Probing the Intramolecular Hydrogen Bond of 2-(2-Hydroxyphenyl)benzotriazoles in Polar Environment: A Photophysical Study of UV Absorber Efficiency

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Received: March 16, 2007; In Final Form: July 6, 2007

An in-depth photophysical study is presented for a series of 2-(2-hydroxyphenyl)benzotriazoles (HBzTs); the structural characteristic of all these photostabilizers is their strong intramolecular hydrogen bridge (IMHB). Tinuvin P (TIN P, **11a**) and six other HBzTs, with no substituent in the 3′-position ortho to the hydroxy function, show pronounced phosphorescence already in the dark (at 77 K in a polar glass). Upon irradiation, the phosphorescence intensity rises further until an equilibrium value is attained (up to 1.5 fold the dark value). A kinetic model is given which excellently reproduces this phosphorescence evolution: it demonstrates phosphorescence to arise from open conformers where the IMHB has been broken. Phosphorescence excitation spectra match the absorption spectra of the open conformer and also that of the *O*-methyl homologue **11A** which cannot form an IMHB. Fluorescence spectra likewise prove the equilibrium between the closed and open conformer for these HBzTs. In unpolar glasses as well as in the crystalline state, TIN P displays a long-wavelength (red) fluorescence (with an enormous Stokes shift of $\sim$10.000 cm^{-1}) which is associated with the excited singlet state of the closed form after proton transfer within the IMHB, $S_1'(C)$. In polar matrixes, on the other hand, a blue fluorescence is observed (with a regular Stokes shift) for all those HBzTs which have no 3′-substituent shielding the IMHB against being opened by the polar solvent. This blue fluorescence, just as the characteristic phosphorescence evolution for these compounds, is associated with the open conformer. For HBzTs with an (alkyl) group ortho to the bridging OH group, however, a long-wavelength (red) fluorescence is again observed. The shielding effect of the 3′-substituent shows a fine gradation, cumyl $\geq$ 1,1,3,3-tetramethylbutyl (isooctyl) $>$ *t*-butyl $\geq$ methyl.

1. Introduction

UV absorbers with a chelate-type intramolecular hydrogen bridge are widely employed as additives for protecting polymer materials against UV radiation. As long as the intramolecular hydrogen bond (IMHB) remains intact, these molecules undergo a very fast excited-state intramolecular proton transfer (ESIPT), followed or accompanied by rapid radiationless deactivation which transforms the absorbed radiation energy into innocuous thermal energy. At low temperatures, one can thus often observe a weak proton-transferred fluorescence (PTF). Shizuka et al.[1] were the first to study such ESIPT processes in 2-hydroxyphenyl triazines by time-resolved fluorescence.

The 2-(2-hydroxyphenyl)benzotriazoles (HBzTs) and the 2-(2-hydroxyphenyl)-1,3,5-triazines (HPTs) constitute two technically important classes of UV absorbers. At least in the electronic ground state, the IMHB of any HBzT, such as TIN P and structurally related compounds studied in this work (cf. Chart 1), is much weaker than that of, for example, 2-(2-hydroxyphenyl)-4,6-diphenyl-1,3,5-triazines (HPTs). This has been established unequivocally from IR, NMR, and emission spectroscopic data as well as by X-ray crystal structure analysis.[2−9]

In polar glasses at 77 K, some HPTs and HBzTs also display a pronounced phosphorescence which increases in intensity upon prolonged irradiation until an equilibrium value is reached;[6−10] we have termed this phenomenon phosphorescence evolution. TIN P and other HBzTs show considerable phosphorescence already at the outset of the irradiation (cf. Figure 1, section 3.1); for HPTs, in contrast, no initial phosphorescence is observed prior to their exposure to UV radiation.[6−9] The corresponding methoxy derivatives (such as the 2-methoxyphenyl benzotriazole **11A** and all methoxy-substituted HPTs investigated so far), however, where the IMHB hydrogen is substituted by a methyl group, exhibit strong phosphorescence from the very beginning of the irradiation, with the intensity independent of the irradiation time.

For both HBzTs and HPTs, the phenomenon of phosphorescence evolution thus must be intrinsically and causally connected with the specific nature of the IMHB. The phosphorescence in

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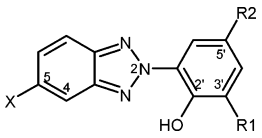
10.1021/jp0721189 CCC: $37.00
Published on Web 09/06/2007

CHART 1: Substituent Pattern and Compound Designation[a] of the 2-(2-Hydroxyphenyl)benzotriazoles Investigated



	X	R^2	R^1	2′-substituent
11A	H	CH_3	H	OCH_3
11B	H	CH_3	H	$OB(C_6H_5)_2$
11a	H	CH_3	H	OH
12a	H	*t*-butyl	H	OH
13a	H	$C_2H_4COOCH_3$	H	OH
13b	H	$C_2H_4COOCH_3$	CH_3	OH
13c	H	$C_2H_4COOCH_3$	*t*-butyl	OH
14d	H	*i*-octyl[b]	cumyl[c]	OH
22a	SC_6H_5	*t*-butyl	H	OH
32a	$SO_2C_6H_5$	*t*-butyl	H	OH
32c	$SO_2C_6H_5$	*t*-butyl	*t*-butyl	OH
34d	$SO_2C_6H_5$	*i*-octyl[b]	cumyl[c]	OH
44d	$SO_2C_4H_9$	*i*-octyl[b]	cumyl[c]	OH
52a	Cl	*t*-butyl	H	OH
54d	Cl	*i*-octyl[b]	cumyl[c]	OH
64a	CF_3	*i*-octyl[b]	H	OH
62c	CF_3	*t*-butyl	*t*-butyl	OH
64e	CF_3	*i*-octyl[b]	*i*-octyl[b]	OH
64d	CF_3	*i*-octyl[b]	cumyl[c]	OH
74d	$COOCH_3$	*i*-octyl[b]	cumyl[c]	OH
81c	OCH_3	CH_3	*t*-butyl	OH

[a] Compound designation is as follows: The first (numerical) digit designates the nature of the substituent X at C-5 in the benzotriazole core (e.g., **1..**, X = H), the second digit characterizes the (alkyl) group R^2 in 5′-position of the hydroxyphenyl moiety (e.g., **.2.**, R^2 = *t*-butyl), and the final, lower case letter denotes the C-3′ (alkyl) group R^1, ortho to the bridging O−H function (e.g., **..a,** R^1 = H; **..d,** R^1 = cumyl). [b] Isooctyl = 2,2,4,4-tetramethylbutyl. [c] Cumyl = α-cumyl = 1-methyl-1-phenylethyl.

fact arises from "open" conformers where the strong, chelate-type intramolecular H-bridge has been broken. In such open conformers, the phenolic OH group forms unspecific intermolecular hydrogen bonds to, for example, basic centers of the glass or solvent matrix. Formation of the open form is a dynamic process which is triggered by the photoexcitation. After a dark period (<1 h at 77 K), the triazines show substantial relaxation[6−10] and thence significantly reduced initial phosphorescence intensity when irradiation is commenced again. For HBzTs such as TIN P, in contrast, this relaxation is negligible (see Figure 1, dark period 2.5 h at 77 K). Detailed kinetic models for the phosphorescence evolution have been presented for both classes of UV stabilizers, HPTs[6,7,10] and HBzTs[8,9] (cf. section 3.1).

Despite their weaker IMHB in the electronic ground state, HBzTs still are of great technical importance. We have therefore studied, in the present work, a broad spectrum of 2-hydroxyphenyl benzotriazoles, with the general structure shown in Chart 1, with respect to both strength (thermodynamic aspect) and stability of the IMHB (kinetic aspect). These two properties which are paramount for the molecule functioning as a UV absorber may be varied systematically by introducing appropriate substituents into the benzotriazole core or the hydroxyphenyl moiety. In this context, the HBzTs investigated here can be classified, for example, according to whether or not they bear an electron-withdrawing substituent X in 5-position. An alternative mode of classification is the presence or not of an (alkyl) substituent at C-3′, that is, ortho to the OH function which constitutes the hydrogen donor for the IMHB ($R^1 \neq$ H, cf. Chart 1). The effective shielding volume of any such substituent R^1 determines whether an "open" conformer can be stabilized by forming a (more or less directed) intermolecular hydrogen bridge to the solvent matrix. Sufficiently bulky groups at C-3′ might even prevent the intramolecular H-bond from being opened at all (cf. 3.2).

The fine-tuning of both the strength of the IMHB and its kinetic stability under constant irradiation becomes manifest primarily from the phosphorescence and, to some extent, also from the fluorescence measurements. The possibility thus can be envisaged to rationally design, on the basis of the respective photochemical data, a UV absorber with an optimum IMHB strength.

