Light-Induced Opening of the Intramolecular Hydrogen Bond of UV Absorbers of the 2-(2-Hydroxyphenyl)-1,3,5-triazine and the 2-(2-Hydroxyphenyl)benzotriazole Type

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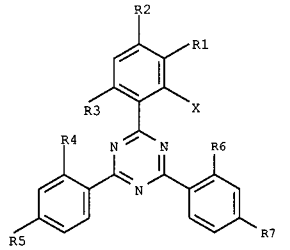
A number of 2-(2-hydroxyphenyl)-4,6-diaryl-1,3,5-triazines (HPTs) and TIN P (2-(2-hydroxy-5-methylphenyl)-benzotriazole) show phosphorescence in polar solvents at 77 K which increases in intensity with UV-irradiation time until an equilibrium value is reached (phosphorescence evolution). TIN P phosphoresces even at the very beginning of irradiation, in contrast to the HPTs, such as M-OH-P (2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine), which exhibit no such initial phosphorescence provided that they were not recently exposed to UV radiation. The corresponding methoxy derivatives (MPTs) of some HPTs, where the H atom of the intramolecular hydrogen bond (IMHB) is replaced by a methyl group, produce intense phosphorescence independent of irradiation time. Considerable relaxation is found for HPTs after dark periods ≤ 1 h at 77 K resulting in a significantly lower initial phosphorescence intensity upon renewed irradiation. TIN P, in contrast, shows much slower relaxation which becomes significant only at elevated temperatures. Phosphorescence evolution is due to open conformers of the molecules, i.e., with intermolecular rather than intramolecular hydrogen bonds, which are formed in polar solvents under the influence of UV radiation. Relaxation, i.e., re-formation of the IMHB of open-form molecules, is faster for the investigated HPTs than for TIN P.

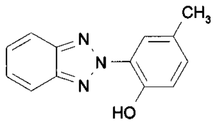
1. Introduction

UV absorbers with an intramolecular hydrogen bond (IMHB) are widely used to protect polymers against photodegradation.[1−5] The most effective compounds, even superior to the well-known 2-(2-hydroxyphenyl)benzotriazoles (HBzTs), are the 2-(2-hydroxyphenyl)-4,6-diaryl-1,3,5-triazines (HPTs) (for structures, see Chart 1). It has been established for such intramolecularly hydrogen-bridged UV absorbers that an excited-state intramolecular proton transfer (ESIPT) takes place after photoexcitation, in accordance with Förster's Theory.[6,7] This is followed by rapid radiationless deactivation which ensures that UV radiation, efficiently absorbed by these compounds owing to their high extinction coefficients, is almost completely transformed into vibrational energy.[7−16] The ESIPT process itself is no absolute prerequisite for effective energy transformation. An intact IMHB in the excited state is, however, necessary for offering the plenitude of vibrational modes which trigger rapid radiationless deactivation processes[11] and which Barbara et al.[17−19] suggested to involve large-amplitude torsional motions. Shizuka et al.[20−23] published the first studies on time-resolved fluorescence from the proton-transferred S_1' state of HPTs. Elsaesser and co-workers have concluded from femtosecond experiments with TIN P that an anharmonic, in-plane deformation mode modulates the separation between proton donor and acceptor atom thus playing a key role in the ESIPT process.[24]

CHART 1: Structures and Designations



	R$_1$	R$_2$	R$_3$	R$_4$	R$_5$	R$_6$	R$_7$	X
M-OH-P	H	OCH$_3$	H	H	H	H	H	OH
M-OH-T	H	OCH$_3$	H	H	CH$_3$	H	CH$_3$	OH
M-OH-X	H	OCH$_3$	H	CH$_3$	CH$_3$	CH$_3$	CH$_3$	OH
TTZ 1	CH$_3$	OC$_6$H$_{13}$	H	H	H	H	H	OH
TTZ 2	H	OC$_6$H$_{13}$	CH$_3$	H	H	H	H	OH
H-OH-B	H	OC$_6$H$_{13}$	H	H	phenyl	H	phenyl	OH
M-MeO-P	H	OCH$_3$	H	H	H	H	H	OCH$_3$
M-MeO-T	H	OCH$_3$	H	H	CH$_3$	H	CH$_3$	OCH$_3$



TIN P

Population of the UV absorber triplet state, in contrast, is highly undesirable since it may initiate photoreactions detrimental to the polymer due to the comparably long triplet lifetime. It has been established for the HBzTs that the triplet state can be populated when the IMHB is disrupted by polar solvents or matrixes.[12,25−29] Turro and co-workers have found from transient absorption spectra that TIN P phenolate ions are formed in DMSO.[30] Although the HPTs have a significantly stronger IMHB than the HBzTs[11,13,31−39] and should, therefore, be insensitive to polar matrixes, they surprisingly show phosphorescence in polar solvents at 77 K indicative of triplet-state population.[11,13,40] This paper aims at giving an interpretation of

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this phosphorescence emission and resolving the apparent contradiction between triplet-state population and the particularly good UV-stabilizing properties of the HPTs. TIN P and its methoxy derivative (MT) as well as the methoxy derivatives (MPTs) of some HPTs are included in this study for comparison.

