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Photophysical Properties of Some 2-(2′-Hydroxyaryl)benzotriazoles: Dramatic Effect of an Ortho-Located Bulky *tert*-Butyl Group

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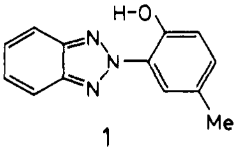
Abstract: Photophysical experiments carried out on 3′-*tert*-butyl and 5′-*tert*-butyl analogues of Tinuvin P provided evidence concerning the origin of the so-called "open" forms. They result from the rotation of the hydroxyl group *followed* by the rotation of the phenyl group, not the other way round. This mechanism is consistent with the negligible amount of "open" forms in the 3′-*tert*-butyl derivative in a base so strong as DMSO. In this series of photoprotectors, a bulky alkyl substituent in ortho position with regard to the hydroxyl group improves considerably their photostability.

The 2-(2′-hydroxyphenyl)benzotriazoles are ultraviolet absorbers which, because of their excellent photostability, constitute one of the most important classes of photoprotecting agents. Their best known representative, the 5′-methyl derivative (Tinuvin P, **1**), exhibits marked photostability in nonpolar solvents, e.g. *n*-hexane, in which $\Phi_R = 1.7 \times 10^{-7}$.[1] However, its photostability is reduced considerably in polar solvents, e.g., acetonitrile, in which $\Phi_R = 2.1 \times 10^{-6}$.[1] Interestingly, parallel solvent-dependent photophysical behavior has also been observed. Thus, in inert solvents,[2-4] e.g. methylcyclohexane–isopentane (1:1), cyclohexane, and *n*-heptane, Tinuvin P neither fluoresces (at room temperature) nor phosphoresces (at 77 K). However, in polar solvents (cf. ref 4), e.g., diethyl ether, tetrahydrofuran, dimethylformamide, methanol, ethanol, or dimethyl sulfoxide and in a mixture of ethanol, ether, and pyridine,[3] very weak fluorescence and phosphorescence were both observed.



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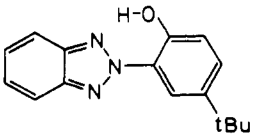

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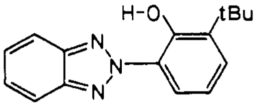

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In the ground state (X-ray determination),[5] Tinuvin P is planar and possesses a strong intramolecular hydrogen bond (IMHB) (see structure **1**), the latter feature being considered to be responsible for its exceptional photophysical properties.[6-11] However, if the IMHB is broken, e.g. by environmental factors, then the molecule loses its planarity, and rotation about the N(2)–C(1′) bond occurs.[6,8,12-18] If this happens, e.g., in solution, then the IMHB is replaced by an *inter*molecular bond involving the OH group and the solvent, presumably at a site in the latter more basic than is either N(1) or N(3). There is general agreement[6] that nonplanar forms of Tinuvin P are luminiscent. Relevant in this regard is the fact that 2-(2′-methoxyphenyl)benzotriazole (Tinuvin P methyl ether, (structure **1** with the OH group replaced by an OMe group), which is nonplanar in the crystalline state (the torsion angle about the N(2)–C(1′) bond is 56°)[3] and does not possess an IMHB, has been found to be luminescent.[3]

It is of course intrinsically desirable that the formation of the luminiscent forms of a photoprotecting agent be avoided. Otherwise, not only is the agent itself likely to be degraded by light but also the substrate being protected (photosensitization of chromophores or impurities in the latter can occur). A possible method for minimizing environmental effects was first suggested by Heller,[7] who reasoned that the introduction of a large alkyl group *ortho* to the OH group would shield the IMHB from being broken. Recently, Wilshire et al.[19-21] have provided support for

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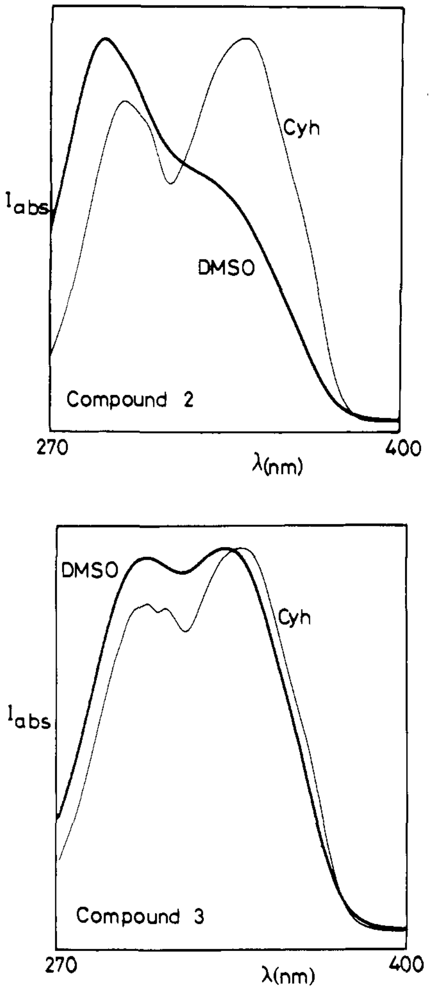


Figure 1. Absorption spectra of compounds **2** and **3** in cyclohexane and in DMSO.

