nm) was determined to be 3 ps. This should correspond with the sum of its decay routes, $k_{VR} + k_{isc^*} + k_{ESIPT^*} = 330 \text{ ns}^{-1}$.

• The lifetime of the S₁(N) state was determined to be 12 ps. This should correspond with the sum of its decay routes, $k_{isc} + k_{ESIPT} + k_{ic} + k_{flu(N)} = 80 \text{ ns}^{-1}$. From the SADS we know that ISC is a major decay route, given the strong absorption of triplet species X.

• The fluorescence quantum yield $\Phi_{420,N}$ from S₁(N) (excitation at 420 nm) = 6 × 10⁻⁴, which should correspond with $k_{\text{flu}(N)}/(k_{\text{tot}})$, sum of all decay rates from S₁(N)). Since the summation in the denominator (see previous point) is 80 ns⁻¹, it follows that $k_{\text{flu}(N)} = 0.05$ ns⁻¹.

• The fluorescence quantum yield of the normal fluorescence upon 330 nm excitation is given by $\Phi_{330,N} = k_{VR}/(k_{VR} + k_{isc^*} + k_{ESIPT^*})$ multiplied with $\Phi_{420,N}$. It was measured as 2.8×10^{-4} (see ref 6). It follows that $(k_{VR}/330) \times (6 \times 10^{-4}) = 2.8 \times 10^{-4}$ 10^{-4} , so $k_{\rm VR} = 150$ ns⁻¹. This means that from the hot state almost half of the molecules will follow Kasha's rule and decay via vibrational relaxation (VR), and slightly more than half will undergo either intersystem crossing (ISC*) or ESIPT*. That same fraction was also concluded in the previous paper.⁶

• The excitation spectrum of the tautomer emission looks normal (similar to the absorption spectrum),⁶ which means that the relative yield of S₁(T) states must be the same for excitation at 330 and 420 nm. With $\lambda_{\text{exc}} = 420$ nm the yield is given by $k_{\text{ESIPT}}/k_{\text{total}} = k_{\text{ESIPT}}/80$.

• With 330 nm excitation there are two routes leading to the tautomer $S_1(T)$, the former has an efficiency of $k_{ESIPT}/330$. The efficiency of the second route is given by $(150/330) \times (k_{ESIPT}/80)$. It follows that k_{ESIPT} must be $2.2 \times k_{ESIPT}$; we assume that k_{ESIPT} is around 10 ns⁻¹ and therefore k_{ESIPT} should be around 20 ns⁻¹ but in fact only the ratio is known. In that case ISC* must be $330 - 150 - 20 = 160 \text{ ns}^{-1}$. The fact that the absorbance values of the tautomeric species are much lower than that of the triplet species X (see Figures 3A and 5A) agrees with this assumption, since the ESIPT rates must be lower than the ISC rates.

• The results of the global analysis indicate that the sum of the decay routes from the $S_1(T)$ tautomer state should correspond to about 350 ps. The fluorescence data are probably more accurate and correspond with 100 ps. This decay is mainly internal conversion, so IC_T can be calculated as 10 ns⁻¹.

• The tautomer quantum yield (at both excitation wavelengths but calculated here for 420 nm), $\Phi_{420,T} = k_{flu,T}/(k_{flu,T} + k_{ic(T)}) \times (k_{ESIPT}/80)$ and was measured as 1.5×10^{-4} ; with k_{ESIPT} estimated at 10 ns⁻¹, it follows that $k_{flu(T)} = 0.02$ ns⁻¹.

• Because the laser powers and the extinction coefficients are comparable, the relative absorbances at 520 nm could be used to calculate the relative yields of species X following excitation at 420 or 330 nm, using the raw absorbance data at 80 ps (Figures 3A and 5A). The absorbance at 420 nm excitation is lower than at 330 nm excitation (0.0045 vs 0.0083), and this agrees with the S/N values in the spectra of X, so apparently the yield of X under 420 nm excitation is lower. The yield at 420 excitation is given by $k_{isc}/80$, whereas with 330 nm excitation and two possible pathways the yield is given by $(k_{isc}/330 + k_{VR}/330) \times (k_{isc}/80)$. It follows that k_{isc*} is $5.7 \times k_{isc}$, which means that if $k_{isc*} = 160 \text{ ns}^{-1}$ the rate of ISC (k_{isc}) would be about 30 ns⁻¹. That would leave $k_{ic(N)} = 80 - 30 - 10 - 0.05 = 40 \text{ ns}^{-1}$.