2. Experimental Section

2.1. Materials. The following compounds were synthesized by Ciba Specialty Chemicals, Inc., Basle, Switzerland (for molecular structures, see Chart 1): M-OH-P, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine; M-OH-T, 2-(2-hydroxy-4-methoxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine; M-OH-X, 2-(2-hydroxy-4-methoxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine; H-OH-B, 2-(4-hexoxy-2-hydroxyphenyl)-4,6-bis(4-biphenylyl)-1,3,5-triazine; TTZ 1, 2-(4-hexoxy-2-hydroxy-3-methylphenyl)-4,6-diphenyl-1,3,5-triazine; TTZ 2, 2-(4-hexoxy-2-hydroxy-6-methylphenyl)-4,6-diphenyl-1,3,5-triazine; M-MeO-P, 2-(2,4-dimethoxyphenyl)-4,6-diphenyl-1,3,5-triazine; M-MeO-T, 2-(2,4-dimethoxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine; TIN P, 2-(2-hydroxy-5-methylphenyl)benzotriazole. The triazines were purified by repeated recrystallization from methylcyclohexane, ethanol, or 2-propanol,and TIN P was recrystallized from toluene. For origin and purification of MT, 2-(2-methoxy-5-methylphenyl)benzotriazole, see ref 12.

Solvents, 3-methylpentane (3-MP), 2-methylbutane (2-MB), methylcyclohexane (MCH), ethanol (EtOH), diethyl ether (Et), and 2-methyltetrahydrofuran (2-MTHF), and solvent mixtures, EPA (Et/2-MB/EtOH, 5/5/2 (v/v/v)) and MCH/2-MB, 3/1 (v/v), for absorption and emission measurements were of spectroscopic grade (Aldrich, Fluka, Merck) and purified by standard procedures.

2.2. Absorption and Emission Spectra. Absorption spectra were measured with a Perkin-Elmer Lambda 7 UV/vis absorption spectrometer. Emission spectra (phosphorescence, phosphorescence excitation) were recorded on a homemade spectrometer described previously[16,27,41] and corrected for the characteristics of the detection system. Both spectrometers could be equipped with an Oxford cryostat allowing cooling with liquid nitrogen to 77 K. Oxygen was removed from the samples for spectroscopic measurements in organic glasses (3-MP, MCH/2-MB, 2-MTHF, EPA, EtOH) at 77 K by several freeze−pump−thaw cycles in quartz cuvettes specially designed for low-temperature conditions. M-MeO-P was employed as standard for the phosphorescence quantum yield determinations ($\phi_P = 1.3 \times 10^{-2}$ in EEP (Et/EtOH/Pyridine 1/1/1, v/v/v); 77 K).[13,40] Triazine and benzotriazole concentrations were $\approx 10^{-5}$ M representing optical densities ≤ 0.2 at λ_{exc}.

3. Results and Discussion

3.1. Phosphorescence Emission from HPTs and MPTs. Table 1 portrays phosphorescence data for a number of HPTs and some of their methoxy derivatives (EPA, 77 K; see Figures1 and 3 for some of the corresponding phosphorescence spectra). The phosphorescence quantum yields given for the HPTs are only approximate because they vary with irradiation time and intensity (see section 3.2), as opposed to those of the MPTs, which are accurate. However, it is evident that the MPTs exhibit phoshorescence with a quantum yield considerably greater than that of the HPTs. In contrast, there are no significant differences between HPTs and MPTs as far as phosphorescence lifetimes and triplet energies are concerned. According to Stueber et al.[13,40] this can be explained by the assumption that the phosphorescence originates from a triplet state of the photoexcited triphenyltriazine core (see refs 42 and 43 for triphenyltriazine phosphorescence spectra). An extension of the mesomeric system should then lead to a bathochromic shift of the phosphorescence maximum as is actually observed for the biphenyl derivative H-OH-B (Table 1). HPT phosphorescence also appears in other polar solvents (EtOH, 2-MTHF), whereas, in nonpolar solvents (3-MP, MCH/2-MB), only M-OH-P phosphoresces, although with very low quantum yield.[13,44] This is analagous to the behavior of HBzTs which phoshoresce only very weakly, if at all, in nonpolar solvents.[16,27,41,45,46] Stueber et al.[13,40] have reported the phosphorescence excitation spectrum of M-OH-P to closely correspond with its absorption spectrum and concluded that the phosphorescence emission arises from the intramolecularly hydrogen-bonded species. However, these authors compared phosphorescence excitation spectra measured at 77 K with absorption spectra recorded at 292 K. Since the absorption spectrum of M-OH-P proved temperature dependent,[44] comparison of phosphorescence excitation and absorption