2. Experimental Section

The following compounds (for structures, see Chart 1) were synthesized in the research laboratories of Ciba Specialty Chemicals Inc., Basle, Switzerland: **11a**, trade name *Tinuvin P*, TIN P, 2-(2-hydroxy-5-methylphenyl)benzotriazole; **11A**, MTIN, 2-(2-methoxy-5-methylphenyl)benzotriazole; **12a**, 2-(5-*tert*-butyl-2-hydroxyphenyl)benzotriazole; **13a**, 2-(2-hydroxy-5-[2-(methoxycarbonyl)ethyl]phenyl)benzotriazole; **13b**, 2-(2-hydroxy-5-[2-(methoxycarbonyl)ethyl]-3-methylphenyl)benzotriazole; and **13c**, 2-(3-*tert*-butyl-2-hydroxy-5-[2-(methoxycarbonyl)ethyl]phenyl)benzotriazole.

The following compounds were synthesized in the research laboratories at Ciba Specialty Chemicals, Tarrytown, New York: **14d**, 2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)benzotriazole; **22a**, 2-(5-*tert*-butyl-2-hydroxyphenyl)-5-phenylmercaptobenzotriazole; **32a**, 2-(5-*tert*-butyl-2-hydroxyphenyl)-5-phenylsulfonylbenzotriazole; **32c**, 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-5-phenylsulfonylbenzotriazole; **34d**, 2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)-5-phenylsulfonylbenzotriazole; **44d**, 5-butylsulfonyl-2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)benzotriazole; **52a**, 5-chloro-2-(5-*tert*-butyl-2-hydroxyphenyl) benzotriazole; **54d**, 5-chloro-2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)benzotriazole; **62c**, 2-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-5-trifluoromethylbenzotriazole; **64a**, 2-(2-hydroxy-5-[1,1,3,3-tetramethylbutyl]phenyl)-5-trifluoromethylbenzotriazole; **64d**, 2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)-5-trifluoromethylbenzotriazole; **64e**, 2-(2-hydroxy-3,5-bis[1,1,3,3-tetramethylbutyl]-phenyl)-5-trifluoromethylbenzotriazole; and **74d**, 2-(2-hydroxy-3-[1-methyl-1-phenylethyl]-5-[1,1,3,3-tetramethylbutyl]phenyl)-5-methoxycarbonylbenzotriazole.

The following compounds were synthesized according to literature procedures: **11B**, 2-(2-diphenylboryloxy-5-methylphenyl)benzotriazole,[11] and **81c**, 2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-5-methoxybenzotriazole.[12]

All HBzTs were purified by repeated recrystallization from, for example, toluene, hexane, or isooctane before the spectroscopic measurements. Measurements at 77 K were performed in solid EPA solution [diethylether/2-methylbutane/ethanol 5:5:2 (v/v/v)], with all solvents purified by standard procedures.

Absorption spectra in the polar EPA solvent mixture were recorded for all compounds with a Perkin-Elmer Lambda 7 UV/vis absorption spectrometer both at 77 K and at ambient temperature. All emission spectra — phosphorescence, fluorescence at λ_{exc} = 313, 333, and 366 nm as well as the respective excitation spectra, and time-resolved phosphorescence (delay time 0.5 μs) — were recorded on an in-house-built spectrometer described previously[13−15] and were corrected for the characteristics of the detection system. Both spectrometers could be equipped with an Oxford cryostat adapted for cooling to 77 K

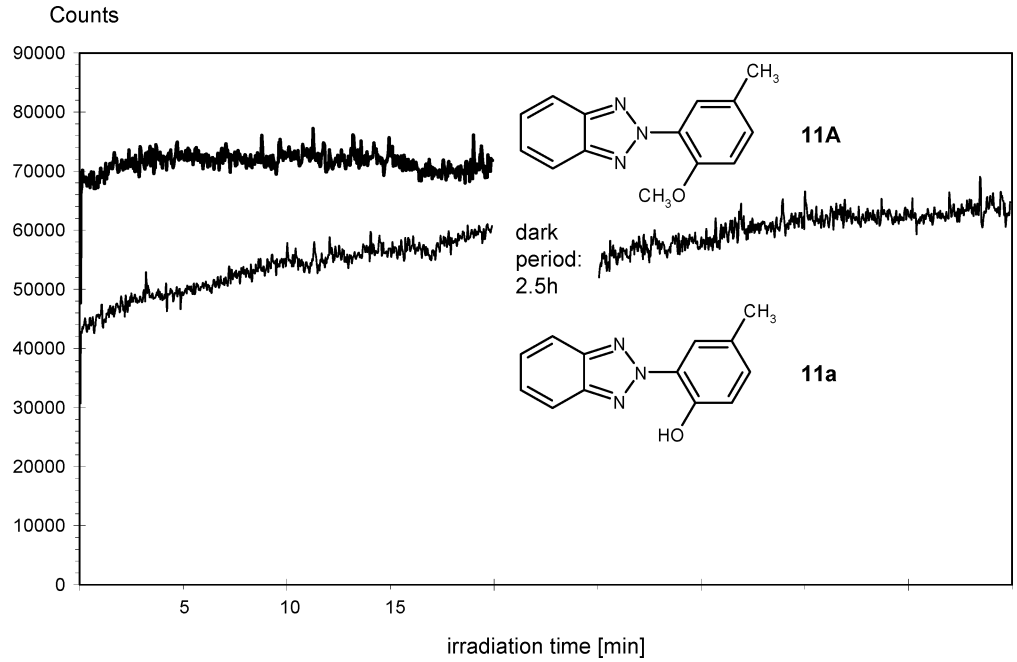


Figure 1. Time-dependent phosphorescence behavior, and relaxation in the dark period, for **11a** and **11A** in EPA at 77 K ($\lambda_{exc} = 333$ nm, $\lambda_{obs} = 512$ nm, $c_{\mathbf{11a}} = 1.4 \cdot 10^{-5}$ mol·L^{-1}, $c_{\mathbf{11A}} = 2.8 \cdot 10^{-5}$ mol·L^{-1}).

with liquid nitrogen. Oxygen was removed from the EPA matrix at 77 K by several freeze−pump−thaw cycles in quartz cuvettes specially designed for low-temperature measurements. HBzT concentrations in EPA ranged between 10^{-6} M and $2 \cdot 10^{-5}$ M, corresponding to an optical density ≤ 0.2 at λ_{exc}.

3. Results and Discussion

As shown in Scheme 1 and outlined already in the Introduction, an equilibrium exists for all HBzT stabilizers between the "closed" form (*C*), with an intact intramolecular hydrogen bridge, and an "open" form (*O*) where this chelate-type hydrogen bond has been broken. In this conformer, the 2-hydroxyaryl ring very likely is twisted relative to the benzotriazole plane, and the phenolic OH group thence can readily form an intermolecular hydrogen bond to, for example, a (basic) solvent molecule. Phosphorescence evolution is directly related to this conformational equilibrium.

A phosphorescing triplet state is not accessible, for either HPTs or HBzTs, from the excited singlet state of the closed form, $S_1(C)$, since this is depleted far too rapidly by the fast and efficient ESIPT process (cf. Scheme 1). If phosphorescence is in fact observed, the intramolecular bridge must have been broken prior to photoexcitation. For the $S_1(O)$ state of this open conformer, an ESIPT process of course is no longer feasible, and so the ground is laid for ISC and population of the triplet, $T_1(O)$, and thence phosphorescence.

3.1. Phosphorescence Evolution. Our kinetic model for the phosphorescence evolution is based on four bulk reactions, presented summarily in Scheme 3; Scheme 1 has the mechanistic details. Reaction 1 in Scheme 3 comprises the photoexcitation of the closed form *C* of the stabilizer molecule, with an intact intramolecular hydrogen bridge, into the $S_1(C)$ state, the subsequent ESIPT process, $S_1(C) \rightarrow S_1'(C)$, and finally the deactivation of $S_1'(C)$ to a form *C** from which an opening of the IMHB is mechanistically feasible. The individual rate constants for all steps involved in the formation of *C** are joined in k_{abs}. Although the exact nature of C* is not important for the model, we assume *C** to be a vibrationally highly-excited state which may either deactivate to the ground state, $S_0(C)$, of the closed form (reaction 2, rate constant k_1), or utilize the excess energy to break the chelate-type bridge and to rearrange to an open conformer *O*, likewise in the respective $S_0(O)$ state (reaction 3, k_2).