Conclusions

A complete elucidation of the excited-state processes that play a role in the unusual fluorophore 2B6M in nonpolar aprotic solvents cannot be achieved by steady-state and time-resolved fluorescence experiments alone. In our earlier paper,⁶ a preliminary scheme was proposed with the main message: there is a significant role of ESIPT starting at a higher (vibronic) state than the lowest vibrational state of $S_1(N)$. This is highly exceptional and constitutes a violation of the Kasha–Vavilov rule.

In this work, it is shown that a much more complete mechanistic scheme can be obtained by combining fluorescence information with transient absorption spectroscopy measurements. In fact, the transient absorption spectra and the associated decay spectra fully support the earlier conclusion that ESIPT* can also start at a higher vibronic level upon short-wavelength excitation, and that an additional decay channel must exist that is sufficiently fast to be in competition with IC. A fourth excitedstate species was needed in order to model the 330 nm data. The transient absorption spectrum and the 3 ps lifetime indicate that this higher state is a hot state $S_1(N)^*$ instead of $S_2(N)$. Furthermore, the transient absorption measurements show that a dark state, most likely the triplet state of the normal configuration $T_1(N)$, plays a main role in the decay pathway.

Acknowledgment. The research visits of A.S.-H. to Amsterdam were supported by the EU access to large-scale infrastructures program, Contract No. 506350.

References and Notes

(1) Youssif, S. ARKIVOC 2001, 242.

(2) Albini, A.; Pietra, S. *Hetrocyclic N-Oxide*; CRC Press: Boca Raton, FL, 1991.

(3) Szemik-Hojniak, A.; Deperasińska, I.; Jerzykiewicz, L.; Sobota, P.; Hojniak, M.; Puszko, A.; Haraszkiewicz, N.; van der Zwan, G.; Jacques, P. J. Phys. Chem. A **2006**, *110*, 10690.

(4) de Klerk, J. S.; Szemik-Hojniak, A.; Ariese, F.; Gooijer, C. Spectrochim. Acta A 2009, 72, 144.

(5) Poór, B.; Michniewicz, N.; Kállay, M.; Buma, W. J.; Kubinyi, M.; Szemik-Hojniak, A.; Deperasińska, I.; Puszko, A.; Zhang, H. J. Phys. Chem. A **2006**, *110*, 7086.

(6) de Klerk, J. S.; Szemik-Hojniak, A.; Ariese, F.; Gooijer, C. J. Phys. Chem. A 2007, 111, 5828.

(7) Turro, N. J. Modern molecular photochemistry; Benjamin/Cummings: Menlo Park, CA, 1978; p 105.

(8) (a) van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R. *Biochim. Biophys. Acta*, **2004**, *1657*, 82. (b) van Stokkum, I. H. M.; Larsen, D. S.; van Grondelle, R. *Biochim. Biophys. Acta*, **2004**, *1658*, 262.

(9) Deperasińska, I.; Makarewicz, A.; Szemik-Hojniak, A. Acta Phys. Pol., A 2007, 112, S-71.

(10) Makarewicz, A.; Szemik-Hojniak, A.; van der Zwan, G.; Deperasińska, I. J. Phys. Chem. A 2009, 113, 3438.

(11) Takezaki, M.; Hirota, N.; Terazima, M.; Sato, H.; Nakajima, T.; Kato, S. J. Phys. Chem. A **1997**, 101, 5190.

(12) Takezaki, M.; Hirota, N.; Terazima, M. J. Chem. Phys. 1998, 108, 4685.

(13) von Benten, R.; Charvat, A.; Link, O.; Abel, B.; Schwarzer, D. Chem. Phys. Lett. 2004, 386, 325.

JP909468H