TABLE 1: Phosphorescence Data for Various HPTs and MPTs in EPA at 77 K with $\lambda_{exc} = 333$ nm

substance	λmax (nm)	ϕ_P	E_T (cm^{-1})	$\Delta\tilde{\nu}_1$ (cm^{-1})	$\Delta\tilde{\nu}_2$ (cm^{-1})	τ_P (ms)
M-OH-P	450	$\approx 5 \times 10^{-3}$	23 100	1000	1100	500
M-OH-T	448	$\approx 5 \times 10^{-3}$	23 400	1000	1200	1400
M-OH-X	450	$\approx 10^{-3}$	23 300	1000	1200	900
TTZ 1	450	$\approx 5 \times 10^{-5}$	23 400	900	1300	*a*
TTZ 2	436	$\approx 10^{-3}$	24 300	1300	1200	*a*
H-OH-B	518	$\approx 10^{-3}$	20 700	1400	1200	2300
M-MeO-P	454	1.3×10^{-2}	23 100	1100	1200	660[c]
M-MeO-T	446	1.9×10^{-2}	23 300	800	1400	*a*

[a] Not determined. [b] No vibrational structure. [c] In EEP.[13]

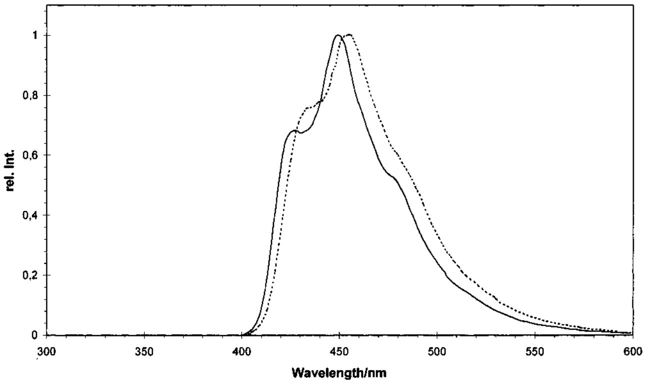


Figure 1. Phosphorescence spectra (normalized to unity) of M-OH-P (—) and M-MeO-P (···) in EPA at 77 K, $\lambda_{exc} = 333$ nm.

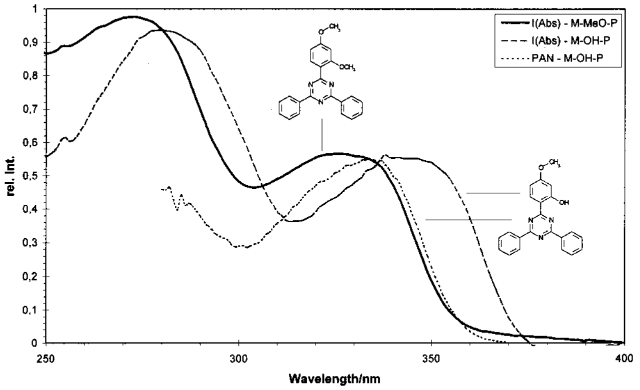


Figure 2. Phosphorescence excitation (PAN, $\lambda_{obs} = 450$ nm) of M-OH-P and relative absorbed intensity (I(Abs)) of M-OH-P and M-MeO-P in EPA at 77 K.

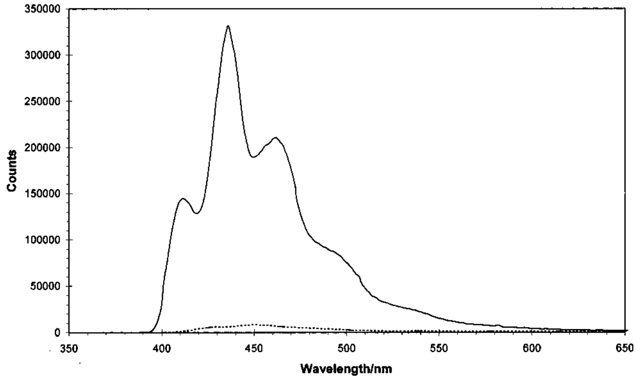


Figure 3. Phosphorescence of TTZ 1 (···) and TTZ 2 (—) in EPA at 77 K with $\lambda_{exc} = 333$ nm.

spectra, now both measured at 77 K, reveal a 20 nm hypsochromic shift for the longer-wavelength maximum of the phosphorescence excitation spectrum (see Figure 2). On the other hand, when the phosphorescence excitation of M-OH-P is compared with the absorption spectrum of M-MeO-P, a striking correspondence in the characteristic longer-wavelength UV region is evident (see also Figure 2). The same holds for M-OH-T/M-MeO-T.