Heller's hypothesis by establishing experimentally that such ortho substitution significantly improves the capability of certain sulfonated 2-(2'-hydroxyphenyl)benzotriazoles to protect wool against light.

In the present work, we have aimed to understand the mechanism by which a large alkyl group located ortho to the OH group enhances the photoprotecting capability of the 2-(2'-hydroxyphenyl)benzotriazoles. For this purpose, we have studied two compounds closely related to Tinuvin P, namely the 5'-*tert*-butyl and 3'-*tert*-butyl derivatives (**2** and **3**, respectively) of 2-(2'-hydroxyphenyl)benzotriazole. We were particularly interested in studying the effect of a hydrogen-bond-breaking solvent, e.g. dimethyl sulfoxide (DMSO), on the photophysical properties of both compounds.

Experimental Section

Materials. Compounds **2** and **3** were prepared according to ref 22.

Photophysics. The absorption spectra were measured by using a Shimadzu UV-2100 spectrophotometer and a matched pair of cells of Suprasil quality of 1-cm thickness at 25.0 ± 0.1 °C (Heto thermostat).

Luminiscence spectra at 77 K corrected for the instrument sensitivity were measured with a SLM 48000S spectrofluorimeter by using a cooled wide-band rf housing for the R928 photomultiplier tube. The samples were contained in sealed quartz tubes of Suprasil quality of 2-mm diameter, which were introduced in the low-temperature SLM accessory. This was modified to keep the samples in a convenient position for excitation and emission. To avoid artifacts, due to polarization effects, the spectra were measured using polarizers in a magic angle arrangement.

The DMSO solutions used to study low-temperature luminiscence were prepared to have identical optical density (OD) at the excitation wavelength. In the present case, the OD at 320 nm was 0.3 for 1-cm optical path cells.

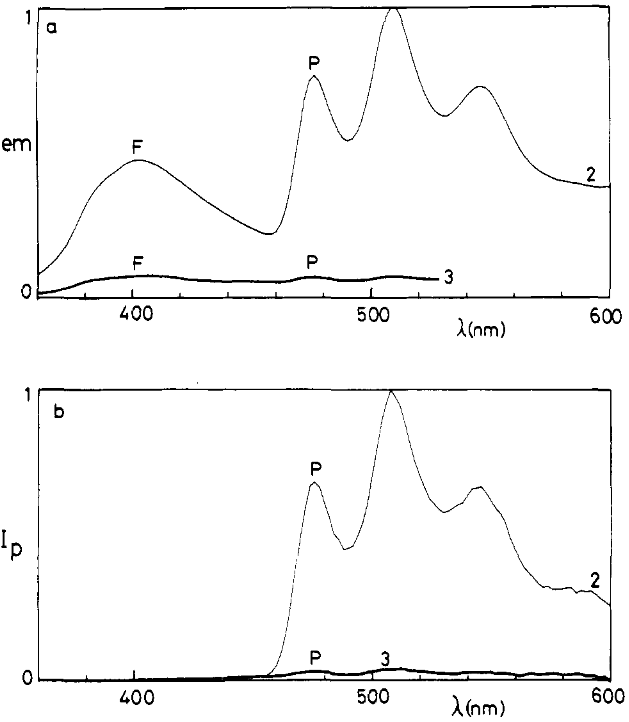
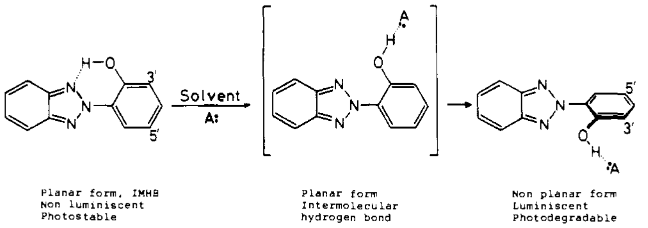


Figure 2. Emission spectrum (77 K; λ_{exc} 320 mm; band pass 4 nm): (a) no delay; (b) delay of 3 ms.

Scheme I



The solvents used were DMSO Merck Uvasol (freshly open bottles) and cyclohexane Merck Uvasol for fluorimetry. The latter one was kept during 24 h over sodium wire.

Results and Discussion

Our experiments have revealed that the UV spectra of solutions of the two *tert*-butyl derivatives in an inert solvent (cyclohexane) (see Figure 1) closely resemble that of Tinuvin P in the same solvent (cf. ref 3). Furthermore, neither compound luminesces in this solvent. However, in DMSO solution, the two compounds differ substantially from one another in their photophysical properties. Thus, the UV spectrum of the 5'-*tert*-butyl derivative **2** changes significantly when cyclohexane is replaced by DMSO (the intensity of the long-wavelength band decreases markedly (cf. the UV spectrum of Tinuvin P in DMSO solution)),[3] whereas that of the 3'-*tert*-butyl derivative **3** remains virtually unchanged. Particularly interesting was the observation that, in DMSO solution, the 5'-*tert*-butyl derivative exhibits weak fluorescence and phosphorescence whereas the 3'-*tert*-butyl derivative hardly luminesces at all (see Figure 2a,b). Indeed, its phosphorescence was estimated to be only ca. 4% of that of the 5'-*tert*-butyl derivative, a finding which indicates that the T_1 states of the open forms of the 3'-*tert*-butyl derivative are practically nonexistent. From these results, we deduce that the ortho *tert*-butyl group shields the IMHB very effectively against the hydrogen-bond-breaking action of DMSO.

