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# Efficient Non-Radiative Deactivation and Conformational Flexibility of *meso*-Diaryloctaalkylporphyrins in the Excited Triplet State

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The excited triplet state deactivation of zinc(II) *meso*-diaryloctaalkylporphyrins (ZnDAOAP) has been studied over a wide temperature range using transient triplet−triplet absorption spectroscopy together with steady-state and time-resolved phosphorescence techniques. The results from transient absorption measurements show that the depopulation of the initially formed triplet state ($T_{1A}$ state) is unusually fast at temperatures above 150 K. The efficiency of the deactivation originates from a spin allowed transition to a second triplet state ($T_{1B}$ state). The transformation process $T_{1A} \rightarrow T_{1B}$ is therefore the dominating deactivation channel of the $T_{1A}$ state in this temperature range, and direct intersystem crossing $T_{1A} \rightarrow S_0$ makes negligible contribution. The subsequent ground-state recovery $T_{1B} \rightarrow S_0$ is also very efficient in comparison to many other porphyrins. Due to the substantial activation energy found for the transformation process, it most likely involves a conformational distortion of the porphyrin macrocycle. At low temperature, however, the relaxation of the $T_{1A}$ state occurs by direct intersystem crossing to the ground state.

## Introduction

The excited-state properties of porphyrins and porphyrin related compounds play a crucial role in processes taking place in various biological systems. Nature's ingenious selection and spatial arrangement of porphyrin derivatives enables the photosynthetic light harvesting pigments to cover about half the visible solar spectrum.[1] The direction and efficiencies of the subsequent energy- and electron-transfer processes are also controlled. To mimic these events, a lot of effort is put into the design and synthesis of artificial supramolecular systems.[1−6] It is, therefore, in this connection important to get insight into what controls the photophysical properties of the individual subunits.

In the past 10 years, a substantial body of experimental and theoretical data has illuminated the conformational flexibility and various nonplanar distortions of the porphyrin macrocycle induced by a sterically encumbered substitution pattern, often represented by dodecasubstituted metal- or free base porphyrins of formal $S_4$ symmetry.[7−19] Interestingly, X-ray structures of bactereochlorophylls in the reaction centers and light harvesting antenna systems also show significant distortion from a planar conformation, probably imposed by the protein framework.[20,21] In addition, semiempirical quantum mechanical calculations suggest that the wide range of bactereochlorophyll absorption maxima observed results from the ability of the macrocycles to adopt different degrees of distorted conformations.[14,22] Spectroscopic and electrochemical characterization of this class of porphyrins showed that the deviations from planarity manifested in substantial changes in redox, excited-state, and light-absorption properties.[8−12,14−16,18,23,24]

Recently, some attention has been drawn to another class of porphyrins, those with geometrical constrains imposed by the peripheral substitution pattern that do not necessarily force the pyrrole ring to severe out-of-plane distortions.[25,26] X-ray structures, NMR data, and spectroscopic measurements on a series of deca-and undecasubstituted porphyrins showed that *meso*-diaryl substituted octaalkylporphyrins show a large degree of conformational flexibility. They exist in both planar and slightly nonplanar conformations, separated by only small energy barriers, but possess light absorption properties comparable to planar porphyrins.[26] Although the behavior on the lowest excited singlet state surface of this class of porphyrins is similar to the normal porphyrins, it was demonstrated by Knyukshto et al. that the characteristics of the lowest triplet excited state were significantly changed.[25] The most intriguing finding was that introduction of one or two aryl substituents in the *meso* positions of zinc- and free-base octaalkylporphyrins dramatically shortened the triplet lifetime at room temperature from the millisecond scale to a few microseconds. It was suggested that the sterical encumbrance induced by torsional librations of the aryl groups initiates nonplanar conformational distortions of the macrocycle. This in turn decreases the energy gap between the $T_1$ and $S_0$ potential surfaces, increasing the nonradiative rate constant.

In this work we have investigated the properties of the excited triplet state in a series of zinc(II)- and free base *meso*-diaryloctaalkylporphyrins (Zn- and $H_2$DAOAP) over a wide temperature range in order to explore the triplet state characteristics of this class of porphyrins. The primary objective has been to formulate a comprehensive kinetic model describing the relaxation dynamics of the triplet state. This work is part of an ongoing project on triplet−triplet energy transfer between zinc- and free-base porphyrins. We have, therefore, concentrated on the properties of the donor moiety, i.e., the zinc porphyrin, and various substituted zinc porphyrins (Figure 1) in this work.

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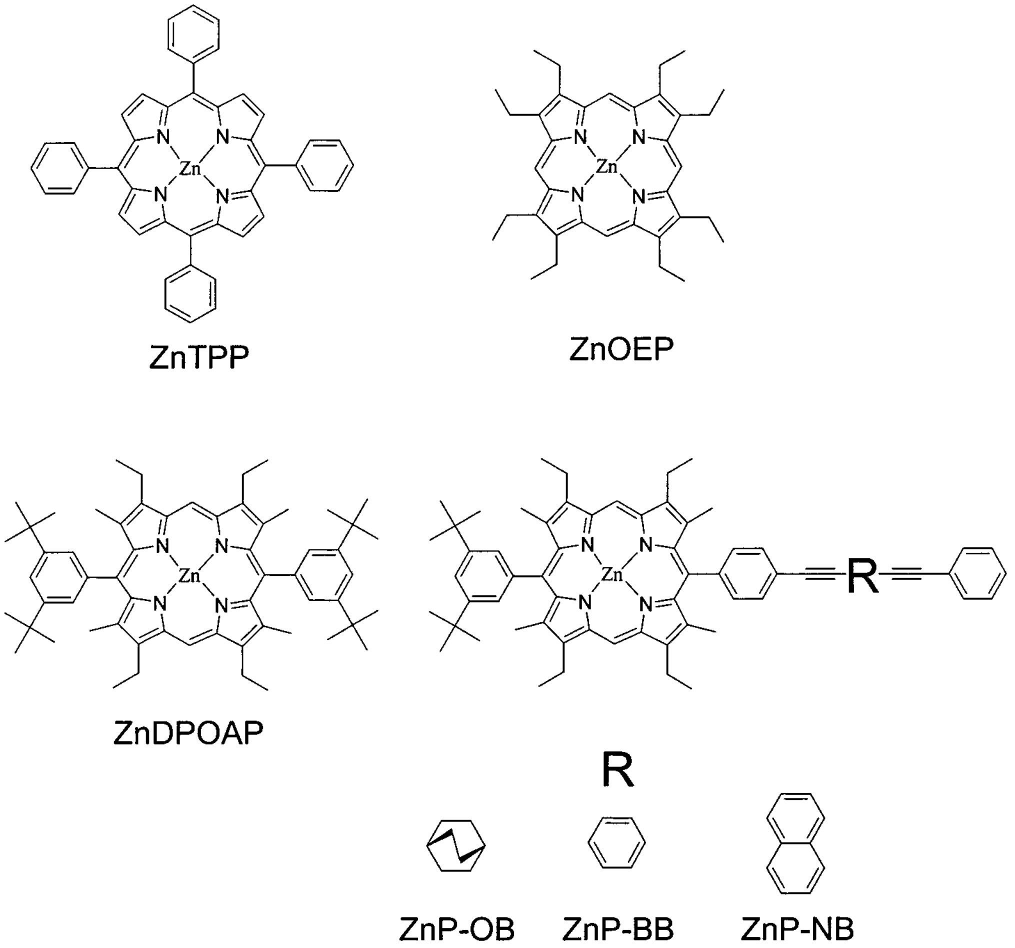