This leads to the conclusion that in the phosphorescent M-OH-P molecules a conformation similar to that of M-MeO-P is present. This conformation is adopted when the IMHB of M-OH-P is converted to an intermolecular hydrogen bond with the (polar) solvent as it has also been found for TIN P.[9,27,45] In this case, an ESIPT cannot take place any more and population of the triplet state becomes feasible. In consideration of the exceptional IMHB strength of the HPTs it might be surprising that polar solvents are able to disrupt this bond. However, there is further experimental evidence for this, e.g. NMR coalescence phenomena observed with HPTs, indicative of IMHB opening and closing processes involving molecular rotations on the NMR time scale.[33] As mentioned above, only very low phosphorescence quantum yields from HPTs are detected in nonpolar solvents which underlines the importance of solvent polarity for the stabilization of the phosphorescent *inter*molecularly hydrogen-bonded molecules. This is also confirmed by comparing the phosphorescence spectra of TTZ 1 and TTZ 2 (Figure 3). The only difference between the structures of these compounds lies in the position of one methyl group on the phenolic aryl moiety (see Chart 1). However, there is almost no phosphorescence emission from TTZ 1 where the methyl group is in the ortho position with respect to the hydroxyl group. A possible explanation would be that the methyl group sterically protects the IMHB from solvent interference, which is in line with the explanation given for the improved solvent resistance of ortho-substituted HBzTs.[46] In TTZ 2 no such steric protection is possible though, so the solvent can freely interact with the IMHB. Furthermore, the methyl group in the 6-position might distort the planar configuration due to steric hindrance, thus weakening the IMHB and facilitating conversion to a twisted conformation with intermolecular hydrogen bonds leading to comparably high phosphorescence quantum yields of TTZ 2 (see Table 1).

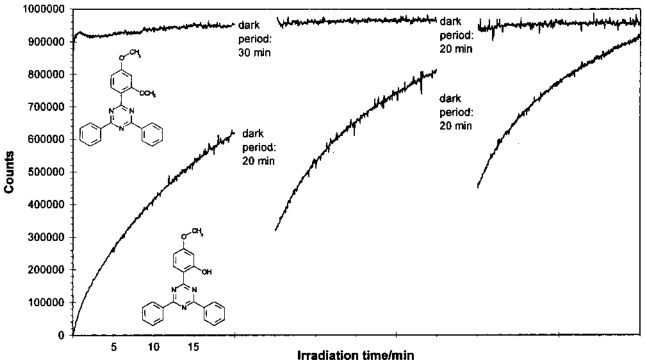


Figure 4. Phosphorescence evolution of M-OH-P (lower curves) and M-MeO-P (upper curves) in EPA ($\lambda_{exc} = 333$ nm, $\lambda_{obs} = 450$ nm, $T = 77$ K).

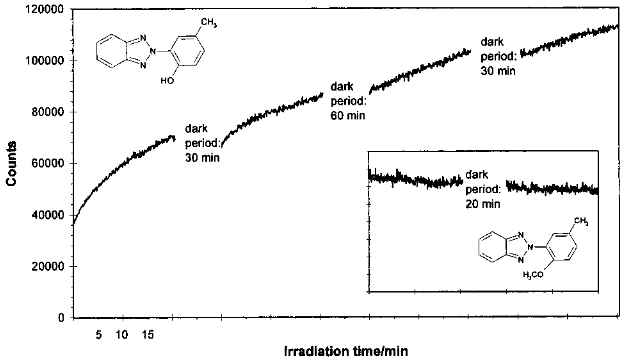


Figure 5. Phosphorescence evolution of TIN P and MT (inset) in EPA ($\lambda_{exc} = 333$ nm, $\lambda_{obs} = 512$ nm, $T = 77$ K).

3.2. Irradiation-Dependent Phosphorescence. As already mentioned in the previous section, the HPTs show an interesting irradiation-time-dependent increase in their phosphorescence intensity in polar solvents at 77 K. At irradiation time t(irr) = 0, no phosphorescence is detected. Then phosphorescence intensity rises quickly and finally approaches an equilibrium value. Figure 4 (lower part) shows this behavior, which is henceforth designated *phosphorescence evolution*, for M-OH-P. After a dark period of 20 min the phosphorescence intensity has significantly decreased with respect to the value from the end of the preceding irradiation period. The observed decrease of phosphorescence intensity after a dark period is termed *relaxation*. In contrast to the HPTs the corresponding MPTs do not show any phosphorescence evolution or relaxation (see Figure 4, upper part). The behavior of TIN P/MT is illustrated in Figure 5. TIN P exhibits phosphorescence evolution just like the HPTs, but there is a considerable initial phosphorescence at t(irr) = 0. However, practically no relaxation is found after dark periods during which the sample was kept at 77 K. MT shows the same characteristics as the MPTs (Figure 5, inset).