All HBzTs studied here show a substantial concentration of open conformer already in the dark (see Figure 1; cf. Scheme 2, equilibrium I), in sharp contrast to stabilizers of the triazine type where the dark concentration of the open form is zero.[6] Upon irradiation, additional molecules are transformed into the open state (equilibrium II) by the sequence outlined above. The closed conformer *C* is reformed, on the other hand, and the IMHB restored via reaction 4 which we have termed relaxation[6] (rate constant k_{rel}; cf. Schemes 2 and 3). The concentration of the open form [*O*] thus becomes a function of the irradiation time *t*:[6−8]

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

with $E = [\mathrm{UVA}] \cdot (k_2 A/B)$, $F = D \cdot (1 + A)$, and $A = k_{abs}/(k_1 + k_2)$. In these terms, [UVA] represents the (initial) concentration of the UV absorber summed over all species, *D* is an integration constant, and *B* is a composite function of the four individual rate constants involved (cf. Scheme 3):

$$B = \frac{k_2 + k_{rel}}{k_1 + k_2} \cdot k_{abs} + k_{rel} \tag{2}$$

Details of how eq 1 is derived are given in ref 6. The initial concentration of the open form $[O]_A$ for any HBzT at the outset of the irradiation ($t = 0$) then is given by

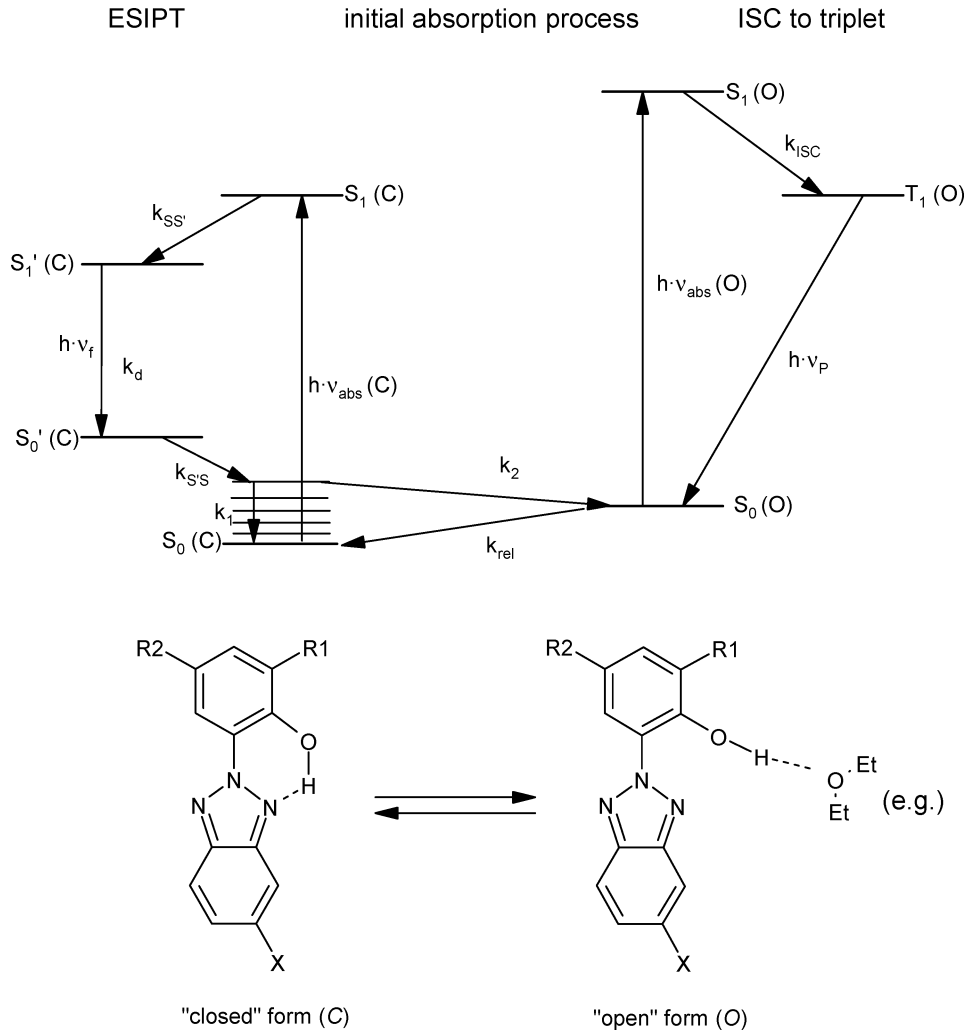
$$[O]_A = E - F$$

and eq 1 is transformed into

$$[O]_t = E - (E - [O]_A) \cdot \exp(-Bt) \tag{1a}$$

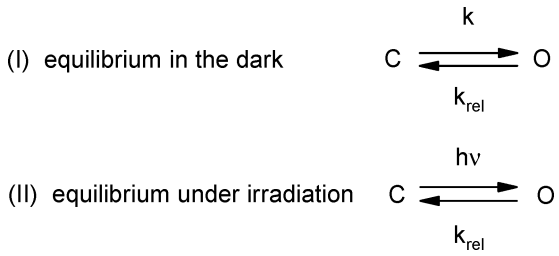
At sufficiently low UV absorber concentrations, the extinction of the open conformer is small, and the phosphorescence

SCHEME 1: Jablonski Scheme[47] for the Interpretation of Phosphorescence Evolution in 2-(2-Hydroxyphenyl)benzotriazoles (HBzTs)[a]

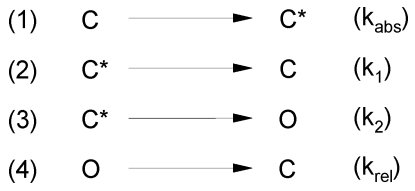


[a] Left-hand side: closed form (*C*) of the respective HBzT, with an intact IMHB; right-hand side: open form (*O*) of the respective HBzT, stabilized (in part) by intermolecular hydrogen bonding to the solvent/matrix.

SCHEME 2



SCHEME 3



intensity I_P which is experimentally accessible thence will be proportional to $[O]_t$:

$$I_P = M - (M - I_P^A)\cdot\exp(-Bt) \qquad (3)$$

with $M = P\cdot E$, and the phosphorescence intensity at the outset of irradiation $I_P^A = P\cdot[O]_A$. The proportionality factor P incorporates I_0 (irradiation intensity hitting the sample), $\epsilon(O)$ (extinction coefficient of the open conformer), d (path length of the sample cell), and ϕ_P (phosphorescence quantum yield).

For TIN P (**11a**), the phosphorescence intensity is pronounced already in the dark; under constant irradiation, it rises to a steady-state equilibrium value (from 50.000 to 60.000 counts). The experimental curve for the phosphorescence evolution (see Figure 2) is reproduced excellently by eq 3 (solid line), despite the simplicity of the kinetic model, with $B = 2.463\cdot10^{-3}$ s^{-1} and $M = 63\,900$ counts.[8,9]

With these experimental data and eq 2, the rate constant k_{rel} was derived for TIN P, following a procedure described for the HPTs in refs 6 and 7. The value for $k_{rel} = 0.7\cdot10^{-3}$ s^{-1} (at 77 K in EPA) represents the capacity of TIN P for restoring the IMHB and corresponds to 24 min average lifetime of the open conformer of TIN P in a glass matrix. For the hydroxyphenyl triazine M−OH−P [2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine], the respective value is $k_{rel} = 1.1\cdot10^{-3}$ s^{-1}, with a corresponding average lifetime of 15 min (likewise at 77 K in EPA).[6,7,10] Even in solid solution, the relaxation process, or better the restoration of the IMHB from the open conformer, thus appears somewhat faster for HPTs than for TIN P (cf. Figures 4 and 5 in ref 6).

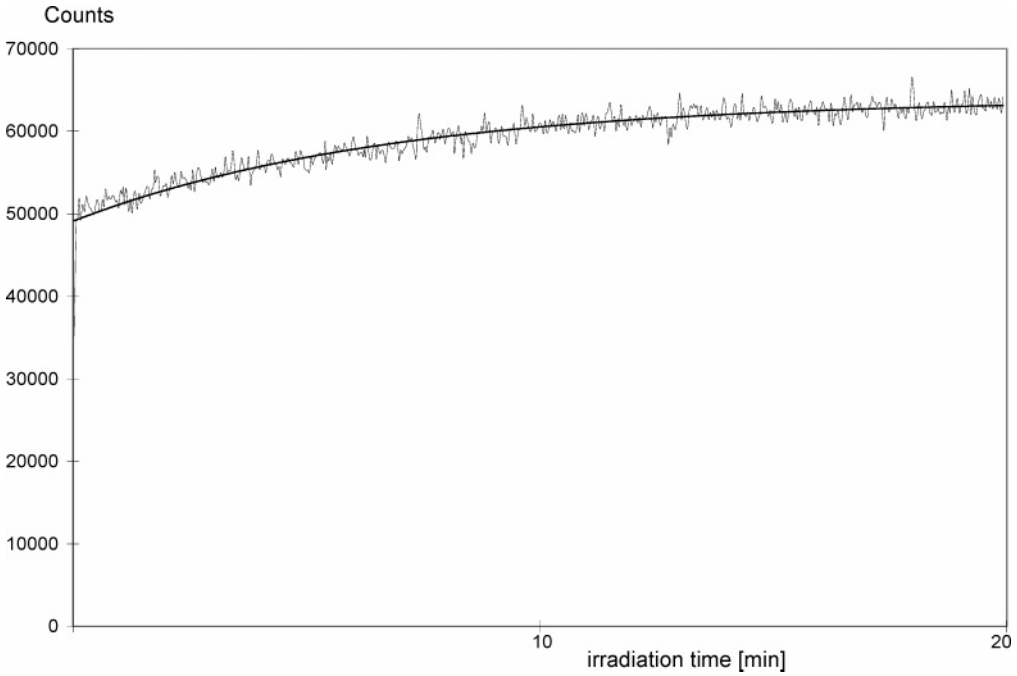


Figure 2. Phosphorescence evolution of **11a** in EPA at 77 K (λ_{exc} = 333 nm, λ_{obs} = 512 nm, $c_{\mathbf{11a}} = 1.4 \cdot 10^{-5}$ mol·L^{-1}).