**Figure 1.** Structures of the zinc porphyrin derivatives studied in this paper.

A similar behavior is also observed for the free-base counterparts, the triplet energy acceptors.

## Experimental Section

**Materials.** All measurements were performed with 2-methyltetrahydrofuran (MTHF), purchased from ACROS, and isotropic PVC films as solvents. The films were prepared by adding the ZnDAOAP derivatives, dissolved in tetrahydrofuran (THF) from MERCK, into a hot 10% (w/w) solution of PVC in THF. After 2 h stirring and heating, the mixtures were gently poured onto glass plates and allowed to dry under controlled vapor pressure. Zinc octaethylporphyrin (ZnOEP) was purchased from SIGMA and used without further purification. Tetraphenylporphyrin (TPP) was synthesized according to the Adler−Longo method,[27] purified by chromatography over dry aluminia,[28] and metalized[29] to ZnTPP by a procedure used by S. Tabushi et al. The synthesis and purification of ZnDPOAP, ZnP−OB, ZnP−BB, and ZnP−NB are described elsewhere.[30,31] The structures of all studied compounds are shown in Figure 1.

**Spectroscopic Measurements.** Ground-state absorption spectra were recorded using a CARY 4B UV/Vis spectrometer. Emission and excitation spectra were measured on either a SPEX Fluorolog $\tau 2$ or a SPEX Fluorolog-3 spectrofluorometer. Triplet lifetimes were determined by laser flash photolysis or by xenon lamp pulsed excitation followed by time-resolved gated phosphorescence detection using a SPEX 1934D3 phosphorimeter. In the flash photolysis experiments the excitation source was the 532 nm second harmonics of a Nd:YAG laser (Spectron Laser Systems SL803G1270). The monitoring system consisted of a pulsed xenon lamp followed by a conventional monochromator photomultiplier system (symmetrical Czerny−Turner arrangement and a five-stage Hamamatsu R928). Data acquisition was performed via a Philips model PM 3323 digital oscilloscope. To minimize interference from triplet annhilation and self-quenching and to avoid kinetic distortions caused by inhomogenieties in the sample distribution, the ground-state absorption at 532 nm was adjusted to 0.05 and the $T_1$−$T_n$ absorption was kept below 0.15.[32] In the temperature interval studied by transient absorption, the triplet lifetimes of the ZnDAOAP derivatives showed no concentration dependence. This excludes that bimolecular processes limit the triplet lifetimes. Ground state absorption spectra recorded after the transient absorption measurements showed neither significant bleaching nor additional absorption bands. The kinetic traces were formed by averaging between 16 and 64 recorded decay curves. A minimum of six kinetic traces at different wavelengths was then analyzed by global analysis methodology. All samples were carefully degassed by six freeze−pump−thaw cycles to a final pressure of ca. $10^{-4}$ Torr. Low-temperature measurements were done in a nitrogen-cooled cryostat (Oxford Instruments) equipped with a temperature regulator. The triplet excitation energies of the different species were estimated from the 0−0 phosphorescence transitions measured at 80 K. Room temperature emission quantum yields were directly determined relative to the fluorescence quantum yield of an optically matched sample of Rhodamine B in ethanol ($\Phi_f = 0.97$).[33] Low-temperature emission quantum yields were determined relative to the room-temperature spectra of the compounds recorded with the samples in the cryostat. In this way, any interference from the cryostat is corrected.