The rate of phosphorescence relaxation appears to rise with increasing temperature and the concomitant change of the EPA matrix from the solid to the liquid state as is implied by the experiment documented in Figure 6. After a dark period of 3 h, during which a M-OH-P sample was heated close to room temperature and then cooled again, complete relaxation was found whereas another sample, which was kept permanently at 77 K, still produced initial phosphorescence at the beginning of the second irradiation period due to incomplete relaxation.

3.3. Interpretation of Phosphorescence Evolution and Relaxation. Phosphorescence evolution of intramolecularly hydrogen-bonded compounds has been observed earlier by Nagaoka et al.[47,48] with *o*-hydroxybenzaldehyde, *o*-hydroxyacetophenone, and *o*-hydroxypropiophenone. They postulated a light-induced formation of rotamers representing one closed and two open forms of *o*-hydroxybenzaldehyde and *o*-hydroxyacetophenone, respectively. The observation that phosphorescence evolution of the latter compounds only occurred in nonpolar 3-MP but not in EtOH, where the phosphorescence intensity remained constant, was explained by a complete preformation of the phosphorescent species in polar solvents.[47] For *o*-hydroxypropiophenone, in contrast, phosphorescence evolution was detected in EtOH but not in 3-MP. Nagaoka et al.[48] suggested that in this case intermolecularly hydrogen-bridged species to the solvent are formed upon irradiation. However, no relaxation was reported by these authors.[47,48] Formation of photorotamers was also demonstrated by Orton et al.[28] and Morgan et al.[49] for isolated molecules of salicylic methyl ester, salicylic amide, and *o*-hydroxyacetophenone in cryogenic matrixes at 12 K. These findings along with our own experimental results lead us to the following interpretation of phosphorescence evolution and relaxation of the HPTs and HBzTs: Phosphorescence emission is produced by those molecules whose IMHB is disrupted already in the electronic ground state. This can be concluded from the fact that the long-wavelength UV band in the phosphorescence excitation spectrum is shifted to the blue compared to the absorption spectrum of the hydroxy compound with intact IMHB (see section 3.1) and that the phosphorescence excitation spectrum of the hydroxy compound corresponds to the absorption (and phosphorescence excitation) spectrum of its methoxy derivative.

The methoxy derivatives, as well as the open-form hydroxy compounds, are significantly distorted from planarity.[11,27] Their long-wavelength UV-absorption band, which is due to an intramolecular charge transfer transition in the planar molecule, is weakened and shifted hypsochromically or missing completely.[13,46] Without previous UV irradiation practically all HPT molecules have an intact IMHB (closed form), and thus, no initial phosphorescence is observed at the beginning of the first irradiation period. When the closed form has completed the intramolecular Förster Cycle, it ends up in its electronic ground state where the molecule has a lot of thermal (vibrational) energy stemming from the conversion of the original electronic excitation energy. Wiechmann et al.[50] estimated the corresponding temperature at 1000 K for TIN P in C_2Cl_4 solution. These thermally activated molecules can easily open their IMHB to form an intermolecular bond with a polar solvent. Upon excitation of this open form no rapid intramolecular proton transfer is possible any more, and thus, the slower intersystem crossing (ISC) process comes into play leading to population of the triplet state T_1 and subsequent phosphorescence emission. On the basis of these plausible assumptions we present a Jablonski scheme which reflects the above-mentioned processes (Scheme 1).

Of course it is also imaginable that the IMHB is opened in the singlet states S_0' or S_1' (proton-transferred level). We cannot distinguish between these pathways at the present time. However, it can be definitely excluded that an opening of the IMHB in the S_1' state is immediately followed by population of T_1 because the phosphorescence excitation spectrum should then correspond to the absorption spectrum of the closed form. As already pointed out, this is not the case, implying that a second photon is necessary to excite the open form to its triplet state.

As outlined above, the IMHB of TIN P is weaker than that of the HPTs. Part of the TIN P molecules convert their IMHB into an intermolecular hydrogen bond to the polar solvent (TIN-(inter); see refs 8, 12, 14, 16, 26, 27, 41, 46, and 51). This nicely explains why phosphorescence is observed from TIN P even at the very beginning of irradiation (Figure 5). For the corresponding methoxy derivatives of HPTs and HBzTs, no increase in phosphorescence intensity upon irradiation is expected in accordance with our experimental results (see section 3.2).