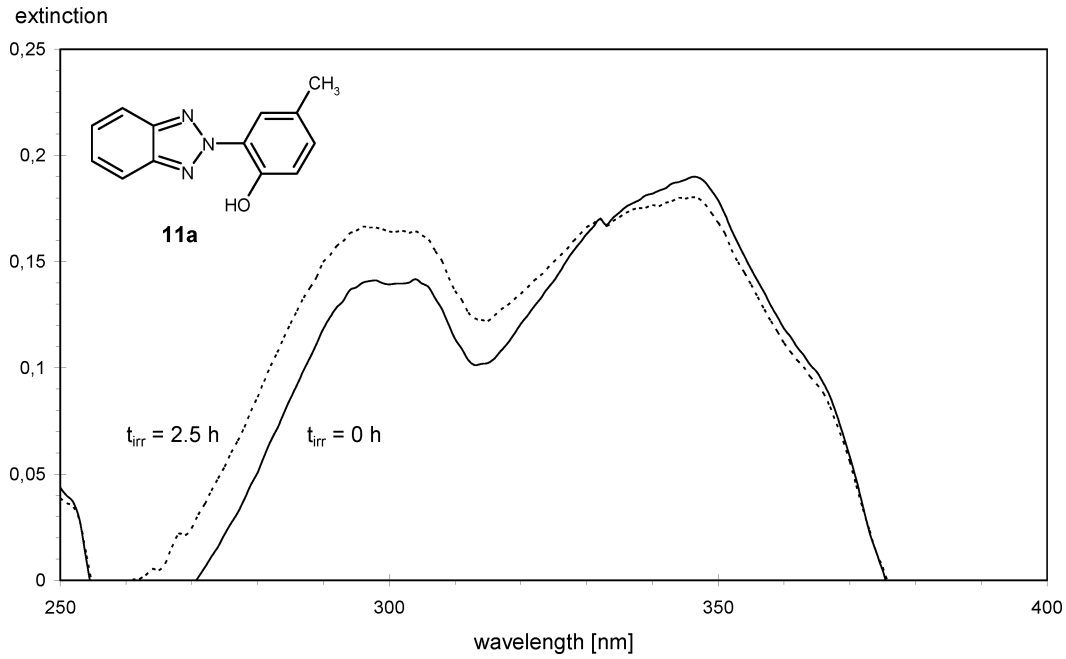


Figure 3. Absorption spectrum of **11a** (in EPA, 77 K) before (—) and after 2.5 h of irradiation (---; λ_{exc} = 333 nm).

The equilibrium constant $K_{h\nu}$, defined as the ratio of the concentrations of open and closed form under constant irradiation (eq 4; cf. Scheme 2, equilibrium II), of course depends on the respective irradiation intensity; it was calculated for TIN P as[8,9]

$$K_{h\nu} = \frac{[O]}{[C]} = 8._3 \qquad (4)$$

Thence, in EPA at 77 K, 89% of the TIN P molecules exist as the open conformer under the given irradiation intensity (100W-HBO lamp, λ_{irr} = 333 nm, photonic flux $I_0 = 6.03 \cdot 10^{13}$ photons·cm^{-2}·s^{-1}); actinometry has shown these conditions to be roughly equivalent to sunlight exposure.[8] The corresponding value for the hydroxyphenyl triazine M−OH−P is smaller by 2 orders of magnitude;[6,7] with $K_{h\nu}$ = 0.05, 95% of the M−OH−P molecules have their IMHB conserved at the irradiation equilibrium under elsewise identical conditions. The increased concentration of open conformers under constant irradiation manifests itself also from the respective absorption spectra (cf. Figure 3).

Since the highly efficient ESIPT process forestalls the triplet state of the IMHB conformer to be populated at all, the observed phosphorescence intensity may be considered as an indicator for the strength of the IMHB in the ground state or rather for the ratio k_{rel}/k_2, that is, for the capacity of a given stabilizer molecule to restore its IMHB once it has been broken following photoexcitation. It is important to realize, in this context, that k_{rel} will be much faster at ambient temperature than in a glass matrix at 77 K. This is crucial for the application of a given

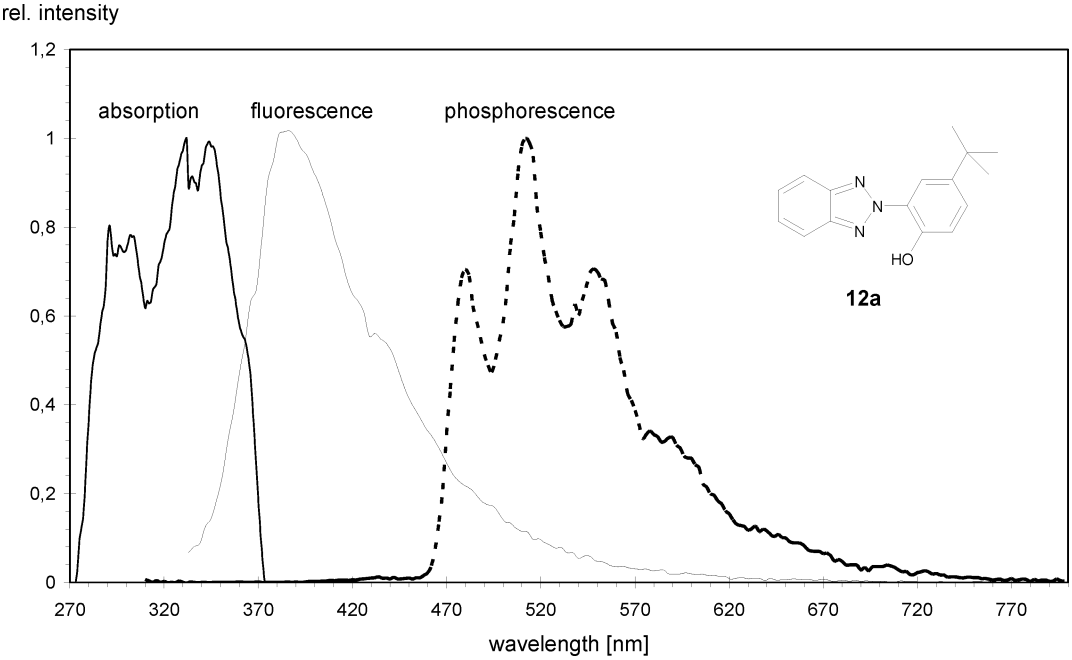


Figure 4. Normalized absorption (—), fluorescence (—; λ_{exc} = 313 nm), and phosphorescence spectrum (---; λ_{exc} = 313 nm) of **12a** (in EPA, 77 K).

compound as UV absorber since a long-lived triplet can and will initiate destructive processes in the matrix that it is supposed to protect and since, on the other hand, the desired fast deactivation pathway via an ESIPT process is accessible only for molecules with an intact IMHB.

3.2. Phosphorescence Spectra. Among the hydroxyphenyl benzotriazoles investigated in the course of the present study, distinct phosphorescence evolution is restricted to those seven compounds (all compounds **..a**, cf. Chart 1) that have no (alkyl) substituent in the 3′-position of the 2-phenyl ring (at C-3′), that is, ortho to the hydroxy function which constitutes the hydrogen donor for the IMHB (R^1 = H), regardless of whether there is a substituent or not in 5-position of the triazole ring and regardless also of its electronic nature (±*M*, ±*I*).[12] If the IMHB is broken as a sequel of photoexcitation (cf. 3.1), subsequent photoexcitation of any such open conformer will result in population of the triplet $T_1(O)$ by intersystem crossing (k_{ISC}, cf. Scheme 1), and phosphorescence is observed besides fluorescence from the excited singlet state $S_1(O)$ of the open conformer (with normal Stokes shift; see below, 3.4). The phosphorescence spectra display a distinct three-maximum fine structure (see Figure 4), with the maxima of the respective most intense emission lying in a very narrow range (512−516 nm,[16] see Table 1). This is exactly the same wavelength as that found for the phosphorescence of the *O*-methyl derivative **11A** (λ_{max} = 514 nm) which of course cannot form an IMHB and thus constitutes further clear proof that phosphorescence in fact arises from the open conformer.

For three other HBzTs, with a substituent R^1 ortho to the phenolic OH function but no C-5 substituent (**13b**, **13c**, **14d**), no phosphorescence is detected exceeding the emission of the solvent (Figure 5, thin line). The C-3′ substituent apparently shields the 2′-hydroxy function to such an extent from the polar matrix that the open conformer cannot be properly stabilized anymore by an intermolecular hydrogen bond. As a consequence, either k_2 (cf. Scheme 1) will be attenuated or, more likely, the rate k_{rel} for restoration of the IMHB from the open form will become much higher; both effects may of course also operate jointly. Each way, the concentration of the open form is reduced drastically, and the phosphorescence intensity concomitantly pushed below the detection limit. A methyl group, as in **13b** versus **13a**, already suffices to definitely shift the equilibrium in favor of the IMHB conformer; neither the bulky *t*-butyl (**13c**) nor the space-filling cumyl residue (**14d**) is required (see Table 1). This strikingly demonstrates the delicate free-energy balance between the two HBzT conformers.