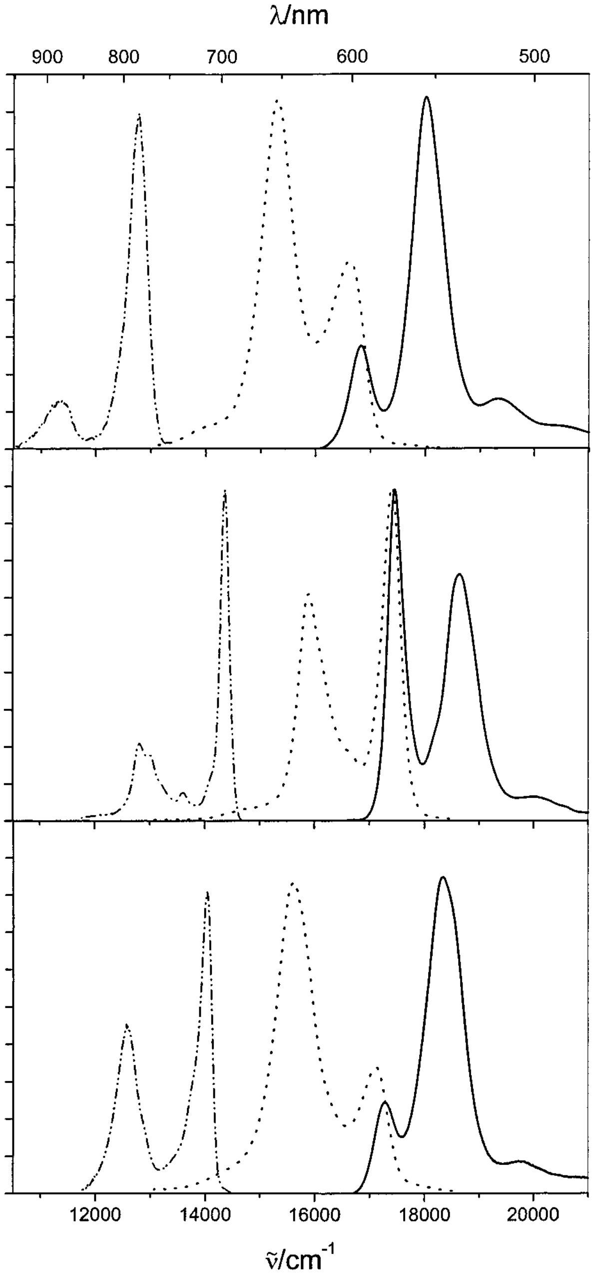

**Figure 2.** Ground-state absorption and emission spectra of ZnTPP, ZnOEP and ZnP−NB (top to bottom). The absorption (—) and fluorescence (••••••••) spectra are recorded at room temperature, while the phosphorescence (—••—) spectra are measured at 80 K.

## Results

The primary objectives of this work have been to investigate the triplet state relaxation dynamics in the series of *meso*-diaryl substituted zinc(II) octaalkylporphyrins (ZnDAOAP) shown in Figure 1. To be able to ascribe the characteristics of the excited triplet state to this particular substitution pattern, we have also included zinc octaethylporphyrin (ZnOEP) and zinc tetraphenylporphyrin (ZnTPP) that serve as representatives of the "normal" planar porphyrins with well documented singlet- and triplet excited state properties. In the following sections, the experimental results (spectra and transients) will be shown only for one of the *meso*-diaryl substituted octaalkylporphyrins (ZnP−NB), whereas the evaluated photophysical parameters of all compounds studied will be collected in the tables.

First, we show that the properties of the lowest excited singlet state of ZnDAOAP do not significantly deviate from the "normal" class of porphyrins. Second, time-resolved $T_1-T_n$ absorption measurements establish that the nonradiative deactivation of the ZnDAOAP triplet state at temperatures above 150 K is unusually efficient and involves two different triplet states, with a "mother−daughter" relationship. Finally, steady-state and time-resolved phosphorescence measurements at low temperature show that the relaxation dynamics is abruptly changed between 150 and 120 K to parallel the behavior of the "normal" class of porphyrins. In addition, phosphorescence is observed from the ZnDAOAP derivatives at room temperature in a highly viscous PVC film. These observations indicate that the efficient deactivation at higher temperatures involves conformational changes of the porphyrin macrocycle.

**TABLE 1: Ground State Absorption and Emission Properties at Room Temperature**[a]

| | $\lambda_{Q(0,0)}$/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ | $\Phi_F$ | $\tau_F$/ns |
|---|---|---|---|---|
| ZnOEP | 573 | 30 | 0.049 | 2.0 |
| ZnTPP | 595 | 170 | 0.047 | 1.9 |
| ZnDPOAP | 578 | 180 | 0.022 | 1.5 |
| ZnP−OB | 578 | 180 | 0.027 | 1.4 |
| ZnP−BB | 578 | 180 | 0.027 | 1.4 |
| ZnP−NB | 578 | 180 | 0.027 | 1.4 |

[a] The peak absorption wavelength of the Q(0,0)-transition ($\lambda_{Q(0,0)}$), Stokes shift ($\Delta\tilde{\nu}$), fluorescence quantum yield ($\Phi_F$), and the fluorescence lifetime ($\tau_F$) are listed. The data for ZnOEP and ZnTPP agree well with values reported in the literature.

**Ground-State Absorption and Fluorescence Spectroscopy.** Figure 2 shows the absorption and fluorescence spectra of ZnTPP, ZnOEP, and ZnP−NB at room temperature and the corresponding phosphorescence spectra at 80 K. The emission spectra are recorded on samples with matched optical densities at the excitation wavelength, 535 nm. Excitation spectra at 80 K with the emission wavelengths in the fluorescence- and the phosphorescence bands do not show significant deviations (not shown). A moderately intense fluorescence is observed for all compounds studied, with Stokes shift ranging between 30 cm$^{-1}$ (ZnOEP) and 170−180 cm$^{-1}$ (ZnTPP and ZnP−NB). The position of the Q(0,0)-band is shifted toward longer wavelength in the order ZnOEP < ZnP−NB < ZnTPP. In Table 1 it is also seen that the quantum yield and lifetime of fluorescence do not vary much among the compounds in the studied series.

**Transient Absorption at Room Temperature.** The $T_1-T_n$ transient absorption profiles of ZnP−NB at different probe wavelengths are shown in Figure 3. Upon comparison with the corresponding transient of ZnTPP and ZnOEP (inset), it is obvious that the decay kinetics of the triplet states differ significantly. In addition to the considerably shortened triplet lifetime, it is evident that the transients are biphasic (biexponential), and the rise time seen in the transients at longer wavelengths suggests a "mother−daughter" type of kinetics. Nevertheless, it must be excluded that that the biexponential behavior originates from two parallel deactivation pathways to the ground state, i.e., two nonconsecutive intersystem crossing processes from two distinct triplet species. The ground-state recovery is possible to monitor in the Soret-band region (418 nm) becasue of the very strong ground-state absorption ($\epsilon \approx 5 \times 10^5$ M$^{-1}$ cm$^{-1}$). Figure 4 shows a transient recorded at 418 nm, and the absence of a fast recovery, corresponding to the fast decay/rise time in the $T_1-T_n$ absorption decays (see Figure 3), clearly rules out two parallel processes. Consequently, we can establish that the relaxation of the excited triplet state is governed by a consecutive excited-state reaction