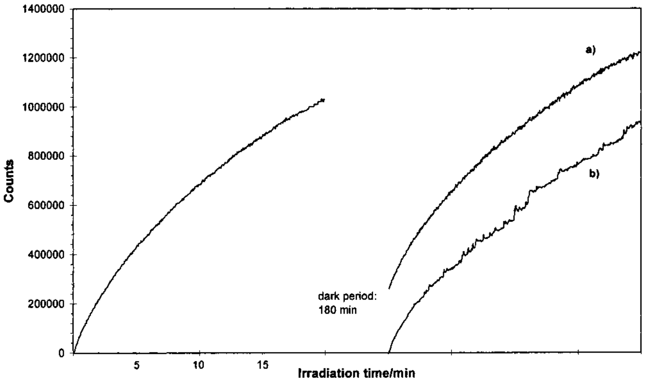
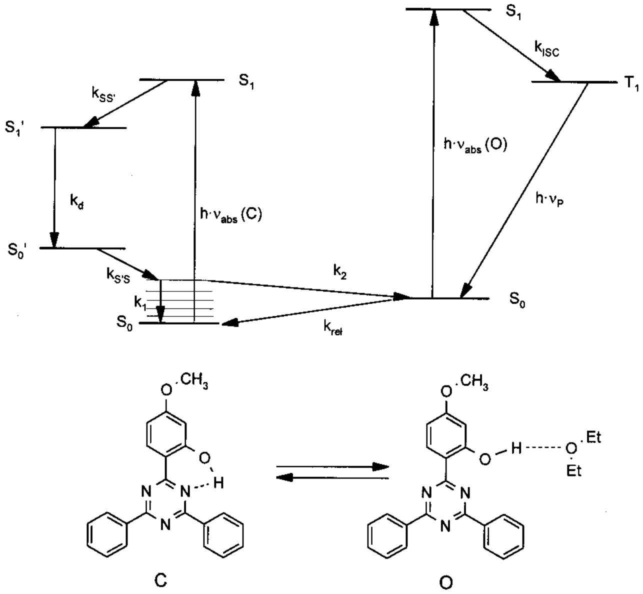


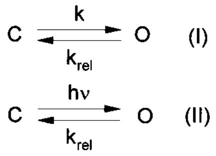
Figure 6. Phosphorescence evolution of M-OH-P in EPA at 77 K: (a) dark period at 77 K; (b) heated to 292 K during dark period and then cooled down again to 77 K (λ_{exc} = 333 nm, λ_{obs} = 450 nm).

SCHEME 1: Jablonski Scheme for the Interpretation of Phosphorescence Evolution (C, Closed Form; O, Open Form)

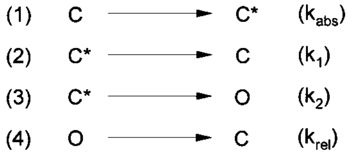


The stronger IMHB of the HPTs leads to a faster and more complete relaxation; i.e., the IMHB of the HPT-based UV absorber molecule is restored more effectively than that of the HBzTs. Thus it is understandable that phosphorescence emission from HPTs starts from a lower intensity level after a given dark period than it is the case for HBzTs. A rise of temperature is expected to accelerate restoration of the IMHB due to the increased thermal energy facilitating a crossing of the activation barrier which, furthermore, is reduced by the concomitant decrease of matrix viscosity. In our above-mentioned experiment (see Figure 6), there could also be an influence on the result due to diffusion of previously nonirradiated molecules into the irradiation zone enabled by the melting of the matrix. To minimize such matrix effects, measurements in a polymeric environment are in progress, where the state of aggregation does not change upon heating from 77 K to room temperature. In this way mainly the influence of temperature on k_{rel} can be studied, which will be reported in a forthcoming paper. It should also be borne in mind that a different equilibrium between both open and closed forms, which is dependent on the temperature, is present in the dark (see Scheme 2, I, thermodynamic aspect[13]). On the other hand, the time needed to reach the equilibrium between open and closed forms under irradiation and thus, whether the equilibrium is established at a given temperature,

SCHEME 2: Equilibrium between Closed (C) and Open Forms (O) in the Dark (I) and under Irradiation (II)



SCHEME 3: Reactions for the Kinetic Model of Phosphorescence Evolution



is governed by the kinetic aspect[13] (Scheme 2, II) and also depends on temperature (activation energy for k_{rel}).