The remaining eight HBzTs have a shielding group R^1 at C-3′ and, additionally, a C-5 substituent in the benzotriazole core. Four of these display a weak yet unequivocal phosphorescence that is distinctly set off from the solvent emission (Figure 5, bold line; see also Table 1). The 5-phenyl- and -butylsulfonyl derivatives (**34d**, **44d**), both with a cumyl substituent at C-3′,

TABLE 1: Phosphorescence Maxima, Quantum Yields, and Phosphorescence Lifetimes of the HBzTs (11a−81c, in EPA, 77 K, λ_{exc} = 313 nm)

	λ_p (nm)	Φ_p	τ_p (s)	phosphorescence evolution	relaxation
aniline[48]	420	0.85	5.4_0	no	no
11A	514	0.168	1.0_9	no	no
11a	512	0.091[a]		yes	yes
		0.127[b]			
12a	512	0.231[b]	1.3_1	yes	no
13a	512	0.283[a]	1.3_3	yes	no
		0.417[b]			
13b				no	no
13c				no	no
14d				no	no
22a	546	0.743[b]	1.3_8	yes	no
32a	512	1.00[b]	1.3_3	yes	yes
32c	512	0.035	1.2_0	no	no
34d	508	0.005	1.2_8	no	no
44d	502	0.005	1.4_5	no	no
52a	512	0.673[b]	1.4_5	yes	no
54d				no	no
64a	516	0.743[b]	1.2_8	yes	no
62c	512	0.011	1.3_7	no	no
64e				no	no
64d				no	no
74d				no	no

[a] Before irradiation. [b] Equilibrium value after ≥2 h irradiation when phosphorescence intensity has reached a steady state.

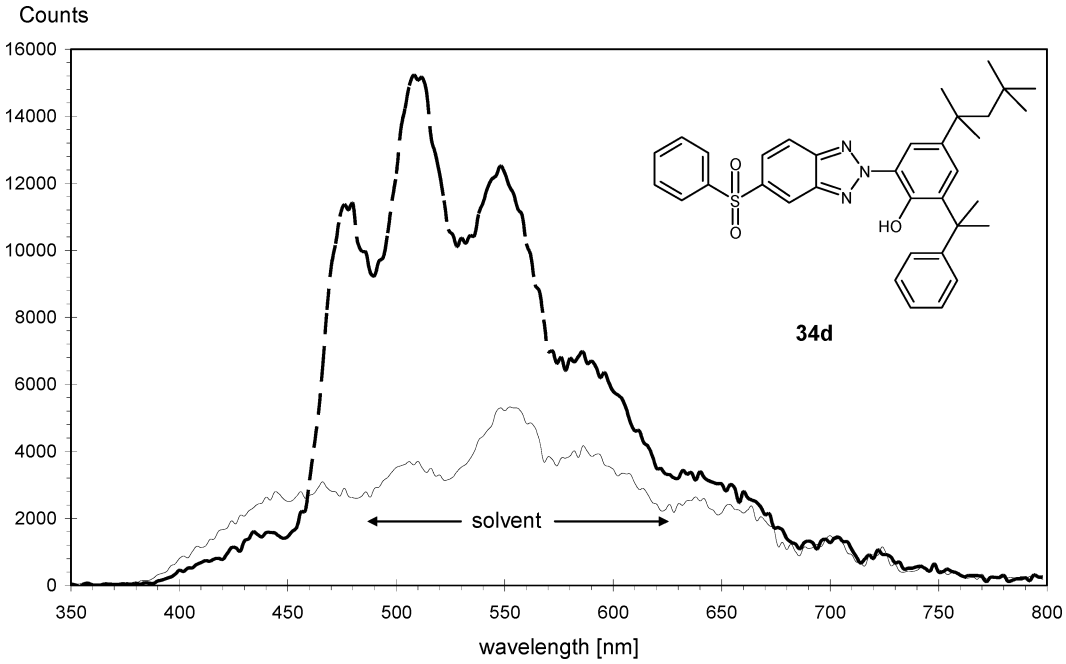


Figure 5. Phosphorescence of **34d** in EPA and of pure solvent EPA (both at 77 K, $\lambda_{exc} = 313$ nm, $c_{\mathbf{34d}} = 9.9 \cdot 10^{-6}$ mol·L^{-1}).

show the same minute residual phosphorescence ($\phi_P = 0.005$). The *t*-butyl group in **32c** apparently does not block the space around the hydroxy group as effectively, so the quantum yield is significantly higher ($\phi_P = 0.035$). The same gradation is found in the series of the 5-CF_3 homologues: while the cumyl and isooctyl compounds (**64d**, **e**) show no phosphorescence beyond the background solvent level, the *t*-butyl derivative (**62c**) does ($\phi_P = 0.01$).

Sulfonyl functions are strong $-M$ substituents, and the CF_3 group has the largest $-I$ effect.[8,17] It seems reasonable, therefore, to assume that electron withdrawal by the 5-X substituent, either mesomeric or π-inductive, additionally stabilizes the open form or destabilizes the IMHB conformer (thermodynamic aspect) and so at least in part compensates for the missing solvent bridge stabilization.[18] The R^1 ortho substituent, on the other hand, impedes the formation of a regular directed hydrogen bond to the solvent matrix, and the rate k_{rel} for reformation of the IMHB thence still is substantially enhanced (kinetic aspect). The concentration of the open conformer thus cannot build up with prolonged irradiation, and no evolution of phosphorescence intensity is in fact observed.

A systematic investigation on compounds with R^1 = cumyl[19a,b] has demonstrated a remarkable stabilizing effect of electron-withdrawing substituents at C-5 (e.g., X = CF_3, CN, sulfonyl) on the photostability of HBzTs in the polar matrix of melamine coatings (relative to **14d**, X = H) although these groups decrease the strength of the IMHB in the ground state.[19b] Photodegradation is triggered by population of the triplet state via photoexcitation of the open form. The decisive effect of electron-withdrawing groups at C-5 in the benzotriazole core thence must be in how they influence the opening of the IMHB in the vibrationally excited state C* (k_2) or the relaxation rate k_{rel}.

In comparing the ϕ_P values, determined in the course of this study, with any phosphorescence intensities reported previously for other HBzTs, one has to keep in mind that because of phosphorescence evolution the phosphorescence emission actually observed crucially depends on both the intensity of the light source and, of course, the effective irradiation time (cf. 3.1). Even recording the phosphorescence spectrum itself will already cause some additional IMHBs to be opened and thus will result in an enhanced emission intensity.

To ensure reproducible and comparable quantum yields, all phosphorescence data listed in Table 1 were therefore determined at the respective irradiation equilibrium and at a constant irradiation wavelength ($\lambda_{exc} = 313$ nm). Each sample was irradiated at this wavelength for ≥ 2 h; before recording the spectrum, we carefully ascertained whether phosphorescence intensity had in fact attained the (constant) equilibrium value.

To get a rough estimate for the possible margin of error in case such provisions are not taken, we have determined ϕ_P also for frozen samples of **11a** (TIN P) and **13a** that had not been exposed to any light (UV/vis radiation) before the spectrum was recorded. The phosphorescence emission observed under these conditions can originate only from open conformers, present already at the thermal equilibrium, or from such molecules where the IMHB has been opened as a consequence of primary photoexcitation during the measurement ($\sim$15 min). The respective values for ϕ_P are 0.09 (**11a**) and 0.28 (**13a**) as compared with 0.13 and 0.42 at the irradiation equilibrium (cf. Table 1); that is, the equilibrium values are about 50% higher, at least for these two representatives.

Table 1 also lists phosphorescence lifetimes for the various HBzT stabilizers at 77 K in EPA, ranging from 1200 to 1500 ms ($\lambda_{obs} = 512$ nm).

3.3. Phosphorescence Excitation and Transient Absorption Spectra. Phosphorescence excitation spectra characterize the species from which the experimentally observed phosphorescence in fact arises. The phosphorescence excitation spectrum of TIN P (**11a**, 77 K in EPA),[9,11,13,20−22] for example, does not match the absorption spectrum of TIN P itself, that is, that of the respective closed form. Rather, it closely resembles the absorption spectrum of the *O*-methyl homologue MTIN (**11A**, Figure 6) where the methoxy group can at most act as acceptor for an intermolecular hydrogen bond. This same homology has already been observed for the phosphorescence spectra themselves (cf. 3.2).