$$T_{1A} \xrightarrow{k_A} T_{1B} \xrightarrow{k_B} S_0 \qquad (1)$$

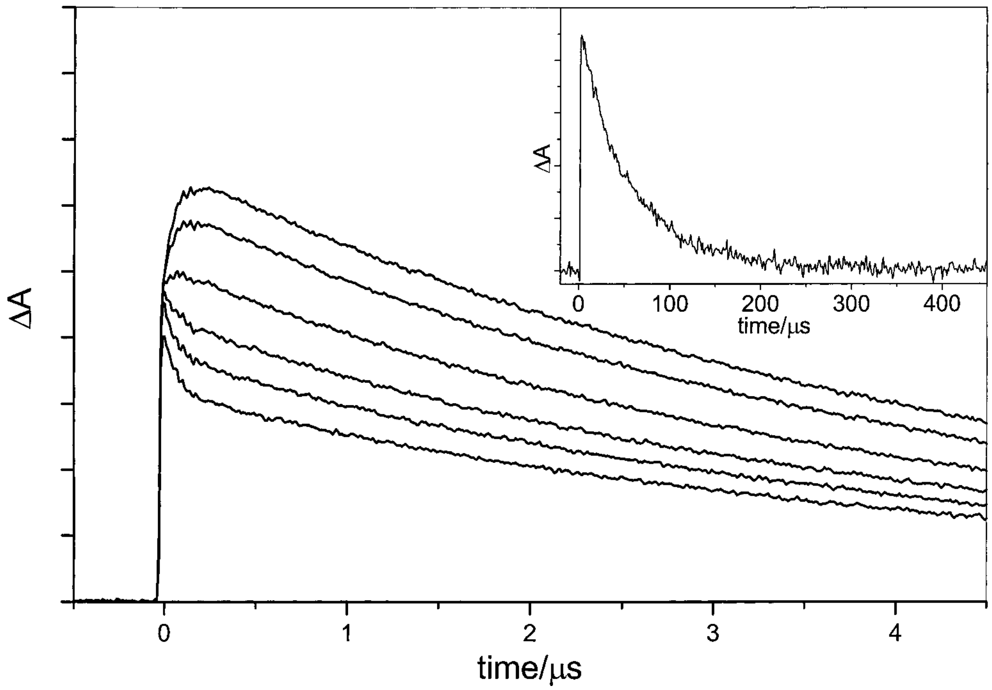

**Figure 3.** Room temperature transient $T_1-T_n$ absorption profiles of ZnP−NB monitored at, from bottom to top, 450, 454, 458, 462, 466, and 470 nm. Inset: Corresponding transient of ZnOEP at 450 nm.

In a wavelength region where ground-state bleaching can be neglected,[34] the kinetic profiles of the reaction shown in (1) are described by[35]

$$\Delta A_{\mathrm{tot}}(t) = \epsilon_A(\lambda)\cdot[T_{1A}]_t + \epsilon_B(\lambda)\cdot[T_{1B}]_t = [T_{1A}]_0\left\{\exp(-k_A t)\left[\epsilon_A(\lambda) + \epsilon_B(\lambda)\cdot\frac{k_A}{k_B - k_A}\right] - \exp(-k_B t)\left[\epsilon_B(\lambda)\cdot\frac{k_A}{k_B - k_A}\right]\right\} \quad (2)$$

where $\epsilon_A(\lambda)$ and $\epsilon_B(\lambda)$ are the $T_1-T_n$ absorption coefficients at wavelength $\lambda$ of the $T_{1A}$- and $T_{1B}$ states, respectively, and $[T_{1A}]_t$ and $[T_{1B}]_t$ are the concentrations of the respective triplet states at time, $t$. Judging from the transients shown in Figure 3, the process $T_{1A} \rightarrow T_{1B}$ is much faster than $T_{1B} \rightarrow S_0$, i.e., $k_A \gg k_B$, simplifying Equation 2 to

$$\Delta A_{\mathrm{tot}}(t) = \alpha_A \exp(-t/\tau_A) + \alpha_B \exp(-t/\tau_B) \quad (3)$$

where $\alpha_A = [T_{1A}]_0(\epsilon_A - \epsilon_B)$, $\alpha_B = [T_{1A}]_0\epsilon_B$, $\tau_A = 1/k_A$, and $\tau_B = 1/k_B$. Biexponential global analysis of the transients at 298 K using eq 3 gives $\tau_A$ = 73 ns and $\tau_B$ = 5.4 μs. Corresponding values for the other porphyrins are shown in Table 2. If the long lifetime, $\tau_B$ (5.4 μs), and the triplet lifetimes of ZnOEP and ZnTPP under identical conditions (60 and 210 μs, respectively)[36] are compared it is seen that the deactivation from the excited triplet manifold at room temperature is much more efficient in the ZnDAOAP derivatives. Analyzing the transients over the wavelength region 436−520 nm gives the triplet absorption spectra in Figure 5, where $\Delta A_A = \alpha_A + \alpha_B$ and $\Delta A_B = \alpha_B$ (cf. eq 3). In comparison between Figures 5a and b it is seen that the time evolution of the triplet spectrum is consistent with a consecutive excited-state reaction $T_{1A} \rightarrow T_{1B}$.

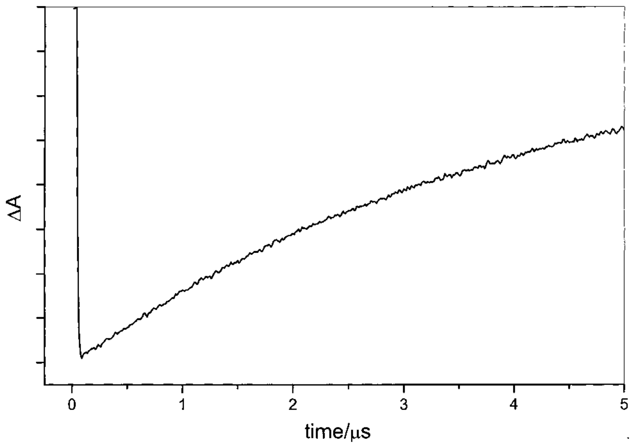

**Figure 4.** Transient ground-state recovery of ZnP−NB with the probing wavelength in the Soret band region (418 nm). The absence of a fast recovery in the early part of the transient establishes the "mother−daughter" relationship between the two triplet states.