3.4. Kinetic Model. For a kinetic model of phosphorescence evolution we consider the four reactions depicted in Scheme 3 (see also Scheme 1 for further details). Reaction 1 reflects photoexcitation of the closed form C into its S_1 state with subsequent ESIPT and further deactivation to C* from which an opening of the IMHB is possible. The corresponding rate constants are contained in k_{abs}. The exact nature of C* is not important for our model. We assume C* to be a highly vibrationally excited state which can either deactivate to the ground state of the closed form, C (rate constant k_1, reaction 2), or reacts by formation of the open form, O (k_2, reaction 3). O can be transformed into C via reaction 4 (k_{rel}) where the IMHB is reestablished. For the change in concentration of the open form the following equation holds at constant irradiation intensity:

$$\frac{\mathrm{d}[\mathrm{O}]}{\mathrm{d}t} = k_2[\mathrm{C}^*] - k_{\mathrm{rel}}[\mathrm{O}] \tag{1}$$

Application of the Bodenstein principle for C* provides

$$\frac{\mathrm{d}[\mathrm{C}^*]}{\mathrm{d}t} = k_{\mathrm{abs}}[\mathrm{C}] - (k_1 + k_2)[\mathrm{C}^*] = 0 \tag{2}$$

Incorporating (2) in (1):

$$\frac{\mathrm{d}[\mathrm{O}]}{\mathrm{d}t} = \frac{k_2 k_{\mathrm{abs}}}{k_1 + k_2}[\mathrm{C}] - k_{\mathrm{rel}}[\mathrm{O}] \tag{3}$$

The initial concentation of the UV absorber [UVA] is related to [O] as follows:

$$[\mathrm{O}] = [\mathrm{UVA}] - [\mathrm{C}] - [\mathrm{C}^*] = [\mathrm{UVA}] - (1 + A)[\mathrm{C}] \tag{4}$$

with $A = k_{\mathrm{abs}}/(k_1 + k_2)$. Inserting (4) into (3) leads to

$$\frac{\mathrm{d}[\mathrm{O}]}{\mathrm{d}t} = B[\mathrm{C}] - k_{\mathrm{rel}}[\mathrm{UVA}] \tag{5}$$

with $B = k_2A + k_{\mathrm{rel}} + k_{\mathrm{rel}}A$. Furthermore, it is evident that

$$\frac{\mathrm{d}[\mathrm{O}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} \tag{6}$$

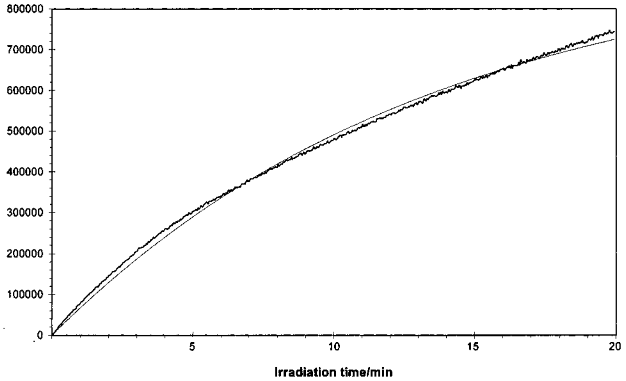


Figure 7. Experimental values (thick line) and fitted curve (thin line) for the phosphorescence evolution of M-OH-P in EPA at 77 K.

and thus inserting (6) into (5) gives

$$\frac{\mathrm{d}[\mathrm{C}]}{\mathrm{d}t} = -B[\mathrm{C}] + k_{\mathrm{rel}}[\mathrm{UVA}] \tag{7}$$

Solution of the differential eq 7 provides

$$[\mathrm{C}] = \frac{k_{\mathrm{rel}}}{B}[\mathrm{UVA}] + D\exp(-Bt) \tag{8}$$

with D being an integration constant. (8) in (4) gives

$$[\mathrm{O}] = E - F\exp(-Bt) \tag{9}$$

with $E = [\mathrm{UVA}](k_2A/B)$ and $F = D(1 + A)$.

If we assume that no open form is present at the beginning of irradiation and, therefore, $E = F$, we can write

$$[\mathrm{O}] = E(1 - \exp(-Bt)) \tag{10}$$

Equation 10 written out thus leads to

$$[\mathrm{O}] = [\mathrm{UVA}]\left(\frac{k_2 k_{\mathrm{abs}}}{k_2 k_{\mathrm{abs}} + k_{\mathrm{rel}}(k_1 + k_2 + k_{\mathrm{abs}})}\right) \times \left(1 - \exp\left[-\left(k_{\mathrm{abs}}\frac{k_2 + k_{\mathrm{rel}}}{k_1 + k_2} + k_{\mathrm{rel}}\right)t\right]\right) \tag{11}$$

At low concentrations of O the phosphorescence intensity I_{p} is proportional to [O] and thus we get from eq 10

$$I_{\mathrm{P}} = M(1 - \exp(-Bt)) \tag{12}$$

with $M = E(2.303)I_0(\epsilon(\mathrm{O}))d\phi_{\mathrm{P}}$, where I_0 is the irradiation intensity hitting the sample, $\epsilon(\mathrm{O})$ the extinction coefficient of O, d the path length of the sample cell, and ϕ_{P} the phosphorescence quantum yield. Equation 12 is used to describe the M-OH-P phosphorescence evolution curve (see Figure 7). Despite the simplicity of our kinetic model we found a good approximation of the experimental curve with $B = 1.226 \times 10^{-3}\ \mathrm{s}^{-1}$ and $M = 914\,000$.