The phosphorescence excitation spectra (in EPA, 77 K) of **13a** (Figure 7) and of the three 5-phenylsulfonyl compounds

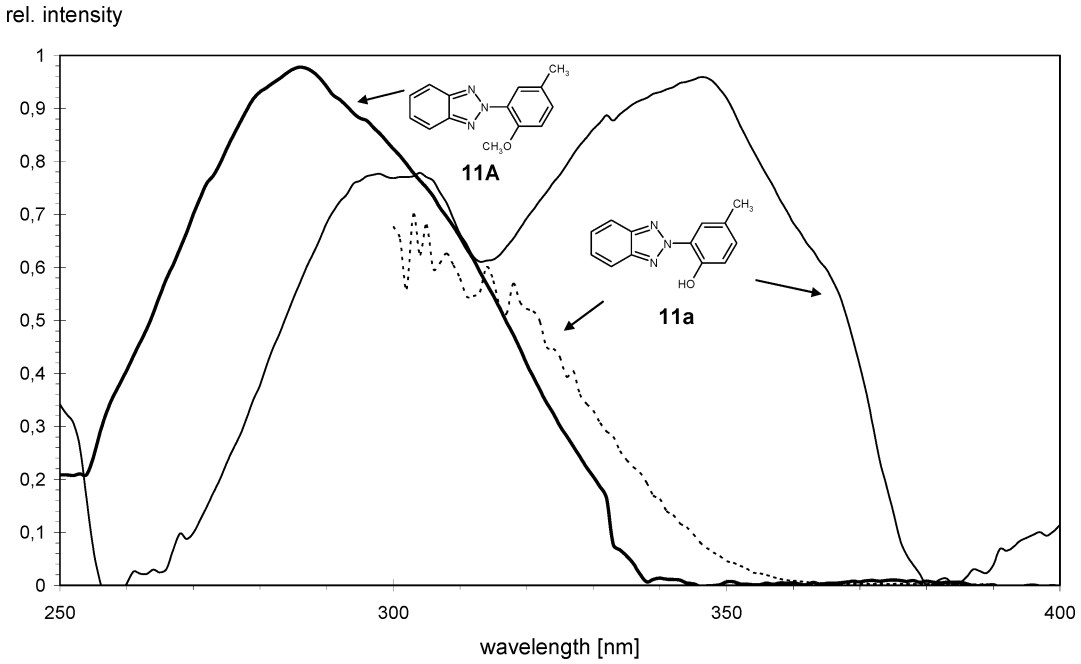


Figure 6. Phosphorescence excitation spectrum of **11a** (---; $\lambda_{obs} = 512$ nm) and normalized absorption spectra of **11a** (—) and **11A** (**—**) ($c_{\mathbf{11a}} = 1.4 \cdot 10^{-5}$ mol·L^{-1}, $c_{\mathbf{11A}} = 2.8 \cdot 10^{-5}$ mol·L^{-1}) (all in EPA, 77 K).

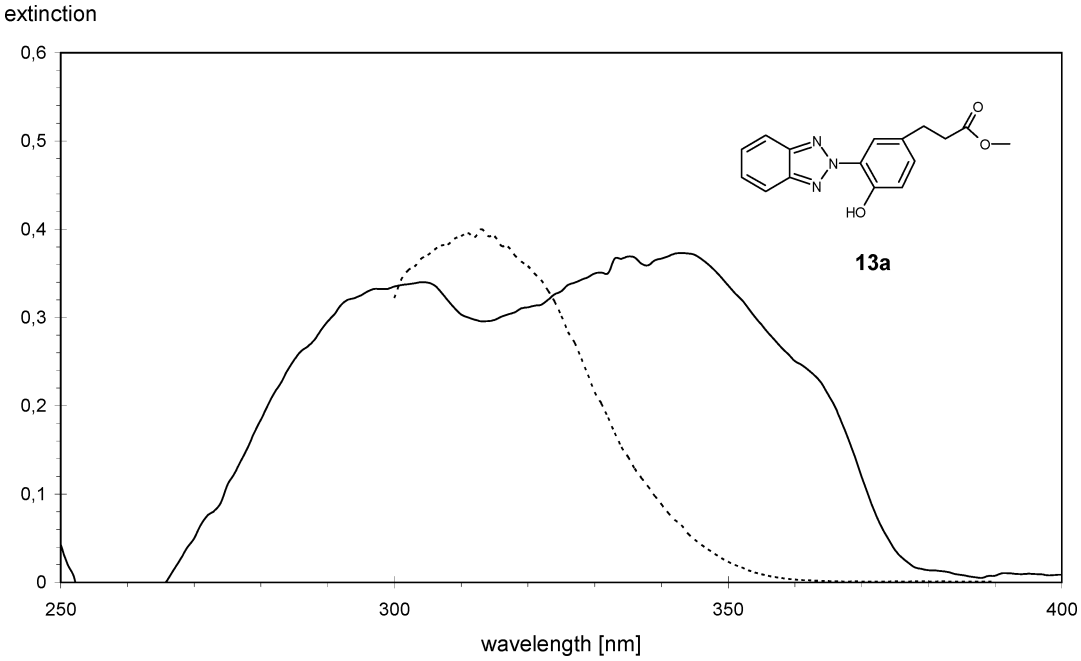


Figure 7. Phosphorescence excitation (---; $\lambda_{obs} = 512$ nm) and normalized absorption spectrum of **13a** (—) in EPA at 77 K ($c_{\mathbf{13a}} = 1.0 \cdot 10^{-5}$ mol·L^{-1}).

32a, **32c**, and **34d** (Figures 8 and 9) all lack a defined maximum in the region of the long-wavelength CT band (λ_2) which is characteristic for the absorption spectrum of any HBzT with an intact IMHB. At 77 K in EPA, the CT band has likewise completely disappeared from the absorption spectrum of **32a** (cf. Figure 9) which has no substituent ortho to the 2′-hydroxy group; at this temperature and in a polar glass matrix, the equilibrium appears to have shifted almost completely toward the open conformer already in the dark (cf. Scheme 1). The absorption spectra of **32c** and **34d**, on the other hand, still show this intensive long-wavelength band at 77 K in EPA ($\lambda_2 = 365/368$ nm). The *t*-butyl and the cumyl substituent both provide sufficient shielding for the *o*-hydroxy group to effectively forestall formation of an intermolecular hydrogen bond in the ground state. The phosphorescence excitation spectra of **32c** and **34d**, however, as well as of **32a** perfectly match the absorption spectrum of **32a** in the long-wavelength region ($\lambda > 315$ nm; all at 77 K in EPA, see Figure 9) rather than the respective absorption spectra. This constitutes additional and independent proof that the phosphorescence of these HBzT stabilizers arises from and is characteristic for their open conformers.

The triplet state of many HBzT-type compounds has been studied by observing the low-temperature (77 K) phosphores-

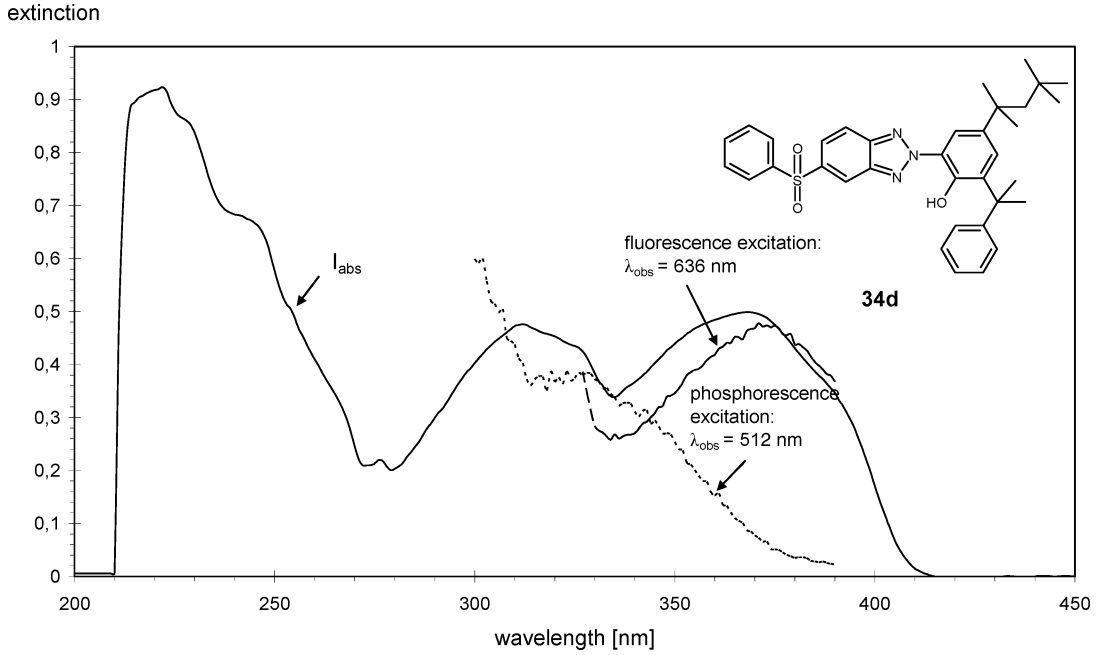


Figure 8. Phosphorescence excitation (λ_{obs} = 512 nm; broken line), fluorescence excitation (λ_{obs} = 636 nm; dashed and solid line, --- −), and normalized absorption spectrum (solid line, −) of **34d** in EPA at 77 K ($c_{\mathbf{34d}} = 9.9 \cdot 10^{-6}$ mol·L^{-1}).