**TABLE 2: Triplet Lifetimes of the ZnDAOAP Derivatives at Temperatures between 298 and 150 K**

| | ZnDPOAP | | ZnP−OB | | ZnP−BB | | ZnP−NB | |
|---|---|---|---|---|---|---|---|---|
| | $\tau_A$/μs | $\tau_B$/μs | $\tau_A$/μs | $\tau_B$/μs | $\tau_A$/μs | $\tau_B$/μs | $\tau_A$/μs | $\tau_B$/μs |
| 298 K | 0.27 | 5.7 | 0.088 | 5.2 | 0.086 | 5.1 | 0.073 | 5.4 |
| 250 K | 3.4 | 9.0 | 0.97 | 7.3 | 0.60 | 6.5 | 0.47 | 6.7 |
| 200 K | 310 | | 24 | 9.0 | 16 | 8.5 | 16 | 8.4 |
| 190 K | 770 | | 48 | 10 | 45 | 10 | 38 | 10 |
| 175 K | 1500 | | 280 | | 180 | | 150 | |
| 165 K | 2500 | | 710 | | 830 | | 520 | |
| 150 K | | | 2400 | | 2600 | | 2400 | |

**Temperature Dependence.** The temperature dependence of the decay kinetics was studied by transient absorption down to 150 K. The triplet lifetime of the initially populated $T_{1A}$ state depends strongly on temperature, whereas the $T_{1B}$ state shows only a moderate dependence. As a result, the lifetime of the $T_{1A}$ state has become longer than the lifetime of the $T_{1B}$ state at 200 K, i.e., $k_B > k_A$, and the population of the $T_{1B}$ state is slower than the subsequent depopulation. This kind of relaxation manifests itself in the transients as "inverted kinetics" because the preexponential factor of the $T_{1B}$ state "decay" will be negative when $k_B > k_A$ (cf. eq 2). The rise time seen in the transients is then attributed to the depopulation of the $T_{1B}$ state. At temperatures of 175 K and lower (200 K in the case of

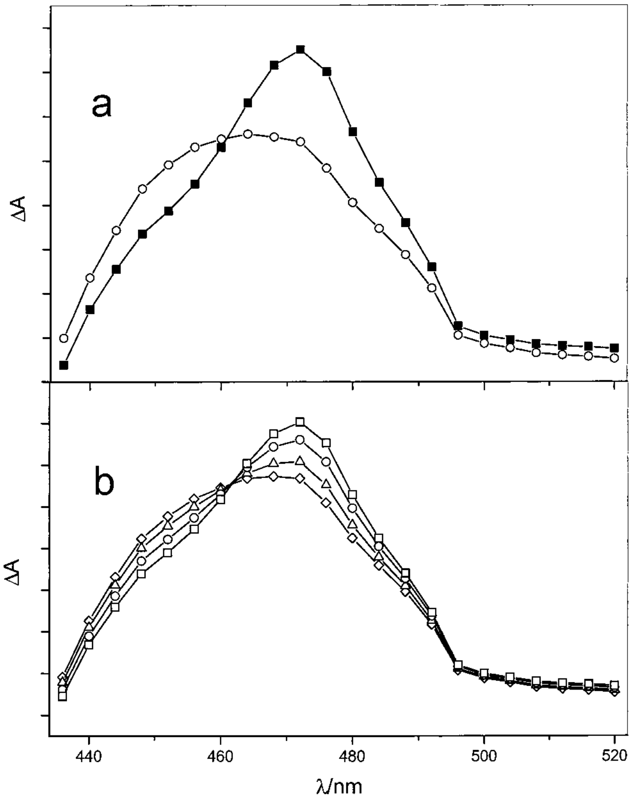

**Figure 5.** Room-temperature triplet absorption spectra of ZnP−NB. (a) Time independent spectra of the $T_{1A}$ (○-○-○) and $T_{1B}$ (■-■-■) species. (b) Time evolution of the total absorption spectrum with 10 (◇−◇−◇), 30 (△−△-△), 70 (○-○-○), and 150 (□−□−□) ns delay after excitation.

**TABLE 3: Excited Triplet State Characteristics at Low Temperatures**[a]

| | 120 K $\tau_P$/ms | 100 K $\tau_P$/ms | 90 K $\tau_P$/ms | 80 K $\tau_P$/ms | 80 K $E_T$/cm$^{-1}$ | 80 K $\Phi_P$ |
|---|---|---|---|---|---|---|
| ZnOEP | | 45 | 93 | 102 | 14370 | 0.061 |
| ZnTPP | | | | 27 | 12810 | 0.0057[b] |
| ZnDPOAP | | | | 82 | 13990 | 0.055 |
| ZnP−OB | 32 | 38 | 52 | 85 | 14000 | 0.065 |
| ZnP−BB | 32 | 39 | 55 | 86 | 14000 | 0.065 |
| ZnP−NB | 34 | 39 | 55 | 86 | 14000 | 0.065 |

[a] The phosphorescence lifetimes ($\tau_P$) at 120, 100, 90, and 80 K are shown together with the triplet excitation energies ($E_T$) and phosphorescence quantum yields ($\Phi_P$) at 80 K. [b] This quantum yield is lower than previously reported by a factor of two,[40] probably because of imperfect corrections of the emission spectrum above 850 nm.

ZnDPOAP), the kinetics of the $T_{1B}$-state cannot be properly resolved because the depopulation is much faster than the formation and therefore shows too vague traces in the transients. The lifetime data are collected in Table 2.