For the following dark period where $k_{\mathrm{abs}} = 0$ and therefore $A = 0$ and $B = k_{\mathrm{rel}}$, we obtain from eq 9

$$[\mathrm{O}] = -D\exp(-k_{\mathrm{rel}}t) = [\mathrm{O}]_0 \exp(-k_{\mathrm{rel}}t) \tag{13}$$

with $[\mathrm{O}]_0$ being the concentration of the open form at the beginning of the dark period. Thus, eq 13 describes the decrease of the open-form concentration with the duration of the dark period. Unfortunately, this equation cannot be used for the determination of k_{rel} via phosphorescence measurements because no emission can be monitored in the dark period, of course.

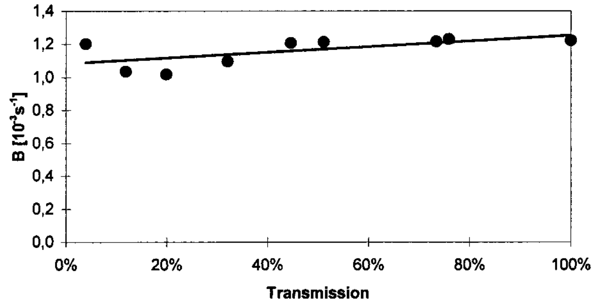


Figure 8. Plot of B vs excitation intensity (represented by the transmission of the respective neutral density filter in the excitation beam) and best linear regression line.

However, k_{rel} can be evaluated from the irradiation-intensity dependence of B. From eqs 9 and 11 follows that

$$B = \frac{k_2 + k_{\text{rel}}}{k_1 + k_2} k_{\text{abs}} + k_{\text{rel}} \tag{14}$$

It is evident from eq 14 that plotting B as a function of k_{abs}, which is assumed to be proportional to I_0, gives k_{rel} as intercept. Variation of the irradiation intensity was achieved by using various neutral density filters with different optical density. Figure 8 shows the result for M-OH-P in EPA at 77 K. B turned out as almost independent of irradiation intensity which is comprehensible upon consideration of eq 14. The slope of the linear-regression line is determined by k_1, k_2, and k_{rel}. The very low steepness of the slope indicates that $k_1 \gg k_2$ and k_{rel}; i.e., deactivation of the highly vibrationally excited molecule C* to its ground-state C is by far the fastest process (see Scheme 1). This appears plausible for it is well-known that distribution of vibrational energy to the environment is a matter of picoseconds in the condensed state.[50,52,53] Formation of the open form (determined by k_2) is much slower than that, otherwise phosphorescence evolution would be much faster. On the other hand, k_{rel} is even smaller than k_2, as can be derived from the obtained intercept giving $k_{\text{rel}} = 1.1 \times 10^{-3}$ s^{-1} corresponding to an average lifetime of 15 min for the open form of M-OH-P (at 77 K in EPA). Furthermore, we find B to be a reasonable approximation of k_{rel} in our investigated system.

4. Conclusions

A plausible answer can now be given to the question why HPTs are such excellent UV absorbers although they are phosphorescent at 77 K. As opposed to the HBzTs, the IMHB of the HPTs is strong enough in the ground state to resist disruption by polar matrixes which accounts for the fact that no phosphorescence is detected at the beginning of irradiation. Photoexcitation is necessary to provide enough energy for open-form formation. This intermolecularly hydrogen-bridged species, however, has a strong driving force to re-form its IMHB, even at 77 K, documented by phosphorescence relaxation, in contrast to the HBzTs which need higher temperatures for efficient relaxation. This, again, demonstrates the greater strength of the IMHB of HPTs. In principle, the comparably high lifetime of the open form, which is of the order of minutes, is not acceptable for a good UV absorber. It must be borne in mind, though, that the mentioned lifetime refers to 77 K and will be significantly reduced at higher temperature as was demonstrated experimentally (section 3.2). In practice, therefore, only a very small fraction of the HPT-based UV absorber molecules is expected to exist in the potentially harmful open form so that there is always a sufficient number of molecules with intact IMHB to guarantee polymer protection. The chosen experimental UV excitation intensities were roughly comparable to outdoor UV radiation from unattenuated sunlight.[37] Since permanent exposure to sunlight is not feasible due to natural dark periods such as clouds or night, there should be enough time for efficient relaxation. For all these reasons, we conclude that the light-induced triplet formation of HPT-based UV absorbers does not bear unfavorable consequences to practical application purposes. To further approach practical conditions, investigations on the phosphorescence properties of HPTs in polymeric matrixes are in progress and will be reported in a forthcoming paper.

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