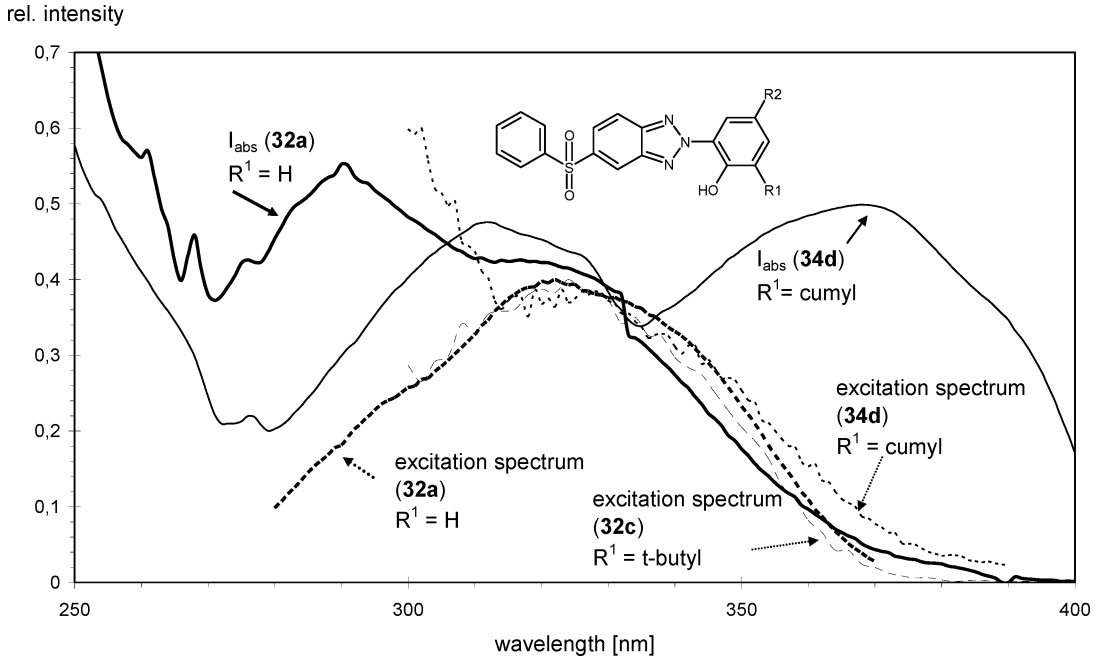


Figure 9. Phosphorescence excitation spectra (λ_{obs} = 512 nm) of **32a** (bold dashed line, ---), **32c** (thin dashed line, ---), **34d** (thin broken line), and normalized absorption spectra of **32a** (bold solid line, —) and **34d** (thin solid line) in EPA at 77 K ($c_{\mathbf{32a}} = 1.2 \cdot 10^{-5}$ mol·L^{-1}, $c_{\mathbf{32c}} = 8.1 \cdot 10^{-6}$ mol·L^{-1}, $c_{\mathbf{34d}} = 8.0 \cdot 10^{-5}$ mol·L^{-1}).

cence (Stein,[23] Waiblinger et al.,[7,24] and Fluegge et al.[8,9]). For practical purposes, the behavior at ambient temperature is more relevant. At this temperature, the triplet lifetime is too short, and its radiationless deactivation is too much favored, so that it escapes observation by phosphorescence measurements. Short-lived triplets of TIN P **11a** and its *O*-methyl homologue **11A** have been monitored by transient absorption spectra in EPA at room temperature.[8] At an excitation wavelength λ_{exc} = 355 nm, where **11A** and the open conformer of **11a** virtually do not absorb, a transient absorption can be observed, though only in degassed, that is, oxygen-free samples, clearly establishing its triplet character. The transient lifetimes have been determined as 58.1 ns (**11a**) and 142 ns (**11A**) at 298 K (λ_{obs} = 460 nm, registration time window 10 μs, Nd:YAG laser power 2.7 mJ/pulse).[8] At lower temperatures, these transient lifetimes increase. However, even at 77 K, they are still shorter by almost 1 order of magnitude than the values obtained from time-resolved phosphorescence measurements (**11a** 1725 ms, **11A** 1089 ms at 77 K in EPA).[8] The respective transients thence probably belong to higher T_n states ($n > 1$) rather than the $T_1(O) \leftarrow S_0(O)$ excitation.

From a practical point of view, it is of paramount importance to stress that the triplets observed at ambient temperature are extremely short-lived and thus are very unlikely to initiate

TABLE 2: Fluorescence (Red and Blue) Maxima and Quantum Yields of the HBzTs (11a-81c, in EPA, 77 K, λ_{exc} = 366 nm)

	λ_{fmax} (nm) (red or blue fluorescence)	Φ_f [10^{-3}] (red fluorescence)
11A	376	*b*
11a	393	*b*
12a	390	n.d.
13a	*a*	*a*
13b	*a*	*a*
13c	*a*	*a*
14d	*a*	*a*
22a	399	*b*
32a	420	*b*
32c	ca. 640	2.39
34d	642	1.60
44d	640	1.44
52a	393	*b*
54d	~630	0.86
64a	405	*b*
62c	637	3.19
64e	~630	7.27
64d	~630	1.41
74d	~630	1.41
81c	610−630[c]	0.8−1.0[c]

[a] No fluorescence observed (neither blue nor red). [b] For the blue fluorescence, no quantum yields were determined. [c] In MCH/2-MB (2:1, v:v).[12]

additional degradation processes as they would be expected to arise from a substantially populated triplet state.

3.4. Fluorescence Spectra. As amply demonstrated above, phosphorescence constitutes unequivocal proof of the presence of an open conformer, for a given HBzT, in equilibrium with the respective IMHB form. The ESIPT is by far the fastest of the individual processes outlined in Schemes 1−3 and, if at all feasible, governs the photochemical behavior of any HBzT-type UV stabilizer. It manifests itself in a (weak) proton-transferred fluorescence (PTF) frequently observed at low temperature.

TIN P (**11a**), for instance, shows a long-wavelength fluorescence at λ_f = 615 nm in nonpolar low-temperature glasses as well as in the crystalline state, with an enormous Stokes shift of 10.000 cm^{-1}.[14,21,22,25] In polar solvent matrixes, for example in EPA at 77 K, however, TIN P fluorescence appears shifted to λ_f = 393 nm (with a normal Stokes shift, cf. Table 2). This matrix dependence of the fluorescence has been demonstrated, over and over again, for TIN P[11−15,20,26−28] and other HBzTs.[12,13,22,29−41] So far, no proton-transferred long-wavelength fluorescence has ever been found for a HBzT stabilizer in a polar solvent or solvent glass matrix.

The respective fluorescence excitation spectra allow these two emissions to be assigned to the two different HBzT conformers. The excitation spectrum of the red, 615 nm emission matches the absorption spectrum of **11a** itself, that is, of the closed form of TIN P with an intact IMHB; that of the blue fluorescence (λ_f = 393 nm), on the other hand, corresponds to the absorption spectrum of the methoxy derivative **11A** which of course lacks any IMHB. As apparent already from the phosphorescence behavior (cf. 3.2), the *O*-CH_3 homologue **11A** thus constitutes an appropriate model for the open conformer of any HBzT molecule. The phenyl ring in **11A** is severely twisted, moreover, with respect to the plane of the benzotriazole moiety, as shown by X-ray diffraction,[11] while TIN P (**11a**) is perfectly coplanar in the crystalline state[14] and thence has the proton-transferred fluorescence preserved even in the solid.

Of the HBzTs investigated in this study, all compounds without a substituent shielding the IMHB (R^1 = H, **..a**) show the same blue fluorescence in EPA at 77 K as **11a**, with a regular Stokes shift (see Figure 4). The maxima are in the range λ_f = 390−400 nm (**11a**, **12a**, **22a**, and **52a**), with a slight red shift for **32a** and **64a** (cf. Table 2; the fluorescence of **13a** is completely buried beneath the intense self-emission of EPA). This blue fluorescence can arise only from the respective open conformers and thus establishes their presence, at least in equilibrium, just as the phosphorescence and the phosphorescence evolution observed for these seven compounds (cf. 3.2).

A painstaking analysis now surprisingly revealed a weak yet well-defined long-wavelength emission, additional to the blue solvent emission, in the fluorescence spectra of eight HBzTs even in the polar EPA matrix at 77 K. The excitation spectra of this red fluorescence match the absorption spectra of the respective HBzTs for which phosphorescence behavior has shown the closed form, with an intact IMHB and thence the capacity for an ESIPT process, to be at least dominant. At ambient temperature, no PTF is detected any more.