The very efficient shielding role played by the ortho *tert*-butyl group can be explained by assuming that it hinders the rotation of the OH group. We propose that the open forms of Tinuvin P and its derivatives arise by rotation of the OH group *followed*

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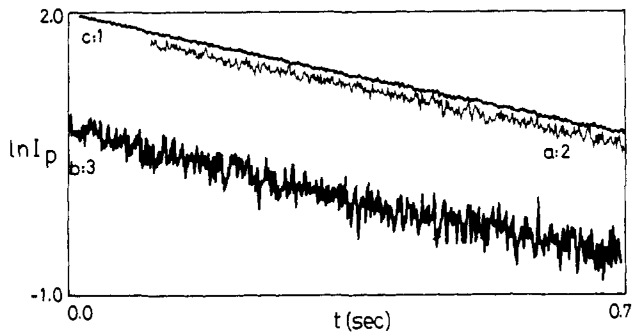

Figure 3. Phosphorescence decay: (a) compound **2**; (b) compound **3**; (c) Tinuvin P. The averaged lifetimes corresponding to five experiments are (a) 0.564 ± 0.007, (b) 0.613 ± 0.003, and (c) 0.611 ± 0.002 s.

by rotation of the aryl group as shown in Scheme I. The inverse order of rotation seems unlikely. It would not explain the role of the *tert*-butyl group since, in that event, the OH group would remain free to form an *inter*molecular hydrogen bond with the solvent.

Other possible explanations for the *tert*-butyl effect can be excluded, at least as the main cause. For instance, the loose bolt effect of the *tert*-butyl group[23] on the ISC $T_1 \rightsquigarrow S_0$[24,25] and the CI $S_1 \rightsquigarrow S_0$[26] cannot be invoked to explain the dramatic reduction in luminescence observed on going from the para isomer to the ortho isomer, because their phosphorescence decays (measurable for the ortho isomer in spite of its exceedingly weak phosphorescence) (see Figure 3) have lifetimes similar to that of Tinuvin P.

It seems likely that the "*tert*-butyl ortho effect" could be used with similar effectiveness in other families of photoprotecting agents (cf. ref 27), e.g., the 2-hydroxybenzophenones and the 2-(2′-hydroxyphenyl)-*s*-triazines.

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A Significant Barrier to 1,2 Hydrogen Migration in Singlet 1-Phenylethylidene. A Laser Flash Photolysis Study

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Abstract: Laser flash photolysis of 1-phenyldiazoethane in heptane releases 1-phenylethylidene which can be intercepted with pyridine to form an ylide (λ_{max} = 475 nm). Oxygen trapping experiments indicate that relaxation of singlet 1-phenylethylidene to the ground triplet state is rapid relative to pyridine trapping. Analysis of the data reveals that the (singlet/triplet) carbene equilibrium constant $K = 2 \times 10^{-2}$ and $\Delta G_{ST}(298\ K) = 2.3$ kcal/mol at ambient temperature in *n*-heptane. Furthermore, the rate constant for 1,2 hydrogen migration in the singlet state ($k_{1,2}$) is less than $6 \times 10^6\ s^{-1}$, and the 1,2 hydrogen shift reaction in the singlet state must traverse an activation energy of at least 4.3 kcal/mol in alkane solvent. The 1,2 hydrogen shift reaction is accelerated by more than a factor of 30 in polar acetonitrile solvent and by substitution of an additional methyl group on the migrating CH group (1-phenylpropylidene).

1. Introduction

Over the past 10 years there has been tremendous activity in the study of the absolute kinetics of carbene processes utilizing laser flash photolysis (LFP) techniques.[1] For the most part, these studies were concerned with aromatic carbenes to take advantage of their benzylic chromophores.

These studies were designed to study carbenes which did not undergo intramolecular rearrangements and thereby facilitate the study of the kinetics of their intermolecular reactions. Recently attention has turned to the study of the intra- and intermolecular reaction rates of alkyl-substituted carbenes. To date, these studies have been confined to alkylhalocarbenes[2] and small-ring dialkylcarbenes,[3] both of which have *singlet* ground states. The absolute Arrhenius parameters associated with the *intramolecular* rearrangements of singlet carbenes which are now known are given in Figure 1. Surprising features of the data are the relatively low Arrhenius preexponential *A* factors and negative entropies of activation. In this paper we report the dynamics of an arylalkylcarbene, 1-phenylethylidene (**1a**), a species with a triplet ground state. The data are consistent with a small singlet–triplet energy separation (ΔG_{ST}) in this carbene and a significant barrier to 1,2 hydrogen migration in the singlet state. We have also found

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