Steady-state and time-resolved phosphorescence measurements were used to characterize the relaxation dynamics of the compounds at temperatures lower than 150 K. Although a bit noisy, the phosphorescence decay curves after xenon lamp pulsed excitation at 544 nm are well described in terms of single exponentials (not shown). The resulting lifetimes together with the phosphorescence quantum yields and the triplet excitation energies at 80 K are shown in Table 3. By assuming the intersystem crossing quantum yield, $\Phi_{isc}$, to be 0.88, which is about the average value reported for a variety of substituted zinc porphyrins,[37] the rate constant of phosphorescence, $k_P$, was determined to be approximately 0.8 s$^{-1}$ for all ZnDAOAP derivatives studied, which is on the same order of magnitude as for both ZnTPP and ZnOEP (0.24 and 0.69 s$^{-1}$, respectively).

**Emission Measurements in PVC Films.** To investigate the effect of a highly viscous media on the relaxation behavior of the ZnDAOAP derivatives, emission spectra were recorded in isotropic PVC films at different temperatures (not shown). In comparison between the spectral position of the emission peaks in the PVC films and the corresponding values in MTHF, no significant changes were observed. Interestingly though, in the PVC films the phosphorescence contributes to the emission spectra already at room temperature, whereas no phosphorescence at all is observed in MTHF at temperatures above 150 K.

## Discussion

**Ground State Conformation of the Porphyrin Macrocycle.** It is established that the introduction of multiple substituents onto the porphyrin macrocycle might cause severe deformations from planarity.[7−18] It is, therefore, not obvious whether the ZnDAOAP derivatives studied in this work will be planar in the singlet ground state or not. However, for porphyrins it is a well demonstrated fact that nonplanar distortions are distinctly reflected in the photophysical properties of the singlet excited state. The changes are manifested in a substantial red shift of the absorption bands, an increased Stokes shift, and a reduced fluorescence lifetime and quantum yield compared to normal planar porphyrins.[8,10,12,14−16,18,24] For example, the Stokes shift for the saddle-shaped zinc(II) octaethyl-tetraphenylporphyrin exceeds the corresponding value for the planar analogue ZnTPP with 1500 cm$^{-1}$, and the fluorescence lifetime and quantum yield is decreased by a factor 10.[15] In comparing the photophysical data of the different zinc(II) porphyrins shown in Table 1, it is obvious that none of the ZnDAOAP derivatives show abnormal values compared to the “reference compounds” ZnOEP and ZnTPP. This suggests planar or near planar conformations of the macrocycles of the ZnDAOAP derivatives in the singlet states. Another observation in favor of this hypothesis is the work by Senge et al., in which several *meso*-aryl porphyrins were characterized by X-ray crystallography, showing that the free-base and Ni(II) counterparts of ZnDPOAP (without *tert*-butyl groups on the phenyl rings) have planar or only slightly nonplanar conformations, respectively.[26]

**Decay Dynamics of the Excited Triplet State at High Temperature.** As is evident from the transient decays in Figure 3, a kinetic model of the triplet state relaxation of the ZnDAOAP derivatives must include two different triplet states, arbitrarily called $T_{1A}$ and $T_{1B}$. Small amounts of impurities, being the origin of the biexponential behavior, are excluded as the fluorescence- and the phosphorescence excitation spectra are very similar in shape. Also taking into account the time evolution of the $T_1-T_n$ absorption spectrum in Figure 5 b, it is seen that the relation between the $T_{1A}$ and the $T_{1B}$ state would have to be that of “mother−daughter” type, i.e., the $T_{1B}$ state is populated from the $T_{1A}$ state via some transformation process, $T_{1A} \rightarrow T_{1B}$. Furthermore, considering the unusually short lifetime of the $T_{1A}$ state at room temperature (see Table 2) and the absence of a fast component in the recovery of the ground state absorption, it is most likely that the $T_{1A}$ state is almost exclusively deactivated via the transformation to the $T_{1B}$ state, i.e., the contribution from direct intersystem crossing to the singlet ground state is negligible. This is also supported by the phosphorescence measurements at low temperatures which show that the intersystem crossing is at least 5 orders of magnitude slower than the transformation process at room temperature (vide

**TABLE 4: Preexponential Factors (*A*) and Activation Energies ($E_a$) of the Excited Triplet State Deactivation Processes**[a]

| | ZnOEP | | ZnDPOAP | | ZnP−OB | | ZnP−BB | | ZnP−NB | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $A$ (s$^{-1}$) | $E_a$ (kcal/mol) | $A$ (s$^{-1}$) | $E_a$ (kcal/mol) | $A$ (s$^{-1}$) | $E_a$ (kcal/mol) | $A$ (s$^{-1}$) | $E_a$ (kcal/mol) | $A$ (s$^{-1}$) | $E_a$ (kcal/mol) |
| $k_{trans}$ | | | $5.8\times10^{12}$ | 8.4 | $7.0\times10^{11}$ | 6.6 | $1.1\times10^{12}$ | 6.7 | $1.0\times10^{12}$ | 6.6 |
| $k_{iscB}$ | | | $1.9\times10^{6}$ | 1.4 | $5.3\times10^{5}$ | 0.6 | $5.8\times10^{5}$ | 0.6 | $5.0\times10^{5}$ | 0.6 |
| | $k_{isc}$=9.0 s$^{-1}$ | | $k_{iscA}$=11 s$^{-1}$ | | $k_{iscA}$=11 s$^{-1}$ | | $k_{iscA}$=11 s$^{-1}$ | | $k_{iscA}$=11 s$^{-1}$ | |

[a] The temperature independent rate constants, $k_{isc}$ and $k_{iscA}$, shown in the bottom row, are estimated from the phosphorescence lifetimes and quantum yields in MTHF at 80 K.