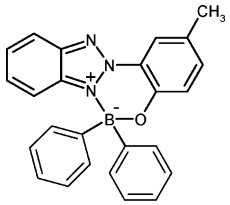
These eight HBzTs all carry an electron-withdrawing substituent at C-5 as well as a shielding group at C-3′. With five of them (**34d**, **44d**, **54d**, **64d**, and **74d**), this is a cumyl moiety; so, the steric shielding of the 2′-hydroxy function in ortho position is identical for all five compounds. Similar quantum yields are in fact observed for their proton-transferred red fluorescence ($\phi_f = 0.9-1.6\cdot10^{-3}$, cf. Table 2); for **32c** and **62c**, with a sterically less demanding *t*-butyl group at C-3′, ϕ_f appears somewhat enhanced. No fluorescence, either red or blue, can be detected, on the other hand, for **14d** which likewise has a 3′-cumyl group but no electron-withdrawing substituent at C-5 in the benzotriazole core. The same holds for the respective 3′-methyl and 3′-*t*-butyl compounds **13b** and **13c**.

These last three HBzTs, just as **54d**, **64d**, **64e**, and **74d**, likewise show no phosphorescence at all. For the remaining four representatives with a 5-substitutent (**32c**, **62c**, **34d**, **44d**), the phosphorescence observed is either weak or very weak, and definitely no phophorescence evolution becomes apparent (cf. Table 1). The complete lack of any phosphorescence for **13b**, **13c**, and **14d** has been attributed above (cf. 3.2) to the hydroxy group of the open conformer, formed in the sequel of photoexcitation, being blocked from the (polar) matrix molecules by the respective ortho alkyl substituent. Thence, the O−H functionality cannot be stabilized by any intermolecular hydrogen bridging, and the equilibrium concentration of the open conformer is reduced to a minimum or even zero. A methyl group is sufficient already for the full effect. At the same time, radiationless deactivation from the S_1' state must be highly effective since not even a trace of the long-wavelength fluorescence is found for these three HBzTs (see Table 2).

An additional electron-withdrawing 5-substituent seems to be able to compensate for this steric shielding effect to a small extent, either by destabilizing the IMHB or by stabilizing the open, nonbridged conformer (cf. 3.2). At the same time, it must increase the lifetime of the proton-transferred S_1' state sufficiently for an (albeit weak) red PTF fluorescence being observed, even in the polar EPA matrix, for each and any HBzT with an alkyl group at C-3′ and an electron-withdrawing substituent at C-5.

Finally, the boryl chelate **11B**[11,15,21,22] strikingly demonstrates how the ESIPT process, by its very rapidity, constitutes the pivot around which the photochemistry of all HBzTs revolves. The diphenylboryl moiety in **11B** is linked, covalently, to both the oxygen and the (coordinatively bonded) nitrogen atom and thus

represents an ironclad chelate bridge. Since no proton transfer is of course possible in this case by which the S_1 state would be rapidly depleted, **11B** consequently displays a highly intensive fluorescence (temperature-independent, non-Stokes-shifted), returning the system directly from the excited S_1 to its S_0 ground state.



Boryl Chelate **11B**

4. Conclusions

Designing the optimum strength of the intramolecular hydrogen bond (IMHB) plays a decisive role in the development of new UV absorbers. In the present work, the effective strength of this chelate-type hydrogen bond has been examined in detail for a wide series of differently substituted 2-(2-hydroxyphenyl)-benzotriazoles (HBzTs; cf. Chart 1) by studying the phophorescence behavior and, more specifically, the phosphorescence evolution of these compounds in a polar low-temperature glass (EPA, at 77 K). The phosphorescence data in fact constitute a highly sensitive tool for probing how the thermodynamic and kinetic stability of the IMHB is affected by the presence and the nature of substituents at C-3′ in the phenyl ring and at C-5 in the benzotriazole backbone. At the same time, the IMHB of the HBzTs is very sensitive to matrix effects, in sharp contrast to that of the 2-(2-hydroxyaryl)-1,3,5-triazines (HPTs), another class of technically important UV absorbers. Even a thermodynamically strong IMHB does not suffice to protect an HBzT against the H-bond being opened in and by a polar medium (energetic respectively enthalpic stabilization). Rather, the IMHB of any HBzT must be sterically shielded from such an outside attack by a substituent R^1 in ortho position to the phenolic OH (kinetic respectively entropic stabilization). A methyl group at C-3′ provides sufficient protection already to suppress any phosphorescence evolution (**13b**, cf. Table 1). For all derivatives with $R^1 \neq H$, no additional irradiation-induced opening of the IMHB is apparent. Even for HBzTs, though, which show no phosphorescence evolution, a certain concentration of open, that is, intermolecularly bridged conformers must be present already in the dark since for all of these compounds a static phosphorescence is observed in EPA at 77 K (cf. Table 1).

From this investigation of the dynamic phosphorescence behavior, a finely graded order can be established for the shielding capacity of the individual substituents R^1 for the IMHB:

$$\text{cumyl} \geq \text{1,1,3,3-tetramethylbutyl (isooctyl)} > \textit{t}\text{-butyl} \geq \text{methyl} \gg \text{H}$$

As the comparable influence of the two isotropic rotor groups methyl and *t*-butyl demonstrates, it is not so much the sheer size of the substituent that is responsible for the steric effect, but rather the volume of space which a freely rotating moiety shields against an outside (solvent) attack. This argument is confirmed by the relative order of isooctyl versus *t*-butyl, and makes it readily understood why the cumyl group constitutes the best safeguard for the IMHB. Compounds in which both effects are combined, that is, steric (entropic) protection by R^1 and energetic stabilization by the substituent X, show proton-transferred fluorescence even in the polar protic medium EPA at 77 K. This is the first time that such a PTF has in fact been observed in a polar glass.

Four criteria can thence be derived for assessing the strength of the intramolecular hydrogen bond in a HBzT-type UV absorber:

(1) The stronger the IMHB is in the electronic ground state, the less prone it is to being cleaved by polar groups in the polymer matrix or, vice versa, the lower the equilibrium concentration of the open conformer is.

(2) As long as the IMHB is conserved in the excited state, it offers a plenitude of vibrational modes, for example, out-of-plane bending, for triggering the radiationless deactivation of the UV absorber molecule and thus can actively protect the polymer matrix against photochemical degradation.

(3) Increasing strength of the IMHB concomitantly raises the activation energy for any vibrational deformation of the increasingly rigid planar bridged HBzT skeleton, and radiationless deactivation thus becomes less and less favorable with a stronger IMHB.

(4) Conservation of the IMHB in the excited state, and thence the availability of a broad spectrum of compatible vibrational modes, is essential for an efficient radiationless decay; complete proton transfer in the excited state, on the other hand, that is, a full-fledged ESIPT process, is no prerequisite at all.[5,8]

There will be an optimum strength of the IMHB, consequently, with respect to the UV absorber efficiency of any given 2-(2-hydroxyphenyl)benzotriazole derivative. An indispensable constituent is the intramolecular hydrogen bond. First of all, the IMHB has to be strong enough in the ground state not to be cleaved already in the dark by competitive intermolecular H-bond formation to polar functions, either in a solvent molecule or in the polymer matrix, thus keeping the equilibrium concentration of any open conformer at a minimum. Moreover, the IMHB must have sufficient strength to remain intact also in the excited state. On the other hand, the IMHB has to be soft, that is, flexible enough to still allow for substantial vibrational deformation and thence effective radiationless deactivation.

One problem still remains to be resolved, though. The intramolecular hydrogen bond in 2-(2-hydroxyaryl)-1,3,5-triazines (HPTs) is far stronger than that in any HBzT.[2,4,42] Crystal structure data have established a true chelate character for this IMHB.[5,25,42] Its strength has been determined, by dynamic NMR spectroscopy, as $\Delta G^{\ddagger} = 55-60$ kJ mol^{-1}, more or less regardless of any additional substituents in the 2-hydroxyaryl moiety, and also of the nature of the respective aryl groups at C-4 and C-6.[2,4,42] Why then are the 2-(2-hydroxyaryl)-4,6-diaryl-1,3,5-triazines such excellent and technically important UV stabilizers despite the extreme strength of their hydrogen bridge?

This apparent inconsistency is readily resolved if one considers the overall molecular structure of the two classes of UV absorbers. Even though the rigid chelate bridge "freezes" the 2-hydroxyaryl moiety at C-2 in the triazine ring plane as in the boryl chelate **11B**, the two additional aryl substituents (phenyl, tolyl, xylyl, mesityl, methoxyphenyl) in 4- and 6-position still offer the requisite vibrational deformation modes for a highly effective radiationless deactivation, for example, by the intensive out-of-plane aryl C−H bending vibrations. The UV absorber potential of the HPTs is lost almost completely, on the other hand, if these 4- and 6-aryl substituents are replaced by methoxy or dimethylamino groups.[43]

In a 2-(2-hydroxyaryl)benzotriazole, in contrast, the vibrational modes for an efficient radiationless deactivation are

associated with the same aryl moiety which constitutes the hydrogen bridge donor. The stronger the IMHB in such a benzotriazole is, the more rigidity it confers to the overall molecular structure, and the more effectively it forestalls any out-of-plane deformation (see above, criterion 3).

Acknowledgment. The paper is dedicated to Professor Dr. André Braun in recognition of his contributions to the field of photochemistry.

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