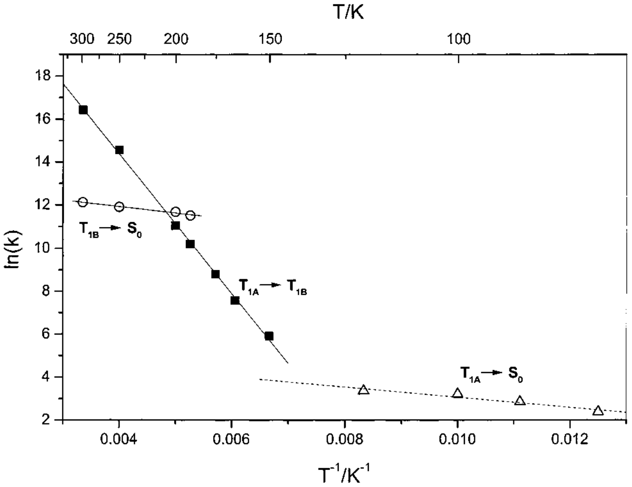

**Figure 6.** Arrhenius plots showing the temperature dependence of the transformation process $T_{1A} \rightarrow T_{1B}$ (■), and the nonradiative decay of the $T_{1A}$- (△) and $T_{1B}$ states (○) of ZnP−NB. Solid lines show the best fit to the Arrhenius equation and the dashed line shows the least-squares fit to the low-temperature data (see text for details).

infra). Therefore, it is possible to express the lifetime of the $T_{1A}$ state in terms of one single rate constant, $k_{trans}$ (corresponding to $k_A$ in eq 1), which is the rate constant of the transformation process, $T_{1A} \rightarrow T_{1B}$.

Assuming the temperature dependence of $k_{trans}$ to follow the Arrhenius equation,

$$k_{trans}(T) = A \exp(-E_a/RT) \tag{4}$$

$\ln(1/\tau_A)$ plotted versus $1/T$ will give the preexponential factor *A* and the activation energy $E_a$ through the intersection and the slope, respectively. Figure 6 shows the Arrhenius plot for ZnP−NB, and the Arrhenius parameters for all ZnDAOAP derivatives are comprised in Table 4. As inferred from the very good agreement between the experimental data points and the fitted line in Figure 6, it is a fair assumption that all of the other relaxation paths from the $T_{1A}$ state can be neglected in the presence of the transformation process, though a small deviation was corrected for at 150 K. This deviation will be explained later in formulating a comprehensive kinetic model (vide infra).

Treating the lifetime data of the $T_{1B}$ state in a similar fashion, i.e., assuming that the deactivation can be ascribed exclusively to a nonradiative temperature dependent rate constant, $k_{iscB}$ (corresponding to $k_B$ in eq 1), described by an Arrhenius expression gives the plot shown in Figure 6. As indicated by the moderate temperature dependence of the $T_{1B}$ state lifetime, the activation energy of this process, $E_a = 0.6$ kcal/mol, is found to be 1 order of magnitude smaller than the corresponding parameter of the $T_{1A}$ to $T_{1B}$ state transformation, whereas the preexponential factor is about 6 orders of magnitude smaller (see Table 4). As the intersystem crossing process $T_{1B} \rightarrow S_0$ is spin-forbidden, in distinction to the transformation process $T_{1A} \rightarrow T_{1B}$, where the spin is conserved, the observed difference between the preexponential factors is expected.

**Decay Dynamics of the Excited Triplet State at Lower Temperatures.** The time-resolved and steady-state phosphorescence measurements are performed between 120 and 80 K. Because the lifetimes of porphyrin triplet states at these temperatures are on the order of some 10 ms (see Table 3), the phosphorescence starts to contribute to the overall deactivation of the triplet state. Therefore, the rate constant of phosphorescence, $k_P$, has to be included in the evaluation of the lifetime data. Furthermore, comparing the lifetimes at 120 and 80 K (~30 and 85 ms, respectively), it is seen that the temperature dependence in this region is considerably less pronounced than what was found between 298 and 150 K. It is therefore most likely that the deactivation of the excited triplet state in this temperature interval is governed by a route distinct from the transformation process $T_{1A} \rightarrow T_{1B}$, which is dominant at higher temperatures. With the transformation process virtually shut off at temperatures lower than 140 K, the intrinsic relaxation would determine the $T_{1A}$ state lifetime. The rate constant for the intrinsic nonradiative relaxation process at lower temperatures is denoted $k_{iscA}$. Again, assuming Arrhenius type of behavior, i.e., plotting $\ln(1/\tau_P - k_P)$ versus $1/T$, gives the results shown in Figure 6. As indicated by the moderate temperature dependence of the lifetime between 120 and 80 K, the activation energy of the nonradiative process is estimated to be less than 0.5 kcal/mol. Furthermore, as the triplet lifetime in this temperature interval is on the order of some 10 ms, viscosity-dependent bimolecular processes, such as self-quenching, could also contribute to the observed temperature dependence.[38] This notion is supported by the emission measurements in a highly viscous PVC-film, where phosphorescence of comparable magnitude is seen in the spectra recorded at 80 and 298 K. Hence, we assume $k_{iscA}$ to be temperature independent, and the variation of the lifetimes with temperature seen for all the porphyrins studied between 120 and 80 K is ascribed to bimolecular processes. Still, in comparing the phosphorescence lifetimes and quantum yields, it is obvious that the features of triplet excited-state relaxation of the ZnDAOAP derivatives start to parallel the "normal" class of porphyrins, in this case represented by ZnOEP, at a temperature of 120 K or below (see Tables 3 and 4). The nonradiative rate constants for ZnOEP and the ZnDAOAP derivatives, $k_{isc}$ and $k_{iscA}$, respectively, are estimated from the phosphorescence lifetimes and quantum yields in MTHF at 80 K, where bimolecular processes safely can be neglected.

**Kinetic Model of the ZnDAOAP Derivatives.** The deactivation of the excited triplet state of the ZnDAOAP derivatives seems to include three different temperature-dependent processes. Our aim in this section will be to resolve the contribution of the individual processes at different temperatures and elucidate their mutual relationship, i.e., formulate a comprehensive kinetic model. As mentioned earlier, the results from the transient absorption measurements at high temperature cannot be explained without including two "mother−daughter"

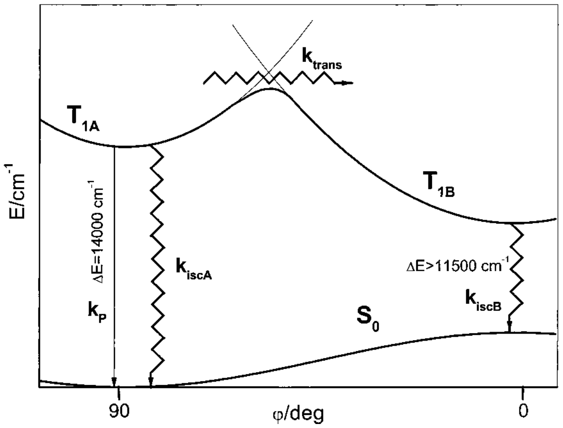

**Figure 7.** Kinetic model of the ZnDAOAP derivatives triplet state deactivation. The reaction coordinate $\varphi$ has been suggested to be the dihedral angle between the aryl- and the porphyrin planes, although any other relaxation coordinate that red shifts the $T_{1B}$ species could be used (see text for details).

related excited triplet states. The absence of a fast recovery in the ground state absorption probed in the Soret band region rules out the possibility for two independently formed triplet states. Furthermore, the time evolution of the $T_1-T_n$ absorption spectra is also in favor of the hypothesis that the initially formed $T_{1A}$ state depopulates through the $T_{1B}$ state via a transformation process. Also taking into account the high linear correlation in the Arrhenius plot of the transformation process, it is most likely that any other deactivation channel from the $T_{1A}$ state can be neglected between room temperature and 165 K. However, below 165 K a slight deviation from linearity was seen in the Arrhenius plots for all of the ZnDAOAP derivatives, indicating that another process begins to contribute to the deactivation at lower temperatures than 165 K. Extrapolation of the dashed line describing the low-temperature intersystem crossing process shows that the "apparent" value of the rate constant $k_{\mathrm{iscA}}$ is of the order of 50 $\mathrm{s}^{-1}$ at 150 K (see Figure 6). Assuming that the transformation and the intersystem crossing processes are two separate processes, i.e., subtracting 50 $\mathrm{s}^{-1}$ from $k_{\mathrm{trans}}$ at 150 K, corrects for much of the deviations from linearity. This is a good indication that the processes are distinct and not one single process that abruptly changes character between 150 and 120 K. One possible conclusion is that the deactivation of ZnDAOAP derivatives at higher temperatures originates from a process that is absent in the "normal" class of porphyrins, most likely the suggested transformation to a different electronically excited triplet state. However, at low temperature, the nonradiative relaxation of the triplet states formed in "normal" porphyrins and in the ZnDAOAP derivatives seem to occur by a common mechanism.

The photophysical properties of the $T_{1B}$ state at temperatures lower than 190 K are not easily determined. Its lifetime at these temperatures is at least 20 times shorter than the lifetime of its precursor state, why it is expected to make only small contributions to the transients. The expected very low $T_{1B}$ state concentration at low temperatures also makes it very difficult to conclude anything about the $T_{1B}$ state emission. However, all experimental data available are consistent with the model shown in Figure 7. The Arrhenius parameters of the different rate constants are comprised in Table 4, and the corresponding plots are collected in Figure 6.

**The Nature of the Transformation Process.** We have no experimental observations that definitely confirm the nature of the transformation process. The considerable activation energy of 7−8 kcal/mol, however, indicates that some degree of conformational change is involved in going from state $T_{1A}$ to $T_{1B}$. Another observation in favor of this hypothesis is that in a highly viscous media where conformational changes should be hindered, $T_{1A}$ state phosphorescence is observed in the emission spectra already at room temperature. The idea of multiconformational excursions in the excited state of multiply substituted porphyrins has been suggested by different groups,[8,9,11,12,15,18,39] and some attempts have been made to characterize the mode of structural change.[8,11,18,39] Of particular interest is the work by Knyukshto et al. in which a series of mono- and diaryl *meso*-substituted zinc and free-base octaethylporphyrins were investigated with respect to their triplet state deactivation properties.[25] They suggest that the dramatically shortened triplet lifetime seen in this group of molecules arises from torsional librations of the aryl groups in the *meso* position initiating non planar conformations of the porphyrin macrocycle. This in turn leads to a decreased $T_1-S_0$ energy gap. As the substitution pattern and the singlet and triplet excited-state properties of our ZnDAOAP derivatives are similar to the *meso*-diaryl substituted zinc(II) octaethylporphyrins, it is reasonable to apply the same argument to explain the behavior seen here. The reaction coordinate in Figure 7 would then be the dihedral angle, $\varphi$, between the planes of the aryl groups and the porphyrin macrocycle. As $\varphi$ in the ground state conformation is approximately 90°, rotation will force the aryl groups into the plane of the macrocycle, i.e., $\varphi \rightarrow 0°$. It should be pointed out, though, that any other reaction coordinate that will red shift the daughter state could be employed to explain the observations made. In a related study on triplet energy transfer between the zinc porphyrins studied here and the corresponding free base porphyrin, we observed that the $T_{1A}$ and the $T_{1B}$ states of the zinc porphyrins function as energy donors. Hence, the lower limit of the $T_{1B}$ state energy is approximately 11500 $\mathrm{cm}^{-1}$, which is the value reported for structurally similar free base porphyrins.[37] The concept of conformational changes accompanying the transformation process should also put some restrictions onto the intersystem crossing process $S_1 \rightarrow T_1$. As the singlet lifetimes of the DAOAP derivatives studied are almost a factor 100 shorter than the $T_{1A}$ state lifetime, it is not very likely that the porphyrins will adopt the B-state conformation in the singlet excited state. Hence, the $T_{1B}$ state is not populated by direct intersystem crossing but has to be preceded by the $T_{1A}$ state.

## Conclusions

We have investigated the excited triplet state deactivation in a series of *meso*-diaryloctaalkylporphyrins. From this study the following has been learned: (1) Two triplet species with vastly different photophysical properties participate in the overall deactivation process. (2) At room temperature, the ground state recovery is unusually fast (a few $\mu$s) compared to the majority of porphyrins. (3) The triplet species have a "mother−daughter" relationship. The pronounced temperature dependence of the transformation process suggests conformational changes to be involved. (4) The ground state recovery at room temperature is governed exclusively by a route via the daughter state, as the direct intersystem crossing from the mother state is slow (some 10 ms).

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